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HIDRÓLISE SUBCRÍTICA DE BIOMASSAS RESIDUAIS DE NOGUEIRA-PECÃ: CARACTERIZAÇÕES FÍSICO-QUÍMICA, MORFOLÓGICA E OBTENÇÃO DE AÇÚCARES REDUTORES

Santa Maria, RS
2020

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Dissertação apresentada ao Curso de Mestrado do Programa de Pós-Graduação em Engenharia Agrícola, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Mestre em Engenharia Agrícola**.

Orientador: Prof. Dr. Marcus Vinícius Tres
Coorientador: Prof. Dr. Giovani Leone Zabot

Santa Maria, RS
2020

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Aprovado em 6 de março de 2020:

Marcus Vinícius Tres, Dr. (UFSM)
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Kátia Rezzadori

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Santa Maria, RS
2019

DEDICATÓRIA

Ao maior amor da minha vida, minha mãe Elenara; meu pai Arioli; minha irmã Angélica e minha sobrinha Heloísa.

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(Theodore Roosevelt)

RESUMO

HIDRÓLISE SUBCRÍTICA DE BIOMASSAS RESIDUAIS DE NOGUEIRA-PECÃ: CARACTERIZAÇÕES FÍSICO-QUÍMICA, MORFOLÓGICA E OBTENÇÃO DE AÇÚCARES REDUTORES

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Neste estudo, diferentes biomassas de nogueira-pecã, como pericarpos, folhas, talos e cascas foram submetidas à hidrólise em água subcrítica, o que resultou em uma solução hidrolisada rica em açúcares redutores. Os ensaios foram realizados em uma unidade multiuso localizada no Laboratório de Engenharia de Processos Agroindustriais (LAPE) e pertencente à Universidade Federal de Santa Maria (UFSM), *Campus* Cachoeira do Sul. Esta unidade contém um reator de hidrólises de 50 mL aquecido por resistência térmica, sensores e controladores de temperatura, vazão e pressão, uma vez que diferentes condições foram consideradas para este estudo. Para os ensaios, foram consideradas as variáveis temperatura (180, 220 e 260 ºC), razão mássica água/sólidos (R) (15 e 30 g água/g biomassa inicial, o que corresponde às vazões de 20 e 40 mL/min, respectivamente) e tempo de reação (0,5 a 15 minutos). A pressão utilizada foi de 30 MPa. Várias respostas foram analisadas, como os rendimentos de açúcares redutores por espectrofotometria no UV, teores de açúcares e inibidores por meio de cromatografia líquida de alta eficiência (CLAE) e caracterização morfológica das diferentes biomassas, através de microscopia eletrônica de varredura (MEV), espectroscopia no infravermelho com transformada de Fourier (FT-IR) e análise termogravimétrica (TGA). Em relação às biomassas dos pericarpos de nogueira-pecã, os resultados encontrados mostraram o maior rendimento de 26,5 g/100 g de biomassa sob 220 ºC e R de 15 g água/g biomassa (220 ºC e R – 15, referente à vazão de 20 mL/min). Já para as folhas e talos, os rendimentos maiores de 26,3 g/100 g de biomassa foram encontrados nas condições de 260 ºC e R de 15 g água/g biomassa (260 ºC e R – 15, vazão de 20 mL/min). Para as cascas, o rendimento maior foi de 27,1 g/100 g de biomassa, encontrado na condição de 220 ºC e R de 15 g água/g biomassa (220 ºC e R – 15, vazão de 20 mL/min). As análises das soluções hidrolisadas por CLAE apontaram a presença de arabinose, celobiose, glicose e xilose, além de furfural e hidroximetilfurfural. As análises de MEV evidenciaram a ruptura da estrutura dos materiais *in natura* e o aumento da presença de microestruturas superficiais nas biomassas. A partir das análises em TGA, observou-se as alterações mássicas dos resíduos, a partir de diferentes condições térmicas. Por fim, as análises em FT-IR expressaram a identificação dos diferentes componentes das biomassas, compreendendo os teores de celulose, hemicelulose e lignina.

Palavras-chave: Noz-pecã. Hidrólise. Açúcares redutores. Biomassas agrícolas. Resíduos agroindustriais. Tecnologia subcrítica.

ABSTRACT

SUBCRITICAL HYDROLYSIS OF PECAN RESIDUAL BIOMASSES: PHYSICOCHEMICAL, MORPHOLOGICAL CHARACTERIZATIONS AND OBTAINING REDUCING SUGARS

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In this study, different pecan biomasses, such as husks, leaves, stalks and shells were submitted to hydrolysis by subcritical water (SWH), which resulted in a hydrolyzed solution rich in reducing sugars. The assays were carried out in a multipurpose unit located at the Laboratory of Agroindustrial Processes Engineering (LAPE) and belonging to the Universidade Federal de Santa Maria (UFSM), *Campus* Cachoeira do Sul. This unit contains a 50 mL hydrolysis reactor heated by thermal resistance, sensors and controllers of temperature, flow and pressure, once different conditions were considered for this study. For the assays, the variables temperature (180, 220 and 260 ºC), water/ solids mass ratio (R) (15 and 30 g water/ g initial biomass, corresponding to the flow rates of 20 and 40 mL/min, respectively) and reaction time (0.5 to 15 minutes) were considered. The pressure used was 30 MPa. Several responses were analyzed, such as yields of reducing sugars by UV spectrophotometry, sugar contents and inhibitors by high performance liquid chromatography (HPLC), and morphological characterization of the different biomasses by scanning electronic microscopy (SEM), Fourier-transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Regarding the pecan husks biomass, the results showed the highest yield of 26.5 g/ 100 g biomass in 220 ºC and R of 15 g water/ g biomass (220 ºC and R - 15, referring to the flow rate of 20 mL/min). For leaves and stalks, the highest yield, 26.3 g/ 100 g biomass, was found in the conditions of 260 ºC and R of 15 g water/ g biomass (260 ºC and R - 15, flow rate of 20 mL/min). For shells, the highest yield of 27.1 g/ 100 g biomass was found in 220 ºC and R of 15 g water/ g biomass (220 ºC and R - 15, flow rate of 20 mL/min). The analysis of HPLC hydrolysed solutions showed the presence of arabinose, cellobiose, glucose and xylose, as well as furfural and hydroxymethylfurfural. SEM analysis showed the rupture of the structure of fresh materials and the increase of superficial microstructures in the biomass. According to the TGA analysis, mass changes in the residues were observed different thermal conditions. Finally, FT-IR analysis expressed the identification of different components of the biomasses, comprehending the contents of cellulose, hemicelluloses and lignin.

Keywords: Pecan nut. Hydrolysis. Reducing sugars. Agricultural biomasses. Agroindustrial residues. Subcritical technology.

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LISTA DE ABREVIATURAS E SIGLAS

CLAE	Cromatografia Líquida de Alta Eficiência
DNS	Ácido Dinitrosalicílico
FT-IR	Espectroscopia no Infravermelho com Transformada de Fourier
HMF	Hidroximetilfurfural
KBR	Brometo de Potássio
KN	Kilonewton
KV	Kilovolt
MEV	Microscopia Eletrônica de Varredura
R	Razão Mássica Água/Sólidos
RPM	Rotação por Minuto
TGA	Análise Termogravimétrica

SUMÁRIO

ESTRUTURA, CONTRIBUIÇÃO TEÓRICA, CONCLUSÕES E RECOMENDAÇÕES PARA TRABALHOS FUTUROS

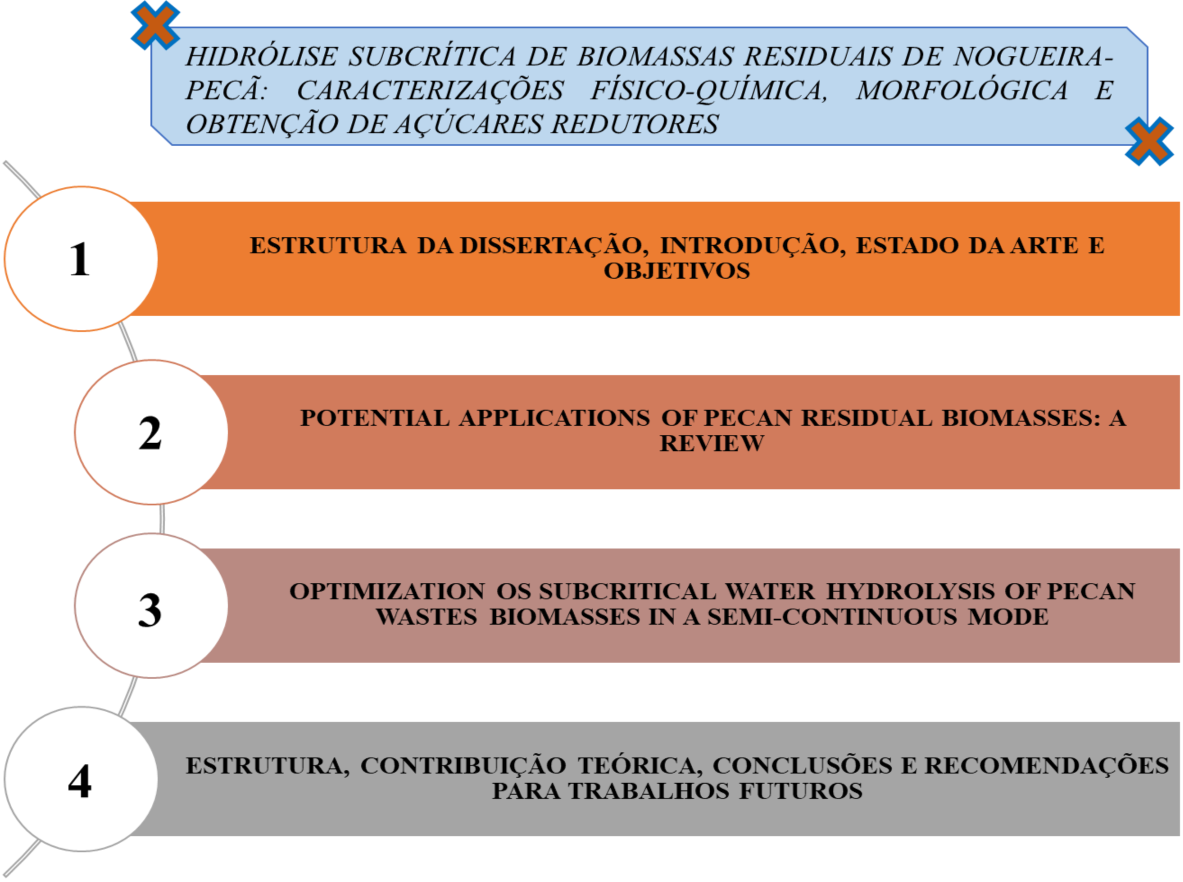
CAPÍTULO 1

ESTRUTURA DA DISSERTAÇÃO, INTRODUÇÃO, ESTADO DA ARTE E OBJETIVOS

1.1 ESTRUTURA DA DISSERTAÇÃO

O presente Capítulo, intitulado ***ESTRUTURA DA DISSERTAÇÃO, INTRODUÇÃO, ESTADO DA ARTE E OBJETIVOS***, introduz amplamente os tópicos iniciais acerca do trabalho, salientando-se o tema principal da pesquisa, a literatura existente, a carência de trabalhos acadêmicos a respeito do tema e os objetivos esperados com este estudo. Também, evidencia-se a configuração das etapas e procedimentos realizados para o desenvolvimento do trabalho, delineando, desta forma, a estrutura desta Dissertação. Para melhor compreensão dos tópicos abordados nesta Dissertação de Mestrado, a estrutura do trabalho é apresentada na Figura 1.

Figura 1 – Estruturação do desenvolvimento da Dissertação



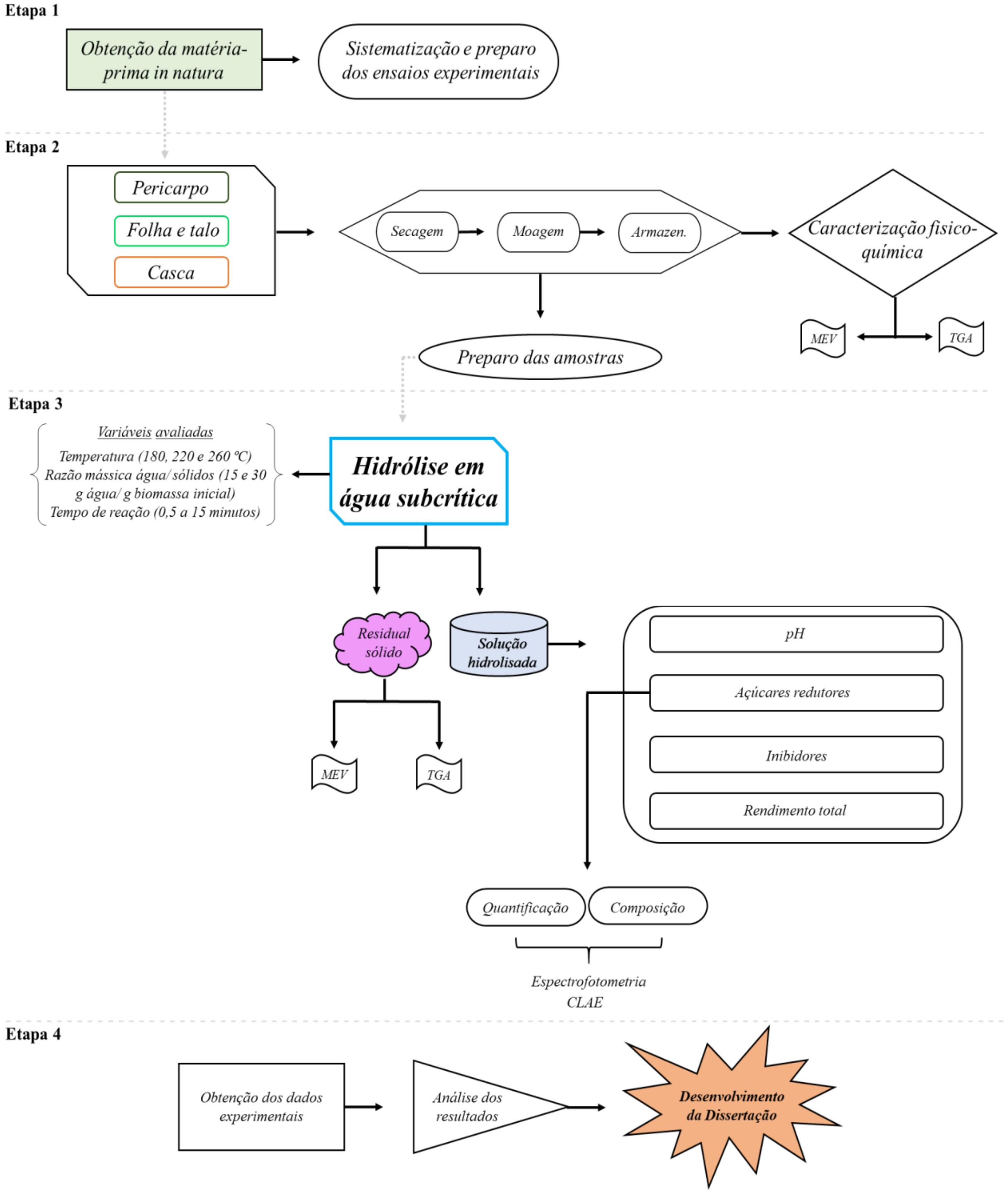
Fonte: (Autor).

O **Capítulo 2**, denominado ***POTENTIAL APPLICATIONS OF PECAN RESIDUAL BIOMASSES: A REVIEW***, retrata uma revisão da literatura relacionada à dinâmica da utilização de biomassas de nogueira-pecã e técnicas e ferramentas de processamento destes resíduos**,** compreendendo estudos que discutem a obtenção de produtos originados a partir de matéria-prima vegetal. Inicialmente, foram discutidas a caracterização dessas biomassas e as suas implicações práticas abordadas na literatura. Posteriormente, foram apresentadas as principais tecnologias e ferramentas para o processamento das biomassas. Por fim, foram retratadas as principais expectativas para trabalhos futuros.

O **Capítulo 3**, designado ***OPTIMIZATION OF SUBCRITICAL WATER HYDROLYSIS OF PECAN WASTES BIOMASSES IN A SEMI-CONTINUOUS MODE***, aborda os resultados dos experimentos referentes às hidrólises com água no estado subcrítico de biomassas residuais de nogueira-pecã. Neste Capítulo, foi apresentada uma introdução acerca do assunto. Ainda, foi descrita a metodologia proposta para o desenvolvimento das hidrólises e dos métodos analíticos realizados para avaliação das soluções hidrolisadas e *in natura*. Após, foram apresentados os resultados obtidos e discorrida uma discussão sobre os mesmos e, por fim, a conclusão geral do trabalho. Ressalta-se que o principal enfoque do Capítulo foi avaliar os teores de açúcares totais em biomassas de pericarpo, folhas e talos e cascas de nogueira-pecã, remanescentes de processamentos industriais.

Finalmente, no **Capítulo 4**, ***ESTRUTURA, CONTRIBUIÇÃO TEÓRICA, CONCLUSÕES E RECOMENDAÇÕES PARA TRABALHOS FUTUROS***, são fornecidas as principais conclusões do trabalho. Inicialmente, foi reportada uma síntese das principais contribuições teóricas deste estudo. Por fim, foram apresentadas a conclusão do estudo e recomendações para trabalhos futuros. Para melhor compreensão das etapas realizadas neste estudo, um fluxograma está apresentado na Figura 2.

Figura 2 – Fluxograma da metodologia aplicada para o desenvolvimento desta Dissertação



Fonte: (Autor).

1.2 INTRODUÇÃO

A nogueira-pecã [*Carya illinoinensis* (Wangenh.) K. Koch] é uma das principais espécies produtoras de nozes. O cenário de produção da noz-pecã tem evoluído nos últimos anos e, em 2019, sua produção foi superior a 140 mil toneladas mundialmente (INC, 2019). Os maiores produtores de noz-pecã são os Estados Unidos e o México, responsáveis por cerca de 55% e 38% da produção global, respectivamente (FRONZA et al., 2018). Entretanto, outros importantes países no cenário agrícola mundial correspondem a uma produção significativa, como Israel, África do Sul, Austrália, Egito, Peru, Argentina e Brasil (THOMPSON & CONNER, 2012). Estima-se que, em 2018, a produção em território nacional foi de, aproximadamente, 7,3 mil toneladas em uma área de cerca de 3,8 mil hectares (IBGE, 2018). No entanto, destaca-se que a produção está concentrada nas regiões sul e sudeste, predominantemente nos estados do Rio Grande do Sul, Santa Catarina e Paraná (BILHARVA et al., 2018). O Rio Grande do Sul é o maior produtor nacional, respondendo por cerca de 74% da produção brasileira e Cachoeira do Sul é o município com a maior área plantada (aproximadamente, 1050 hectares) (BOSCARDIN & COSTA, 2018; FRONZA et al., 2018).

Segundo a Food and Agricultural Organization (FAO, 2017), a produção de noz-pecã no Brasil se encontra em um momento promissor, uma vez que a produção tem avançado significativamente, de cerca de 2,2 mil toneladas em 2007 para mais de 7,8 mil toneladas em 2017. Diante deste cenário, a quantidade de resíduos de nogueira-pecã gerados como resultado dos processos de colheita e processamento industrial tem aumentado consideravelmente nos últimos anos.

Neste sentido, grandes quantidades de materiais residuais são produzidas a partir do processamento das nozes em indústrias e nos processos de colheita. Ainda, destaca-se que para o consumo do produto final das nozes, diversos procedimentos são realizados, como classificação e dimensionamento, fracionamento, descasque e secagem, o que acarreta em maiores volumes destes elementos no ambiente (ÁLVAREZ-CHÁVEZ et al., 2017). Paralelamente, boa parte do fruto da nogueira-pecã não é comestível e o quadro de expansão da produção da cultura tem resultado no aumento de seus coprodutos lançados no ambiente (ALVAREZ-PARRILLA et al., 2018). É um cenário bastante preocupante, considerando-se que até 80% (25 a 30% – pericarpo e 49% – casca) do peso total das nozes é referente a esses resíduos, caracterizados como bioprodutos de grande potencial (IDOWU et al., 2017).

As biomassas de nogueira-pecã constituem materiais ricos em lignocelulose (lignina, celulose e hemicelulose) e de grande potencial de uso (OZCARIZ-FERMOSELLE et al., 2018).

Além disso, a lignina apresenta características de uma matéria-prima biodegradável, o que é de grande vantagem ao meio ambiente. Nas células vegetais, moléculas biológicas, como celulose, hemicelulose e lignina, são fortemente ligadas, formando estruturas rígidas da parede celular e compreendendo a biomassa lignocelulósica que deve ser decomposta para isolar a lignina (GANEWATTA et al., 2019). Entretanto, um dos fatores que impossibilita a conversão eficiente da biomassa lignocelulósica em produtos com valor agregado é sua recalcitrância inerente à desconstrução enzimática. Além disso, as barreiras físicas e químicas proporcionadas pela lignina e hemicelulose às enzimas celulolíticas são apontadas como agentes notáveis dessa resistência (NITSOS et al., 2019). Desta forma, salienta-se a importância de desenvolver estudos que explorem tecnologias eficientes para a desfragmentação do complexo lignocelulósico de modo a agregar valor às biomassas, e que investiguem a composição química, morfologia da estrutura vegetal e detecção de compostos potenciais nestes materiais.

Considerando-se o potencial de aplicabilidade dessas biomassas, é importante destacar a necessidade de atribuir maior atenção ao reaproveitamento destes materiais, explorando a sua potencialidade, agregando valor aos coprodutos e possibilitando a aplicação de tecnologias ambientalmente promissoras no seu processamento. Nesta perspectiva, inúmeros procedimentos e tecnologias inovadoras que visam agregar valor às biomassas residuais ricas em lignocelulose têm sido usados nas etapas de pré-tratamento dos processos de hidrólise (AKHTAR et al., 2016). No entanto, diversos atributos devem ser considerados de modo que ocorra otimização do processo de exploração eficiente da biomassa, como a utilização de tecnologias que requerem baixo consumo energético, degradação mínima e máximo aproveitamento dos componentes empregados (HRNČIČ et al., 2016).

Frente a métodos convencionais, a tecnologia hidrotérmica consiste na decomposição hidrolítica de materiais ricos em lignocelulose em água quente pressurizada, convertendo a celulose e outros polissacarídeos em açúcares redutores, sem a necessidade da adição de solventes orgânicos, de altos custos e ambientalmente indesejáveis, com uma alta taxa de seletividade e altas taxas de reação (FUNAZUKURI & OZAWA, 2019). O tratamento hidrotérmico pode obter produtos com porcentagens mais baixas de defeitos (FREITAS et al., 2019). Ainda, esta técnica possui a capacidade de produzir grandes quantidades de açúcares e modificar as características estruturais dos resíduos vegetais (SANTANA et al., 2017).

Com isso, a tecnologia utilizando água subcrítica surge como uma alternativa em destaque, caracterizando-se como uma prática ambientalmente amigável e de baixo custo, atuando diretamente no campo da sustentabilidade (MOHAN et al., 2015a). Ainda, a tecnologia subcrítica permite prontamente a conversão da biomassa em açúcares, contidos nas matriz lignocelulósica, o que oferta um amplo potencial de aplicabilidade destes resíduos (LIANG et al., 2017; PARK et al., 2012). Essa prática utiliza a água como solvente, um elemento de baixo custo e ambientalmente viável (ZAKARIA et al., 2017). Com isso, gastos com solventes orgânicos, substâncias de alto custo e ambientalmente indesejáveis, são descartados (TODD & BAROUTIAN, 2017). No estado subcrítico, o produto iônico da água aumenta com a temperatura, resultando na formação de íons hidrônio (H_3O+) e hidróxido (OH–), permitindo que a água nestas condições atue como um catalisador ácido ou básico (POWELL et al., 2017).

Vários estudos utilizando a abordagem da tecnologia subcrítica têm sido retratados na literatura em modo descontínuo, semi-descontínuo e contínuo com diferentes biomassas lignocelulósicas (POSMANIK et al., 2017; PRADO et al., 2015; SHITU et al., 2015). Em modo descontínuo, a biomassa e a água, aquecidas, são carregadas simultaneamente no reator e nenhum produto é removido durante a reação, resultando na degradação dos açúcares. Já em modo semi-contínuo, determinada quantidade de biomassa vegetal é carregada no reator enquanto a água flui continuamente, removendo os produtos da reação de modo que não ocorra degradação dos açúcares (MARULANDA-BUITRAGO & MARULANDA-CARDONA, 2017). Desse modo, o emprego de tecnologias hidrotérmicas tem sido promissor para a conversão de resíduos com altos teores de lignocelulose. Grande parte das reações hidrotérmicas requerem altas temperaturas e pressões, mas tecnologias de reação eficientes com recuperação de calor e baixas temperaturas foram desenvolvidas para minimizar o custo energético (ZHAO et al., 2014). Ainda, o tratamento hidrotérmico oferece inúmeras outras vantagens, como rápida taxa de reação e substituição de ácidos/bases por um solvente mais ambientalmente aceitável, compatibilidade com alimentos úmidos, uma vez que a água presente pode ser utilizada, desprezando a etapa de secagem utilizada em métodos convencionais (LACHOS-PEREZ et al., 2017).

Também, a água em estado subcrítico (T_c = 100 a 374 ºC e P_c = 22 MPa) caracteriza-se como um solvente viável para os processos de hidrólise. Esta tecnologia tem visado a utilização da biomassa residual como fonte de matérias-primas para novos produtos e redução da geração de grandes volumes de resíduos lançados no ambiente (YOSHIDA et al., 2015). Em condições de alta pressão e altas temperaturas, há uma maior penetração da água na matriz da estrutura lignocelulósica. Isso se dá em função da influência da temperatura e pressão nas propriedades físico-químicas da água, mantendo a água em estado líquido durante a reação (COLORADO et al., 2019; COCERO et al., 2017).

As características dos solventes influenciam diretamente a seletividade do processo e as taxas de transferência de massa entre os elementos. A utilização de água, somente, ou como parte de uma mistura de solventes miscíveis é eficiente nos processos de extração de compostos polares a moderadamente polares, em diversos materiais residuais de grande potencial de aplicabilidade. Em função de suas características fisico-químicas, antioxidantes, compostos fenólicos e carboidratos estão entre os principais compostos extraídos usando água como solvente. A temperatura é uma variável de grande importância nesse processo. Salienta-se que um aumento na temperatura de extração aumenta a taxa de extração em constantes de difusão e solubilidade crescentes. A última etapa do processo de extração é controlada por difusão e pode resultar em maior eficácia com o aumento da temperatura da reação (LACHOS-PEREZ et al., 2017).

Desta forma, é de grande interesse o uso de alternativas que resultam na agregação de valor destes coprodutos de forma eficiente e, ao mesmo tempo, sustentáveis. Uma importante estratégia é a aplicação de tecnologias de processamento visando à obtenção de açúcares redutores através do processo de hidrólise da matéria-prima lignocelulósica, concedendo ampla valorização às inúmeras aplicabilidades destes materiais.

1.3 ESTADO DA ARTE

É importante salientar a carência de trabalhos científicos que tem como propósito abordar o processo de hidrólise em produtos de nogueira-pecã, tampouco àqueles relacionados aos materiais remanescentes da espécie. Particularmente, o mesmo cenário é observado a respeito da tecnologia que utiliza água no estado subcrítico em modo semi-contínuo no processo de hidrólise de materiais originados de matéria-prima da nogueira-pecã ou biomassas residuais de demais espécies vegetais.

A partir de uma investigação detalhada utilizando a combinação dos termos ‘pecan’, ‘hydrolysis’, ‘subcritical water’ e ‘reducing sugars’ nas principais plataformas no meio científico, como Scopus®, Scielo®, Web of Science®, Science Direct® e Questia Research® não foram encontrados trabalhos científicos que comprovem a abordagem do processo de hidrólise em água subcrítica aplicada em materiais remanescentes de nogueira-pecã. De acordo com a avaliação científica, há um número reduzido de estudos atuais desenvolvidos visando a espécie da nogueira-pecã, focando, apenas, nas demais espécies produtoras de nozes.

Além disso, uma gama de estudos utilizando outros procedimentos com o objetivo de avaliar uma composição de forma mais ampla em biomassas de espécies vegetais têm sido reportados. Boa parte destas pesquisas se concentra na caracterização das matérias-primas visando os setores industrial e econômico e, positivamente, não se limita apenas aos produtos mais desejados das plantas, como frutos e óleos, o que é favorável para o aproveitamento dos materiais remanescentes.

Estudos desenvolvidos com base nas cascas da nogueira-pecã revelaram concentrações de compostos fenólicos, taninos e flavonoides, o que mostra a possibilidade de utilização destes materiais para a obtenção de compostos bioativos (FLORES-ESTRADA et al., 2019; PRADO et al., 2013). A literatura relata a presença de biocompostos, nas cascas, de grande potencial de aplicabilidade em vários setores, o que se caracteriza como um benefício econômico significativo e atua como uma alternativa sustentável (ÁLVAREZ-CHÁVEZ et al., 2017). Ainda, constatou-se que há uma grande concentração de fibras e carboidratos nas cascas de nogueira-pecã, o que, inclusive, pode ser utilizado na alimentação humana (DOLAN et al., 2016; PRADO et al., 2009a). De acordo com as folhas da nogueira-pecã, grandes quantidades de flavonoides e compostos fenólicos têm sido relatados (ALVAREZ-PARRILLA et al., 2018; EL HAWARY et al., 2016). Ainda, grandes concentrações de polifenóis, carboidratos, fibras e taninos foram encontrados na composição dos pericarpos da nogueira-pecã (CORRAL-ESCÁRCEGA et al., 2017). Desta forma, percebe-se a abundância de estudos relacionados à caracterização das propriedades químicas de matérias-primas residuais da nogueira-pecã. Entretanto, em relação à quantificação e caracterização dos açúcares, a literatura se restringe ao uso das nozes, desprezando a aptidão das demais matérias-primas provenientes das plantas (IDREES et al., 2014; KAZANKAYA et al., 2008; VENKATACHALAM & SATHE, 2006).

Além disso, a literatura tem retratado a utilização de inúmeras outras metodologias para os processos das reações de extrações de compostos utilizando matéria-prima vegetal de nogueira-pecã, como o emprego de alcalase (HU et al., 2018), dióxido de carbono (SEABRA et al., 2019), gás liquefeito de petróleo (ALVES et al., 2019), acetona (GAO et al., 2019), substâncias ácidas e alcalinas (ROBBINS et al., 2015; ABE et al., 2010), etanol e metanol (JACOPIČ et al., 2009) e hidrólise enzimática (SUN et al., 2019; QIN et al., 2017).

Em tese, é evidente a escassez de estudos científicos pertinentes à aplicabilidade da tecnologia subcrítica em materiais residuais de nogueira-pecã, bem como aqueles relacionados à utilização destes coprodutos para a determinação de açúcares redutores. Isso evidencia a necessidade de desenvolvimento de pesquisas que possibilitem atribuir agregação de valor e um aproveitamento sustentável destes componentes. Diante disso, o presente trabalho se caracteriza por sua natureza inédita e inovadora, empregando uma tecnologia vantajosa para obtenção de açúcares redutores, e um estudo pioneiro acerca desta temática, viabilizando o interesse de futuras pesquisas relacionadas ao tema.

1.4 OBJETIVOS

1.4.1 Objetivo geral

O objetivo deste estudo foi avaliar o processo de hidrólise de biomassas de nogueira-pecã com água subcrítica visando à obtenção, quantificação e caracterização dos açúcares redutores.

1.4.2 Objetivos específicos

a) Fornecer informações pertinentes ao cenário atual da produção de noz-pecã, caracterização dos materiais residuais resultados desse processo e as tecnologias empregadas para extração de compostos de interesses desses coprodutos e suas principais aplicações;
b) Análise e caracterizações físico-químicas das biomassas de pericarpos, folhas e talos e cascas de nogueira-pecã em condição *in natura* e após a hidrólise por meio da análise termogravimétrica (TGA), microscopia eletrônica de varredura (MEV) e espectroscopia no infravermelho com transformada de Fourier (FT-IR);
c) Análise e caracterização morfológica das biomassas de nogueira-pecã em condição *in natura* e após a hidrólise por meio de microscopia eletrônica de varredura (MEV);
d) Obtenção de açúcares redutores por meio de espectrofotometria e determinação do rendimento e eficiência de conversão para as diferentes biomassas de nogueira-pecã;
e) Parametrização das condições ótimas do processo de hidrólise para as diferentes biomassas da nogueira-pecã em função do ajustamento de variáveis fundamentais para o processo;
f) Caracterização do meio hidrolisado e determinação de açúcares redutores e inibidores através de cromatografia líquida de alta eficiência (CLAE).

CAPÍTULO 2

POTENTIAL APPLICATIONS OF PECAN RESIDUAL BIOMASSES: A REVIEW

Potential applications of pecan residual biomasses: a review

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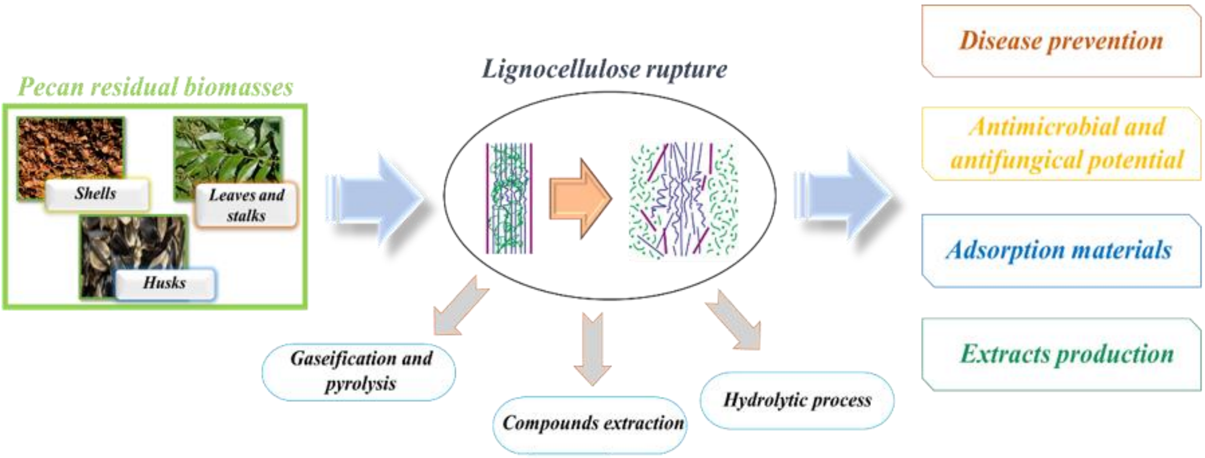
Graphical abstract



Abstract

Considering a large amount of high potential materials coming from the processes to obtaining pecan nut, there are important future perspectives to enable an increase of using pecan materials. For this, structural support and the development of scientific research are needed to reuse the wastes in an environmentally friendly way. Thus, the aim of this scientific research is to present a detailed literature overview regarding the characterization of pecan waste materials, the main applications and technologies used to add value to these materials. The study is fundamentally based on the scientific literature related to obtaining products from pecan wastes and their application in food-related areas. The lack of sufficient data on the proposed theme requires a properly structured approach to provide a clear perspective on the subject and to highlight the current limitations. It is evident that pecan culture has presented a prosperous context with respect to the world and Brazilian production. The scientific literature presented many studies that employ the approach of using remaining pecan materials. Thus, it is clear the range of fields that apply the residuals for the most diverse purposes, which enables them to add value to pecan coproducts.

Keywords: *Carya illinoinensis* (Wangenh.) K. Koch. *Lignocellulosic materials. Pecan coproducts. Sustainability. Vegetable wastes. Food reuse.*

2.1 INTRODUCTION

Considered the diversity of nut-producing species, the pecan [*Carya illinoinensis* (Wangenh.) K. Koch] is characterized as one of the largest nut producers. The International Nut and Dried Fruit Council Foundation (INC) identified that, by 2019, the total production was over 140,000 tons worldwide [1]. These results have shown marked growth in pecan cultivation, considering that in 2008/09 harvest the production was just over 60,000 tons. As a trend observed for years, Mexico and the U.S. dominate pecan nut production, accounting for, approximately, 130,000 tons, which correspond to about 90% of global production. These countries are important exporters of pecan nuts, meeting the demand for this product in various regions, such as Europe, China and South Korea.

The increased production of pecan nuts generates a large amount of waste as a consequence of harvesting and industrial processing. Considering only pecan shells, it is estimated that approximately 420,000 tons are produced worldwide every year [2]. Also, up to 50% of the total weight of a pecan nut is accounted to the shell and up to 80% is accounted to shell and husk [3,4].

It is important to assign high attention to the reuse of pecan wastes biomasses, thus exploring the potential of these materials for resulting in higher added value to their coproducts. These materials contain high concentrations of cellulose, hemicelluloses and lignin [5]. Also, a range of applications of pecan coproducts is known, especially in the extraction of compounds of interest for use in different fields of application, such as the biofuel production, pharmaceutical and food industries. Thus, considering the importance of the pecan nut residue and the materials generated from the processes of obtaining pecan nut, the aim of this scientific research is to present a detailed literature overview regarding the characterization of pecan waste materials, the main applications and technologies used to add value to these materials.

2.2 SCOPE

This review analyzes the existing literature about the importance of the pecan nut in the current panorama. Thus, it is reported the technologies used to process the remaining materials of this species. The main purpose is to expand and to encourage the development of numerous studies on the subject, defining the scenario for this study and helping to identify the most relevant and appropriate points for this research. The work is fundamentally based on the literature related to obtaining materials from pecan wastes and the applicability of these components.

The literature related to waste vegetable materials presents a wide field of study. However, this approach is still scarce considering the pecan culture, which shows the need for more studies about this subject. Therefore, the lack of academic studies on the subject highlights the need to develop properly structured works in order to provide information about the current panorama related to the subject and highlight its main constraints.

Briefly, Section 3 reports the current landscape of pecan culture, focusing on the socio-economic performance of culture at national and international levels. This section provides a historical and economic overview of the culture, providing an economic analysis in Brazil and around the world.

Section 4 explores what the scientific literature addresses the characterization of pecan waste materials. The section begins with studies related to observations pertaining to the husks. Consequently, it describes information about the leaves and stalks. In conclusion, the section discusses the characteristics of pecan shells.

Section 5 examines the current works that employ the approach of using remaining pecan materials. The objective is to understand the range of fields that apply the residuals for the most diverse purposes, which enables them to add value to the coproducts generated from pecan biomasses. Likewise, Section 6 provides information on the key-technologies employed for processing nuts within the main context of this study, namely obtaining pecan hydrolyzed materials.

Finally, Section 7 provides an overview of the various applications of pecan biomass and a discussion of its importance. It also presents a brief report on the fragmented literature on the topic and the main future expectations for the research.

2.3 PECAN FEATURES AND CURRENT PECAN PRODUCTION SCENARIO

Pecan [*Carya illinoinensis* (Wangenh.) K. Koch] is a species belonging to the genus *Carya* of the Juglandaceae family. It is noteworthy that the Juglandaceae family presents several other nut-producing species, standing out the pecan as an important supplier of nuts. The structure of the fruits produced is composed of the pecan, husks, shells and, finally, leaves and stalks, which constitute the residual plant materials (Figure 3).

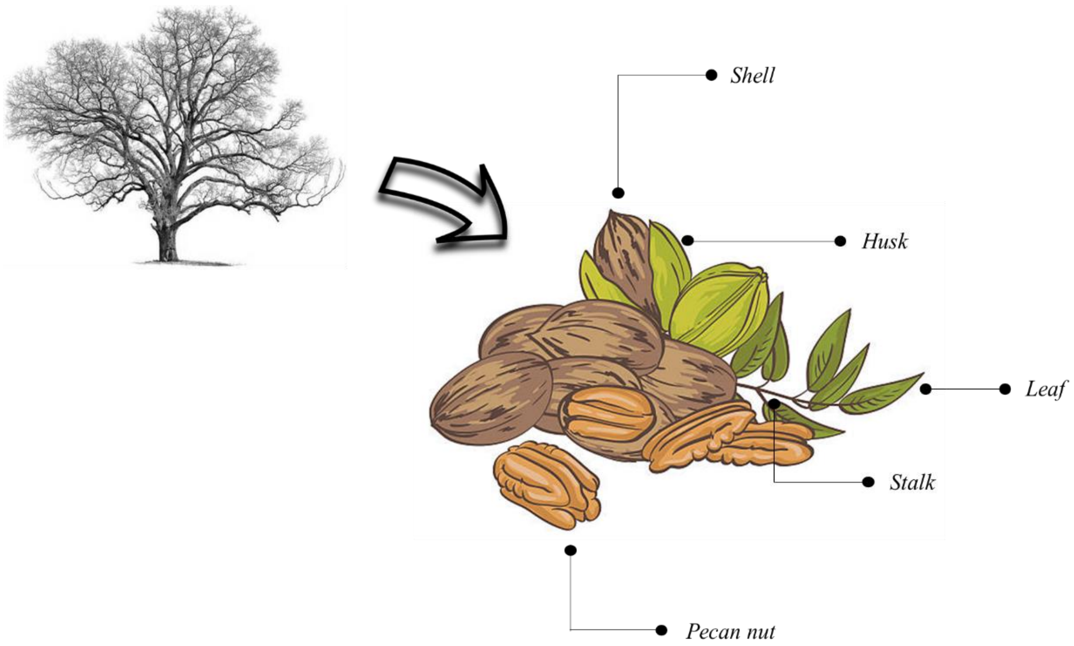


Figure 3. Structural components of pecan trees.

The production status of pecan trees has shown promising results in recent years. According to INC, in 2019 total production exceeded 140,000 tons worldwide [1]. In 2007, this value was close to 60,000 tons. Therefore, it is noteworthy that crop production grows at a rate of approximately 30% annually [1].

The species *Carya illinoinensis* is originated from the Milder Southern U.S. [6]. Mexico (52%) and the U.S. (40%) account for over 90% of pecan nut production. In 2019, these two countries produced approximately 72,000 and 56,000 tons, respectively. In addition, South Africa (7%, 10000 tons) and Australia (1%, 1000 tons), rank as other important leading producers of pecan nuts in the world. However, considering the easy adaptability of the species, its current geographical location covers a significant area around the planet [7,8]. Recently, pecan cultivation presents a globalized panorama, not limited only to the region of origin, but is found in several regions. Countries such as China, Argentina, Uruguay, Peru, Chile and Brazil are also pecan nut producers [9]. Figure 4 presents the current pecan nut production scenario worldwide.

Figure 4. Current pecan nut production worldwide scenario.

2.4 RESIDUAL BIOMASSES CHARACTERIZATION

Pecan processing has as its main purpose to obtain the pecan nut. However, coproducts, or plant biomasses, are generated in the midst of this process, such as husks, leaves, stalks and shells. It is estimated that more than 420,000 tons of pecan shells are produced annually worldwide [2]. Thus, an analysis of the composition of these materials becomes pertinent when it is intended to verify their potentialities, aiming at adding value and applicability in various fields of study.

Also, a perception of the physicochemical properties of pecan lignocellulosic biomasses is essential for the processing of conversion of biomasses to desired products. As presented earlier, these materials are rich in cellulose, hemicelluloses, and lignin (Figure 5). However, there are other compounds of great interest especially using as renewable energy and for the production of bioproducts. Generally, lignocellulosic materials have a mass composition of 35 to 55% cellulose, 20 to 40% hemicelluloses and 10 to 25% lignin, and other elements such as extracts and minerals [10].

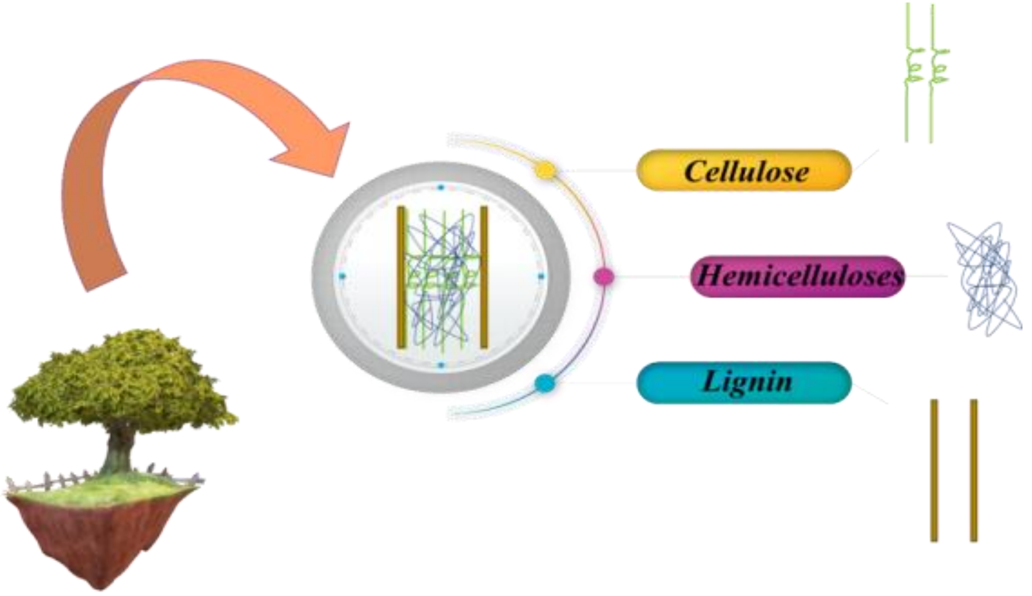


Figure 5. Coproducts generated from processing to obtain pecan nut.

Cellulose is an important polymer in the world, being glucose ($C_6H_{12}O_6$) consisting of chains of 1,4-D-glucopyranose units linked in the β1,4 configuration. It is emphasized that the crystalline portion of the cellulose is insoluble and forms the skeletal structure of the cell. On the other hand, hemicelluloses is shorter and complex polysaccharides, containing several chains that are also located with cellulose in the cell wall. Shorter chains of xylose, arabinose, galactose and monosaccharides are attached to the hemicelluloses chains, creating a branched polymer. In contrast to cellulose, hemicelluloses are heterogeneously branched polysaccharides that bind non-covalently to the cellulose surface. Finally, lignin is characterized as the largest structure of the cell wall. Lignin is composed of three carbon chains attached to six-carbon rings. It is this component that acts on the rigidity of plant cell structure [11].

In general, studies present that lignin and cellulose are abundant constituents in pecan waste materials. The Figure 6 shows some studies that have reported the composition of different parts of the plant, such as shells, husks and branches, with the proportions of the lignocellulosic complex found in the pecan shells (a) [12-15], branches (b) [16] and husks (c) [17].

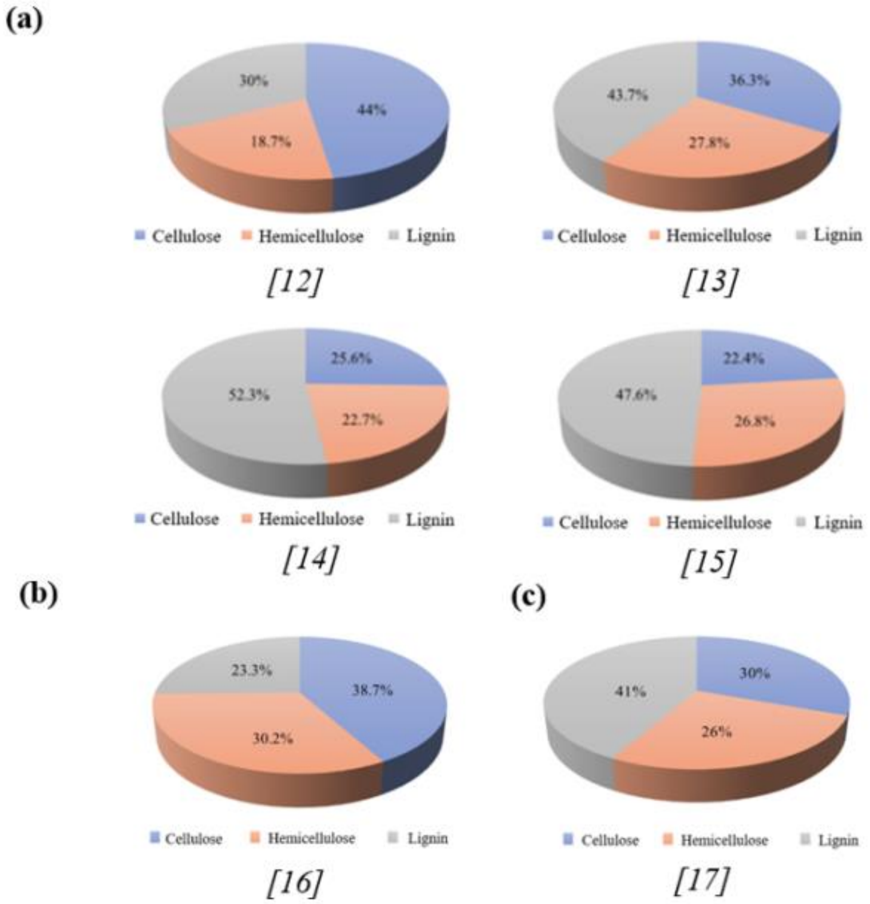


Figure 6. Lignocellulosic composition of pecan shells (a), branches (b) and husks (c).

Also, important biocompounds have been obtained from the exploration of chemical compounds from pecan raw materials. In general, data about these compounds is fragmented and restricted to nuts to a greater extent. However, some studies have been found, where Table 1 presents the parameterization of these components and related studies.

Table 1 - Characterization and applicability of pecan biomasses compounds.

Coproduct	**Observed compounds**	**Objectives**	**Reference**
Shells	Phenolic compounds (acids, catechin, epicatechin, and others)	Chemical composition study for health application	*[18]*
	Lipids, proteins, fibers, carbohydrates and tannins	Modeling and kinetic and adsorption studies	*[19]*
	Phenolic compounds (catechin, and others), tannins and antioxidant extracts	Nutraceutical and food application	*[20]*
	Phenolic extracts and antioxidants	Antioxidant action for biofuel production	*[21]*
Leaves	Flavonoids (rutin, kaempferol, and others) and phenolic compounds (acids)	Potential of chemical composition for health application	*[22]*
	Nutrients (manganese, nitrogen, boron and others)	Nutritional characterization for application in various fields	*[23]*
Husks	Lipids, proteins, fibers, carbohydrates and tannins	Modeling and kinetic studies	*[19]*
	Flavonoids, phenols, acids and others	Chemical characterization and antioxidant, antimicrobial and antiproliferative action	*[24]*

2.5 RECENT APPROACH AND APPLICABILITY OF PECAN RESIDUAL MATERIALS

This section presents a brief review of studies involving the applicability of pecan wastes for various purposes. It is noted that the current studies about this subject are lacking. However, some studies related to the exploration of the potential of pecan biomass have been reported in the academic field, such as its application in the field of medicine due to its many advantageous properties in disease prevention. The purpose of this section is to enable the use of pecan wastes as materials of wide interest in various fields of study, such as disease prevention and extracts production.

2.5.1 Disease prevention

A range of important phenolic compounds is present in plant species. These components are of great nutritional and medicinal concern due to their potent antioxidant capacity. The potential of pecan waste materials in the medical field has recently gained recognition. The use of pecan shells, specifically, has been reported as an efficient alternative in the treatment of various diseases [25].

The shells have a high antioxidant potential due to the high amount of phenolic compounds and fatty acids, which makes pecan as a species of great importance for pharmacological activities [26]. It is estimated that the concentration of these elements can reach 167 mg/ g gallic acid [4]. In this context, studies have shown that aqueous extracts of pecan shells (rich in acids such as gallic, 4-hydroxybenzoic, vanillic, chlorogenic, caelic and ellagic) have the ability to induce breast cancer cell death and increase breast cancer survival time of patients with certain tumors [18, 27]. Also, shell in fresh condition has been used in nutraceutical products against obesity, hypercholesterolemia and as a source for the precaution of metabolic and inflammatory diseases, neurological disorders, gastric ulcers, and cancer [28]. These residues act as antinociceptive and antiedematogenic materials due to the high concentration of rutin, or vitamin P, in its composition [29]. Also, pecan leaves have been reported as antifungal materials, applied as important inhibitors of tuberculosis-causing bacteria activity [26]. Husks have been shown to be special components in antioxidant, anti-proliferative (against lung, colon and cancer diseases) and antimicrobial activities due to the concentration of phenols and flavonoids in their composition [24].

2.5.2 Antimicrobial and antifungal potential

Numerous compounds obtained from plants or plant waste biomasses have a high potential to inhibit microbial and fungal activities. The current studies have shown pecan residues as materials with great potential as new sources of fungicides for the control of pathogenic fungi, as well as the application for bacterial inhibition. Due to a significant accumulation of acids and other phenolic compounds of antioxidant function, it was found that pecan shells act as inhibitors of gram-positive bacterial activities, such as *Listeria monocytogenes*, *Staphylococcus aureus*, *Bacillus cereus* and *Vibrio parahaemolyticus* [30]. Also, antimicrobial activity has been investigated against *Staphylococcus aureus*, *Bacillus cereus*, *Listeria monocytogenes*, *Listeria inoccua*, *Salmonella Enteritidis*, *Aeromonas hydrophila* and *Pseudomonas aeruginosa* [31]. Shells have also been reported to have antifungal action, mainly due to the presence of polyphenols, inhibiting the growth of *Pythium* sp., *Colletotrichum truncatum*, *Colletotrichum* sp., *Alternaria alternata*, *Fusarium solticillio*, *Fusarium sambucinum* and *Rhizoctoniasolani*, which are the major causes of diseases in important crops of agricultural interest [32]. In addition, it has been reported that pecan leaves have antimicrobial and antifungal performance, essentially due to the high concentrations of flavonoids, phenolic compounds (gallic acid, catechin, rutin, among others) and tannins in the action against various bacteria and fungi [33].

2.5.3 Adsorption materials

Activated carbon adsorption is an important and efficient technique for removing contaminants from waste residues treatments. Although many materials are explored for the production of activated carbon, raw materials are widely used due to their wide availability in the environment and reduced costs, making them attractive options and sources of raw materials for activated carbon production [34].

The potential regarding the use of pecan shells as adsorbent material is significant and more efficient compared to other conventional materials, considering characteristics such as surface area (902 m^2/g), density (0.5 g/m^3), friction capacity (12.8%) and conductivity (331 μS) [35]. Another study was developed based on the adsorptive capacity for Cu^{2+}, Pb^{2+} and Zn^{2+} ions, where the shells showed excellent results in the adsorption of these elements [36].

Furthermore, the activated charcoal of pecan shells treated with sodium dodecyl sulfate was efficient in the removal of methylene blue in aqueous solution, allowing the use of these residues as raw material for cost-effective and sustainable charcoal production [37]. These wastes are also efficient in removing up to 100% of the iron present in contaminated water over a surface area of 1516.5 m^2/g and a volume of 0.7 cm^3/g [38]. Also, experiments referent to the economic evaluation to obtain activated carbons from pecan shells were performed and about 1370 kg of steam-activated and 2964 kg of acid-activated pecan shell carbon could be produced everyday with low costs (U$S 18/h and U$S 2.72/kg) [39].

2.5.4 Extracts production

Extracts of pecan residual materials have shown great application potential. Pecan shell extracts, rich in phenolic compounds, were effective in inhibiting cancer cells, decreasing the viability of these cells and preventing the cell cycle. The stimulation of important proteins involved in cell death and cell cycle regulation was the mechanism involved in the observed effects. In addition, it was evidenced that the extracts have the ability to cause DNA damage to tumor cells, indicating that pecan shell extracts can be considered an important alternative to the treatment of some tumors [18].

Studies have also reported that pecan shell extracts have the ability to inhibit the germination of species such as lettuce (*Lactuta sativa* L.) at concentrations higher than 5 kg/m^3, showing that these residues have allelopathic potential and can be employed as natural herbicides [40]. This allelopathic potential was also found when shells were disposed of as mulching, inhibiting weed development in crops of fruit species [41].

Another study involving pecan shell extracts showed that these materials can be used to prevent the degradation in soybean biodiesel production. The addition of these antioxidants is carried out during the soybean biodiesel washing process in an unconventional manner. The concentrations of the extracts that provided the longest induction time for the biodiesel were the ethanol extract of the husks at a concentration of 5 g/L (9.45 h), aqueous extract of the shell at a concentration of 12 g/L (7.40 h) and methanol extract and shell water at a concentration of 12 g/L (7.37 h) [21].

2.6 TECHNOLOGIES FOR EXTRACTION OF COMPOUNDS OF THE BIOMASSES OF PECAN

A range of processing technologies applied in pecan biomasses is presented in the scientific literature, as well as their main benefits and limitations. Gasification and pyrolysis, compounds extraction and enzymatic/ acid/ alkaline hydrolysis have been employed and are reported in the literature.

An indispensable component in the efficiency of lignocellulose rich material extraction procedures is the technology, or technology integration, adopted for the process. The literature reports several technologies employed in order to add value to these materials. However, other factors should be considered, such as minimal energy exploitation and techniques that do not result in environmental contamination [42]. Numerous chemical solvents and procedures involving high energy consumption have been reported as major concerns related to these processes. In addition, the combination of high costs, minimum yields and/or desirable element losses should be considered with full attention [43]. Developed studies that approach technologies of extraction with pecan residual biomass have been evidenced in the academic-scientific environment. These works present several applications associated with these materials, aiming at obtaining value-added products.

2.6.1 Gasification and pyrolysis

Gasification and pyrolysis are some of the main technologies adopted to add value to the reused pecan biomasses. Gasification is the process of transforming liquid and/or solid materials into a gas mixture, widely used for power generation or biofuel production. The expansion of this practice is a result of the growing concern with the environment and the increase in conventional fuel prices [44]. Pyrolysis is one of the main processes involving gasification and is characterized as the conversion of solid material into a carbon-rich compound and a volatile solid, which will be partially condensed into a liquid fraction [45]. It is of great interest to the systematic impact of gasification and pyrolysis process conditions on production studies and characterization of products generated from these technologies [46]. The literature has reported some studies involving the application of these technologies in remaining pecan materials.

Considering the importance of the product generated from pyrolysis, studies have found suitable conditions of this technique to evaluate the behavior of elements and functional groups present in pecan shells. It was found that in a temperature range between 300 and 500 ºC, changes occurred and the removal of functional groups from the surface of the pyrolysis product generated, as well as a change in the shell structure, and an increase of gaseous products, such as methane, carbon dioxide, and ethane [47]. In addition, other studies have reported the adsorptive capacity of pecan waste materials from the application of pyrolysis. Also, the carbon resulting from the pecan shells pyrolysis technique absorbs a large number of different metals and organic elements present in processing wastewater. Approximately 3000 kg of shell-based products can be produced daily and the results are higher than those found in conventional commercial carbon [38]. Similar results were observed from the pecan husks, characterized as a highly efficient bio sorbent in acid and lead adsorption, with a worship performance of up to 79 mg/g of these substances [17].

2.6.2 Compounds extraction

Phenolic compounds are characterized as the main bioactive groups present in plants and include flavonoids, tannins, phenolic acids, among others [48]. Current literature addresses a range of extraction technologies for these compounds in plant species and their wastes materials, such as infusion extraction, ultrasound-assisted extraction, and Soxhlet extraction.

Extraction by infusion is characterized by the contact of vegetable biomass and solvent (normally water) in a given period under boiling conditions. Studies involving pecan shells related to this technique as an extremely efficient method referring to obtaining phenolic compounds, tannins, and antioxidant actions compared to other methodologies such as ethanol extraction and supercritical extraction [30]. Also, it was found that aqueous extracts of pecan shells from the infusion process tests presented inhibitory activities against a variety of pathogenic bacteria of major importance, as well as the potential use of natural conservatives of chemical foods for food industries [31].

Moreover, ultrasound-assisted extraction is an extraction process facilitated by the behavior of mechanical waves under high pressures and temperatures [49]. This technology can be completed quickly and with low consumption of organic solvents, which is extremely advantageous from a sustainable viewpoint [50]. Studies have pointed out the applicability of extraction in the characterization of compounds of pathological interest present in pecan shells.

Finally, Soxhlet extraction is based on the extraction of lipids and other solid-state substances in contact with a solvent at high temperatures [51]. This method has been widely used due to its ease of processing, minimal environmental contamination, strong interaction between samples and solvent, and large-scale application capability [52]. Numerous studies have indicated the application of this technique in pecan waste materials, mainly aiming at characterizing the physicochemical composition and obtaining properties that present activity against pathogens of these residues. Studies have shown that the application of this method and methane as a solvent allowed a detailed analysis of the pecan shell composition, characterizing the phenolic compounds, tannins and lipids present in these materials, as well as a morphological evaluation of their structure [53]. In addition, the obtaining of antioxidant materials from pecan shells by the Soxhlet and methane method as a solvent was effective in inhibiting the activity of a range of bacterial microorganisms [54]. Finally, the use of hexane as a solvent allowed the extraction of important compounds in the shells and pecans, such as polyphenols, acids and antioxidant and antiproliferative substances [55].

2.6.3 Hydrolytic process

Hydrolysis reactions consist of breaking the chemical bonds of substance molecules by the action of water. Chemical materials of different natures (acid and alkaline substances) have been used as solvents in hydrolytic processes, as well as the use of microorganisms (enzymatic biotechnology) capable of hydrolyzing the components of the lignocellulosic matrix. In the current literature, the procedures involving pecan raw materials and the hydrolysis technique as a technology for extracting compounds have been widely portrayed aiming at obtaining walnut oils and compounds [56-60].

Regarding the pecan remaining materials, some studies have reported that the use of substances such as sodium citrate and cellulase and certain conditions in the enzymatic hydrolysis process is effective in obtaining compounds present in the shells, which can be used to produce biofuels [61]. Moreover, hydrolyzed pecan shells solutions subjected to acid/ alkaline hydrolysis (acetone: water, 70:30, v/v) were detected with high concentrations of phenolic compounds of high antioxidant capacity (up to 633 mg CAE/ g) as ellagic acid, gallic acid, and others [62]. In addition, pecan shell hydrolysis by supercritical conditions also resulted in high concentrations of phenolic compounds of high antioxidant capacity, as well as acting as potential antimicrobial materials, inhibiting the development of *Vibrio parahaemolyticus*, *Staphylococcus aureus*, *Listeria monocytogenes* and *Bacillus cereus* [30].

2.7 General background and expectations

Considering the information presented in this review, it is clear that pecan culture has presented a prosperous status with respect to the world and national production. However, as a result of this scenario, there is a large amount of waste materials generated and disposed of in the environment. As previously presented, some authors report that up to 80% (25 to 30%, husk; 49%, shell) of the pecan corresponds to the coproducts produced by the plants. These materials, coming from harvesting processes and industrial processing, remain in nature and can cause serious environmental problems. In common for the husks coproducts, leaves and stalks and shells, high contents of lignocellulosic material are evidenced. This context refers to the various applications of these wastes as renewable sources for biofuel production, energy sources and bioproducts generation.

Recently there has been a major concern about the environment. This situation is due to the alarming situation of population growth experienced in recent years and, consequently, the increased production of food and waste generated from it. Thus, the application of vegetable wastes stands out as an important alternative to be employed in relation to other products in food-related areas. Considering the concept of biorefinery as a sustainable technology, these materials have been applied in a range of studies for various purposes, such as synthesis of polymers, organic fertilizers, human and animal feed and industrial purposes, with pharmaceutical and biotechnological aptitude.

This scenario highlights the expansion of studies that use the approach of reusing these materials, which is characterized as a very optimistic perspective. From an investigation of the modern literature about the applicability of pecan waste materials and the technologies employed for the purpose of exploration and value addition of these coproducts, it is clear that several procedures have been used to extract compounds and elements of interest for various purposes. Furthermore, it is noteworthy that many companies have been using environmentally advantageous techniques for large-scale reuse of plant residues, such as ReGrained®, located in San Francisco, U.S.; Renmatix, Inc®, in Montreal, Canada; AINIA® in Valencia, Spain; and Bio-on® in Bologna, Italy. Also, it is important to note that there are academic-scientific organizations that address the same context, such as The Ohio Bioproducts Innovation Center (OBIC), located at The Ohio State University in Ohio, U.S.

In view of this context, it is evident that many alternatives have been portrayed as promising techniques regarding the processing of these coproducts, considering the concept of biorefinery. Nowadays, about 1/3 of the food produced in the world is wasted. This scenario occurs at the same time as more than 1 billion people suffer from food shortages. Pecan residues constitute only a small portion of this problem. However, as evidenced earlier, more than half the weight of pecan is waste material and a coproduct of great potential. Thus, it is necessary to increase the use of pecan coproducts in large proportions and for multiple purposes. This review presented the main applications of pecan waste reported in the current literature, pointing out the potential use of these materials.

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CAPÍTULO 3

OPTIMIZATION OF SUBCRITICAL WATER HYDROLYSIS OF PECAN WASTES BIOMASSES IN A SEMI-CONTINUOUS MODE

Optimization of subcritical water hydrolysis of pecan wastes biomasses in a semi-continuous mode

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Conflict of interest

The authors inform that there are no conflicts of interest.

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Highlights

1 – Pecan raws were processed by subcritical water hydrolysis to obtain reducing sugars;

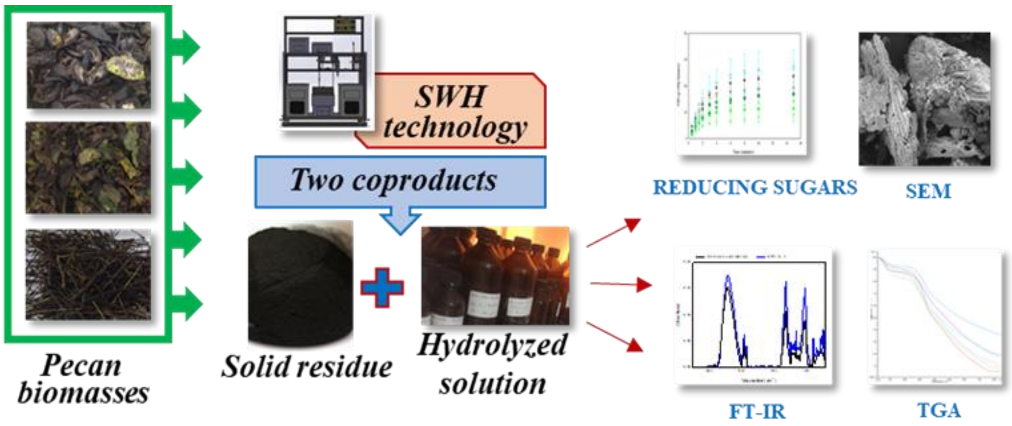
2 – Different process conditions (temperature; water to solid mass ratio) were evaluated;

3 – 27.1 ± 6.9 g reducing sugars/ 100g biomass were obtained at 220 ºC for shells;

4 – Efficiency in producing reducing sugars were up to 78 wt.%;

5 – The strategy proved to be a clean alternative for adding value to pecan coproducts.

Graphical abstract



Abstract

Pecan cultivation has increased in recent years. Consequently, the amount of lignocellulosic residuals from its production has expanded. Thus, there is a necessity to explore and add value to their coproducts. The objective of this work was to obtain reducing sugars from pecan biomasses by the optimization of the subcritical water hydrolysis technology in a semi-continuous mode and the physicochemical and morphological characterization of these materials, such as SEM, TGA and FT-IR analysis. Temperatures of 180, 220 and 260 ºC, water/ solids mass ratio of 15 and 30 g water/ g biomass and total reaction time of 15 minutes were used. The highest reducing sugar yield was 27.1 g/ 100 g of biomass, obtained at 220 ºC and R-15 for pecan shells. TGA, SEM and FT-IR analysis indicated the modifications of structures and compositions of biomasses in fresh and hydrolyzed samples.

Keywords: Lignocellulosic materials. Pecan bagasse. Residual biomasses. Subcritical technology.

3.1 INTRODUCTION

Nut total production has increased significantly in recent years. The results demonstrate a promising scenario, considering that in 2009 the production was 2.8 million tons, approximately 40% lower. In this context, pecan is characterized as a species of great interest. It is estimated that in the 2018/19 harvest, the production was over 140.000 tons [1]. Although the main production is concentrated in countries such as the United States and Mexico, its cultivation has been widely extended to other countries, while Brazil is one of the largest producers.

In 2017, the Brazilian production was approximately 8000 tons in 3800 hectares [2]. In this sense, large quantities of waste materials are generated from nut processing in industries and harvesting processes. Since the increase in the production of remaining materials is proportional to the increase in food production, efficient methods are required for the treatment of these materials, especially due to the loss of high suitability and applicability of residues [3]. It is estimated that 40-50% of the total walnuts produced are waste materials, which can be classified as potential bioproducts [4].

Therefore, it is necessary to assign high importance to the reuse of pecan wastes, thus exploring the potential of these wastes for resulting in higher added value to their coproducts. Pecan biomasses are rich in lignocellulosic materials of high potential for use [5]. Obtaining reducing sugars from lignocellulosic raw material can be achieved through the hydrolysis process, which has been portrayed as an efficient technique for breaking down the lignocellulosic complex and converting these compounds, as well as serving as an alternative to minimize related problems of waste disposal in the environment [6].

Considering the biorefinery concept as a sustainable processing route, the subcritical water hydrolysis (SWH) technique has been reported as an efficient alternative in the process of breaking the lignocellulosic structure of biomasses [7]. This technology is applied to a wide variety of wastes to optimize the process as it has low costs, ease of use and reduced reaction time [8, 9]. This technology uses subcritical water at a temperature below its critical point at high pressures. Temperature significantly influences the physicochemical properties of water, allowing a better penetration in the lignocellulosic matrix. High pressures, on the other hand, help maintaining water at a liquid-like phase, consequently optimizing the mass transfer between the solutes and solvent [10].

The use of subcritical technology focusing on obtaining sugars has been reported in the literature for numerous plant species residual biomasses [11, 12]. However, researches on the application of this technology to pecan biomasses, specifically, is scarce and has not been reported in the current scientific literature. Thus, the importance of studies that evaluate the efficiency of this alternative in pecan waste materials is highlighted. Also, there is a necessity for a database that provides relevant information related to the quantification and composition of sugars and inhibitors present in these materials.

Therefore, it is of great interest to use alternatives that result in adding value to these coproducts efficiently and, at the same time, sustainable. An important strategy is the application of processing technologies aimed at obtaining reducing sugars through the hydrolysis process of the lignocellulosic raw material, granting wide appreciation to the countless applicability of these materials. Thus, the objective of this work was to evaluate the potentiality of different pecan biomasses by using subcritical water hydrolysis technology as an efficient and sustainable technique for the conversion of lignocellulosic matrix into reducing sugars (such as xylose, arabinose, glucose and cellobiose) in semi-continuous mode and to perform physicochemical and morphological analysis of biomasses in fresh and post hydrolysis conditions.

3.2 MATERIAL AND METHODS

3.2.1 Materials

Vegetable biomasses from pecan, such as husks, leaves and stalks, and shells were obtained from the harvest residues of the company Paralelo 30®, located in Cachoeira do Sul, central region of Rio Grande do Sul, Brazil (30º 0' 45” S, 52º 55' 11” W), referring to the 2019/I crop. For all analyses, except for moisture content, the leaves and stalks biomasses were combined to form single sample. Initially, the biomasses were weighed and maintained in a stove at 60 ºC until reaching constant weight. Afterward, the dried biomasses were ground in a Willey Knife Mill (SL 30, Solab, Brazil) to obtain a thin and uniform material. Finally, the ground biomasses were frozen in a refrigerator until the beginning of trials. For a better comprehension, the steps of this study and the analyzes performed are presented in Figure 7.

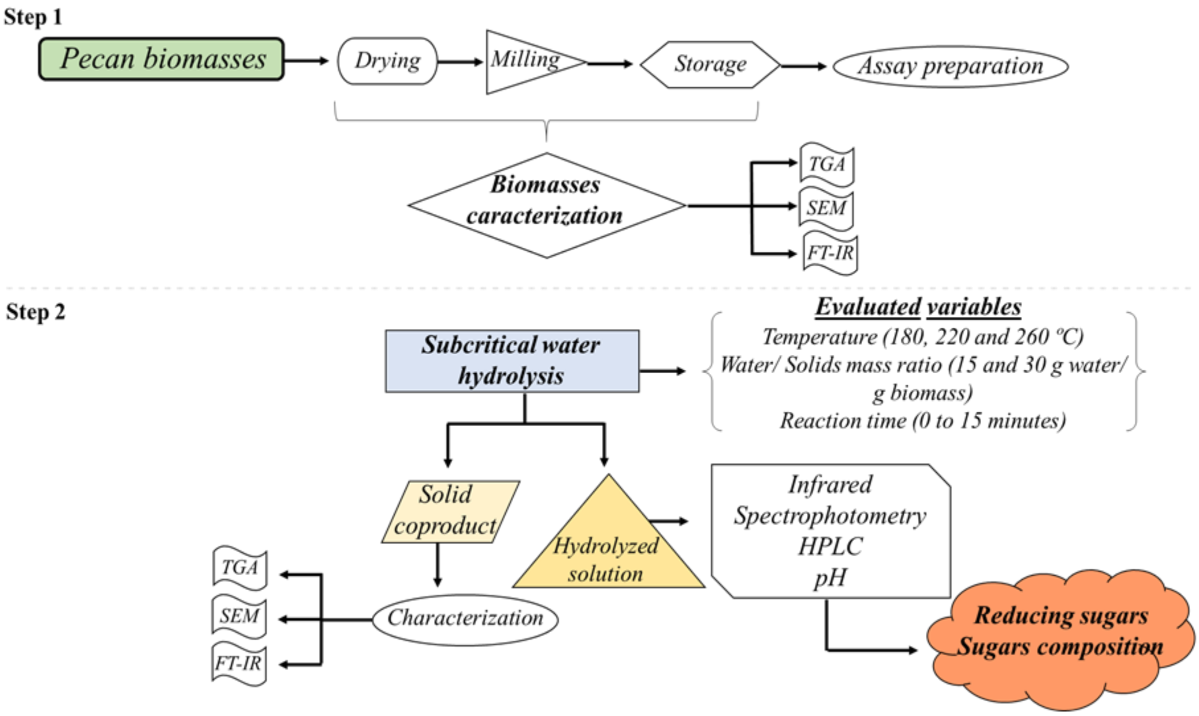


Figure 7. Flowchart of the steps of this study. SEM: scanning electron microscopy; TGA: thermogravimetric analysis; HPLC: high-performance liquid chromatography.

3.2.2 Pecan biomasses characterization

For the moisture content determination, approximately 1 g of each pecan biomass was placed in aluminum trays. Thereafter, the samples were placed in an oven at 105 °C up to reaching constant weight. For moisture, triplicates were used, where the average values and standard deviations were reported.

3.2.3 Pecan biomasses subcritical water hydrolysis

The technological complex where subcritical hydrolysis has been performed according the current literature [7].

For each hydrolysis assay, 20 g of each biomass was loaded in the reactor and distilled water was pumped at a constant flow. After system pressurization, the water was heated and the temperature adjusted according to each assay. The pressure has been adjusted to 30 MPa.

For each test, different temperatures were selected (180, 220 and 260 ºC). In each case, the flow rates used were 20 and 40 mL/min, which corresponds to water/ solids (R) mass ratios of 15 and 30 g water/ g biomass, respectively. The hydrolyzed solutions were obtained in a total reaction time of 15 minutes, at intervals of 0.5 minutes (first 2 minutes), 1 minute (2 to 4 minutes) and 2 minutes (4 to 10 minutes). A final sample was collected within 10 to 15 minutes. Afterward, the samples were stored under refrigeration for pH, ultraviolet/visible spectrophotometry and HPLC analyses. The remaining solid residue from each assay of hydrolysis was collected and dried in an oven at 105 ºC until constant weight for its characterization. A duplicate was performed for each assay and the mean values and standard deviation were considered for the statistical analyses.

3.2.4 Statistical analysis

To evaluate the influence of process variables, such as temperature and water/ solids mass ratio, in the different biomasses and its triplicates, a statistical analysis was carried out using the software Sisvar® 5.6. A significance level of 95% ($p < 0.05$) was considered.

3.2.5 Analytical procedure

3.2.5.1 pH

The pH of the hydrolyzed solutions was determined by a benchtop pHmeter (DM-22, Digimed, Brazil). To measure the pH of the samples, the pHmeter was previously calibrated using pH 4.0 and pH 7.0 buffer solutions.

3.2.5.2 Ultraviolet/ Visible Spectrophotometry

As proposed by Maldonade et al. (2013), the determination of total reducing sugars was performed by the dinitrosalicylic acid (DNS) method, using glucose at 1.0 g.L/L as standard solution. For each 1 mL of hydrolyzed solution sample, 1 mL of DNS reagent was added. Thereafter, the solution containing the mixture of the solutions was agitated and heated in a water bath at 100 °C (boiling) for 5 minutes and then placed in an ice bath at the same interval. In addition, 16 mL of double potassium sodium tartrate solution was added, where 15.1 g of the solute was dissolved in 1 L of distilled water.

The absorbance was measured by a spectrophotometer (UV-1900, Shimadzu, Japan) at a wavelength of 540 nm after calibrating the instrument with the blank solution. The blank solution was based on replacing the sample solution or glucose solution with distilled water (1 mL).

Based on the study reported by Abaide et al. (2019a), for each hydrolyzed solution test, the reducing sugar yield (Y_{RS}, g sugar/ 100 g initial biomass) was determined by the equation 1 and the efficiency (E, g sugar/ 100 g of carbohydrates (hemicelluloses and cellulose)) was defined according the equation 2. A multiple comparison test for Y_{RS} and E was done and Tukey's test was applied at 5% probability.

$$Y_{RS} = (m_{RS}/m_{SA}) \cdot 100 \tag{1}$$

$$E = (m_{RS}/m_{CA}) \cdot 100 \tag{2}$$

Where:

m_{RS}: mass of reducing sugar in the hydrolyzed solution, g;

m_{SA}: initial mass of pecan biomass for the hydrolysis process, g;

m_{CA}: initial mass of carbohydrates (hemicelluloses and cellulose), g.

3.2.5.3 Thermogravimetric Analysis

The thermogravimetric analysis (TGA) of pecan biomasses was performed according to the current literature [7]. The analysis was performed using a thermogravimetric analyzer (Pyris 1 TGA Model, Perkin Elmer, USA). For the TGA analysis, fresh biomasses and biomasses processed in the conditions of the highest sugar contents were used. Derivates thermograms (DTG) were obtained according to the methods recommended in the scientific literature [7, 14].

3.2.5.4 Scanning Electron Microscopy

The morphology of the particles of the different biomasses was analyzed by scanning electron microscopy (SEM) (VEGA3, TESCAN, Czech Republic). The samples were arranged on the equipment and then covered by a thin layer of gold. Finally, the samples were analyzed at a voltage of 5 kV, in the magnifications were defined up to 1500×. For the SEM analysis, fresh biomasses processed in the conditions of the highest sugar contents were used.

3.2.5.5 High-Performance Liquid Chromatography (HPLC)

For the analysis of sugars, the methodology proposed by Fleig et al. (2018) and employed by Abaide et al. (2019a) was used. 2 mL of each sample of hydrolyzed solution was centrifuged at 14.000 rpm for 3 minutes. Samples containing hydrolyzed solution were filtered through a 0.22 μm nylon membrane and the quantification of xylose, glucose, cellobiose, and arabinose were determined by high-performance liquid chromatography (HPLC) (Proeminence UFLC-Nexera XR, Shimadzu, Japan), equipped with a refractive index (IR) detector (RID 10A, Shimadzu, Japan). An Asahipak NH2P-50 (250mm × 4.6mm) amino column (Asahi Kasei, Japan) at a temperature of 50 °C was used. As a method that considers the distribution of the components in two phases, the mobile phase consisted of a solution of acetonitrile: water in the ratio of 69: 31. Subsequently, the mobile phase was vacuum filtered through cellulose esters (Milipore, USA) of 0.45 μm and 47 mm pore diameter and degassed in an ultrasonic bath (USC-1400, Unique, São Paulo). The mobile phase volumetric flow rate was 0.5 mL/min and the injection volume of the samples was 15 μL. In the stationary phase, the compounds were separated and analyzed with an IR detector at 30 ºC for a total run time of 16 minutes. Concentrations of each component were obtained by correlation between chromatogram areas and standard curves previously determined by ᴅ-glucose, ᴅ-xylose, ᴅ-arabinose and cellobiose standards. For the HPLC analysis, the conditions of the highest reducing sugar contents for each biomass in each temperature and R were used.

For the analysis of furfural and hydroxymethylfurfural (HMF), the methodology proposed by Fleig et al. (2018) and employed by Abaide et al. (2019a) was used. Filtered samples were analyzed in a HPLC system (UFLC – Nexera XR, Shimadzu, Japan) equipped with a photodiode array detector (PDA 20-A, Shimadzu, Japan). A Shim-Pak ODS C18 column (Shimadzu, Japan) was used. A solution of acetonitrile: water (1: 8, with acetic acid 1% (v/ v)) filtered in 0.45 mm and diameter 47 mm cellulose esters (Milipore, USA) and degassed in an ultrasound bath (USC-1400, Unique, São Paulo) was used for the mobile phase. The conditions for the analysis were: injection volume of 10μL, flow rate of 0.8 mL/min, column temperature of 30 °C, wavelength of 280 nm, detector temperature of 30 °C, and run time of 10 minutes. The concentrations of each component were obtained by the correlation between chromatogram areas and standard curves previously determined by furfural and HMF standards. The peak areas corresponding to furfural and HMF were used to calculate their concentration in the samples. For this analysis, the conditions of the highest reducing sugar contents for each biomass in each temperature and R were used.

3.2.5.6 Fourier-Transform Infrared Spectroscopy

The alterations in the structure of samples of fresh biomasses and solid coproducts were analyzed by Fourier-transform infrared spectroscopy (FT-IR) (IR Prestige 21, Shimadzu, Japan) by the direct transmittance method using the disc-shaped KBr. The spectra were obtained in the range of 400 to 4500 cm^{-1}, with 45 scans and a resolution of 2 cm^{-1}. The disks were made in the KBr tablet die accessory using a press (Hand Press SSP-10a, Shimadzu, Japan). Approximately 100 mg of KBr and 1 mg of the sample were used, macerated and mixed in a smooth agate pressing under 78.5 kN (8 tons), resulting in thin transparent inserts (less than 1 mm thick) and 13 mm in diameter. For the FT-IR analysis, fresh biomasses and the conditions of the highest reducing sugar contents for each biomass were used.

3.3 RESULTS AND DISCUSSION

3.3.1 Pecan biomasses characterization

The moisture, cellulose, hemicelluloses, and lignin content are shown in Table 2. As reported, the concentration of lignin in all biomasses tends to be higher than that of hemicelluloses and cellulose. These concentrations may affect the SWH process, once this element is responsible for the stiffness of the cell wall in plant species. This scenario can hinder the penetration of water in the lignocellulosic matrix and overestimate the reducing sugars yield efficiency [16]. Interestingly, these results may be related to the values found for E in the different biomasses, since the shells biomasses present higher levels of lignin and higher values of E (Table 3).

In addition, these elements can vary according to the climatic and agronomic conditions, which can influence other compounds presented in pecan biomasses, such as flavonoids, polyphenols and tannins [17]. However, similar results were found for shells, where the lignin content in the samples (38.4%) tends to be higher than hemicelluloses (19.2%) and cellulose (13.1%) [18, 19].

Table 2 - Lignocellulosic composition of fresh pecan biomasses.

	Biomass	**Moisture[a]**	**Cellulose[b]**	**Hemicelluloses[b]**	**Lignin[b]**
Composition (wt.%)	**Husks**	21.1 ± 2.6	17.5	21.2	36.5
	Leaves	23.6 ± 5.2	18.7	22.0	35.2
	Stalks	19.9 ± 0.1			
	Shells	19.9 ± 0.5	13.1	19.2	38.4

[a] Mean ± standard deviation.

[b] Calculated by DTG procedure.

3.3.2 pH

The pH behavior for the different conditions of the hydrolysis process is presented in Fig. 1 for husks (a), leaves and stalks (b) and shells (c).

The kinetic behavior of pH was similar to the husks, leaves and stalks, and the shells biomasses (Fig. 2), where the values decrease in higher temperatures. For the husks and shells biomasses, there was an increase up to 10 minutes of reaction and the maximum value was reached. After, the values showed a slight reduction. Interestingly, for the shells conditions of 180 ºC / R-30 there was an increase of the pH value from 10 to 15 minutes. These results may be related to the management at the pH measurement, since there are exceptions if we compare the kinetic profile of all conditions of the different biomasses.

The behavior of the increase of pH acidity of hydrolyzed solutions with the increase of the temperature can be related to the higher concentrations of soluble materials, as organic acids that come from the degradation of sugars in high temperatures [20]. This performance shows how pH values can give us the magnitude of autocatalytic degradation of sugars to produce acids [21]. Also, as shown in Figure 8, for all the biomasses the lower pH values in lower temperatures shows that these conditions are unsatisfactory for the rupture of the lignocellulosic complex by the SWH process.

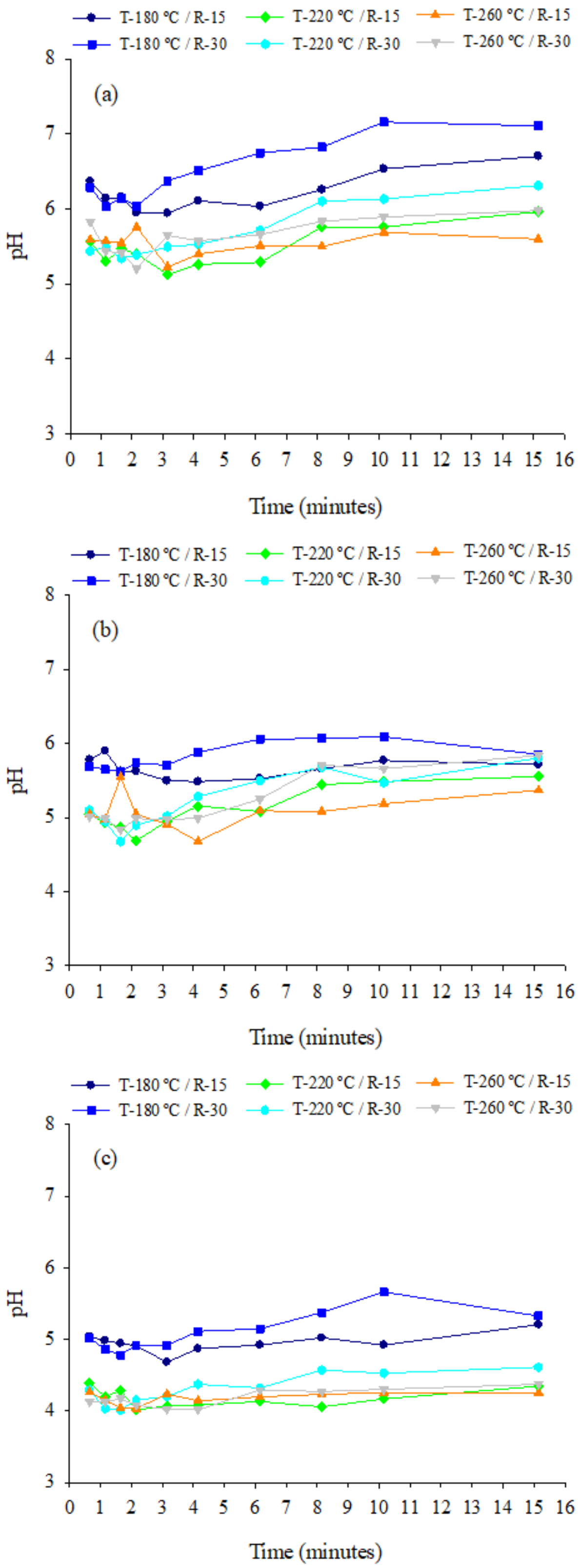


Figure 8. Kinetic profile of pH of hydrolyzed solutions of pecan husks (a), leaves and stalks (b), and shells (c).

3.3.3 Reducing sugars

For the husks, leaves and stalks, and shells biomasses, the Y_{RS} and E obtained at different conditions of temperature and R in a total reaction of 15 minutes are shown in Table 3. Considering the husks, the highest Y_{RS} value was obtained at the condition of 220 °C / R-15 (26.5 ± 7.1 g / 100 g pecan husks), which did not obtain significant difference ($p < 0.05$) of the value obtained in the same temperature condition and in R-30 (18.9 ± 5.0 g / 100 g pecan husks). No statistical differences were observed for assays 3, 1 and 4, where the highest Y_{RS} values were obtained. The lowest Y_{RS} values were found in assays 6, 5 and 2, which were not statistically different one from each other.

Table 3 - Reducing sugars yield (YRS) and efficiency (E) of SWH from pecan husks, leaves and stalks and shells in different conditions of temperature and water/ solids mass ratio in a semi-continuous mode.

Husks assays	Condition	R (g water/ g biomass)	Temperature (ºC)	Y_{RS} (g/ 100 g biomass)	E (g/ 100 g carbohydrates)
1	180 ºC / 20 mL/min	15	180	23.6 ± 3.9^{ab}	50.1 ± 8.3^{ab}
2	180 ºC / 40 mL/min	30	180	17.0 ± 2.6^{bc}	36.1 ± 5.7^{bc}
3	220 ºC / 20 mL/min	15	220	26.5 ± 7.1^{a}	56.4 ± 15.1^{a}
4	220 ºC / 40 mL/min	30	220	18.9 ± 5.0^{abc}	40.1 ± 10.7^{abc}
5	260 ºC / 20 mL/min	15	260	16.7 ±7 .6^{bc}	35.3 ± 16.2^{bc}
6	260 ºC / 40 mL/min	30	260	11.4 ± 5.0^{c}	24.2 ± 10.6^{c}

Leaves and stalks assays	Condition	R (g water/g biomass)	Temperature (ºC)	Y_{RS} (g/100 g biomass)	E (g/100 g carbohydrates)
1	180 ºC / 20 mL/min	15	180	24.7 ± 0.1^{ab}	41.5 ± 0.3^{ab}
2	180 ºC / 40 mL/min	30	180	16.5 ± 0.1^{cd}	27.7 ± 0.6^{cd}
3	220 ºC / 20 mL/min	15	220	24.4 ± 1.5^{ab}	40.9 ± 2.5^{ab}
4	220 ºC / 40 mL/min	30	220	19.9 ± 1.4^{bc}	33.5 ± 2.6^{bc}
5	260 ºC / 20 mL/min	15	260	26.3 ± 1.6^{a}	44.2 ± 2.7^{a}
6	260 ºC / 40 mL/min	30	260	12.8 ± 1.1^{d}	21.5 ± 1.8^{d}

Shells assays	Condition	R (g water/g biomass)	Temperature (ºC)	Y_{RS} (g/100 g biomass)	E (g/100 g carbohydrates)
1	180 ºC / 20 mL/min	15	180	26.9 ± 0.8^{a}	78.1 ± 2.4^{a}
2	180 ºC / 40 mL/min	30	180	18.0 ± 3.3^{ab}	52.4 ± 9.8^{ab}
3	220 ºC / 20 mL/min	15	220	27.1 ± 6.9^{a}	78.7 ± 20.3^{a}
4	220 ºC / 40 mL/min	30	220	19.7 ± 1.5^{ab}	57.2 ± 4.4^{ab}
5	260 ºC / 20 mL/min	15	260	21.0 ± 0.1^{ab}	61.0 ± 0.4^{ab}
6	260 ºC / 40 mL/min	30	260	11.7 ± 1.1^{b}	33.9 ± 3.3^{b}

When analyzing the kinetic profile (Figure 9 (1a)), the reaction rate seems to follow different behaviors for the conditions of higher and lower yields. For the conditions of 220 °C / R-20, there was an increase in Y_{RS} until the reaction time of 10 minutes. After this time, the conversion rate was minimal and the maximum value of 26.5 ± 7.1 g / 100 g pecan husks was reached. In the conditions of 260 ºC / R-40, which was the one with the lowest Y_{RS} values, the yield became constant after 4 minutes of reaction, where the lowest value was obtained (11.4 ± 5.0 g / 100 g pecan husks).

The yield increased with the temperature increase from 180 ºC to 220 ºC in both conditions of R. A greater production of soluble oligomers and monomeric sugars, such as cellobiose and fructose and glucose, respectively [22]. Also, in short reaction times, cellulose and hemicelluloses are hydrolyzed to higher proportions of fermentable sugars [7]. At 260 ºC, a reduction in yield was observed in both conditions of R. In high temperatures, the compounds tend to suffer thermal degradation, which affects the sugar concentrations in the samples [22].

The kinetic behavior of E was similar to the Y_{RS} (Figure 9 (1b)), where for the conditions of higher Y_{RS} (220 °C / R-20), there was an increase up to 10 minutes of reaction. After, the conversion rate was minimal and the maximum value of 56.4 ± 15.1 g / 100 g pecan husks was reached. At 260 ºC / R-40, the efficiency became constant after 4 minutes of reaction, where the lowest value was obtained (24.2 ± 10.6 g / 100 g pecan husks). For the three temperature conditions, the efficiency was higher in lower R, which can be attributed to the residence time [23]. The authors observed a significant increase in Y_{RS} efficiency when the residence time was increased in palm materials.

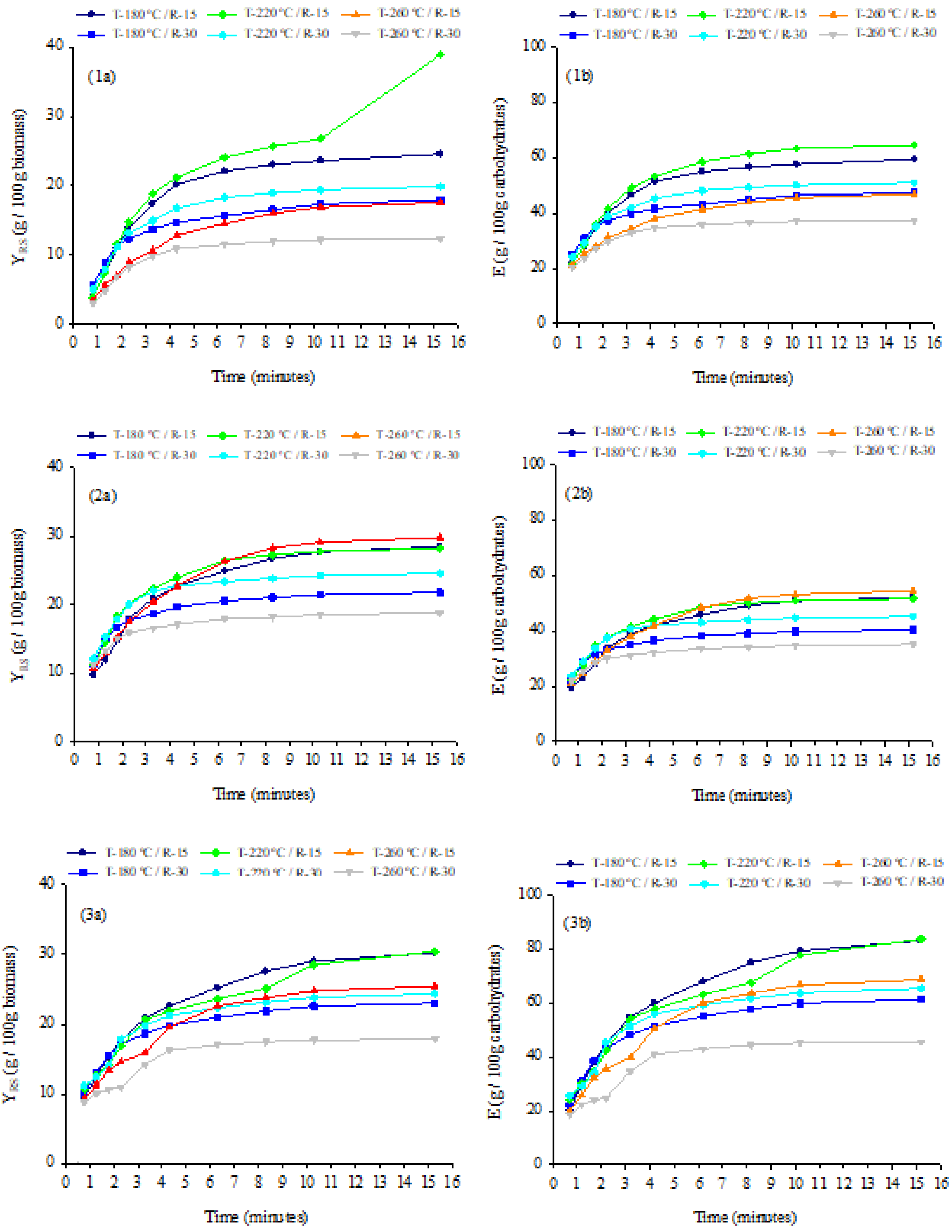


Figure 9. Kinetic profile of reducing sugars yield and efficiency (accumulated samples) of hydrolyzed solutions of pecan husks (1a, 1b), leaves and stalks (2a, 2b) and shells (3a, 3b), in different conditions of temperature and water/ solids mass ratio in a semi-continuous mode; the bars refer to the standard.

The SWH process was also applied to hydrolyze palm oil [24]. The authors found a reduction in the efficiency of reducing sugars produced by SWH procedure at temperatures above 240 ºC. Similar results were obtained when subcritical hydrolysis was applied in a microcrystalline cellulose material, where the influence of temperature (150 to 250 °C) in a range of 10 to 60 minutes was evaluated for the production of total reducing sugars [22]. By increasing the temperature from 150 to 225 °C, the Y_{RS} increased from 1.9% to 26.6% and reduces to 4.4% at 250 °C.

Differently from the husks assays, the leaves and stalks hydrolyzed solutions showed the highest Y_{RS} value at the condition of 260 °C / R-15 (26.3 ± 1.6 g / 100 g pecan leaves and stalks). A significant difference ($p < 0.05$) of the Y_{RS} values obtained in the same temperature condition and in R-30 (12.8 ± 1.1 g / 100 g pecan leaves and stalks) was observed. According to Table 2, no statistical differences were observed for assays 5, 1 and 3, where the highest Y_{RS} values were obtained at R-15. The lowest Y_{RS} values were found in assay 6 (12.8 ± 1.1 g / 100 g pecan leaves and stalks) which, interestingly, was submitted to the same temperature conditions as the samples with the maximum Y_{RS} value (260 ºC). Assays 2 and 4 were not statistically different one from each other and the assay 4 was significantly different from the assay 6, which had the lowest Y_{RS}.

As verified for husks biomasses, the kinetic profile of the leaves and stalks biomasses (Figure 9 (2a)) showed that the reaction rate follows different profiles for the conditions of higher and lower yields. For conditions of 260 °C / R-20, there was an increase in Y_{RS} up to the reaction time of 10 minutes. After, the conversion rate was minimal and the maximum value of 26.3 ± 1.6 g / 100 g pecan leaves and stalks was reached. In the conditions of 260 ºC / R-40, which was the one with the lowest Y_{RS} values, the yield became constant after 6 minutes of reaction, where the lowest value was obtained (11.4 ± 5.0 g / 100 g pecan leaves and stalks).

Specifically for leaves and stalks biomasses, the Y_{RS} decreased with a temperature increase from 180 ºC to 220 ºC, under the condition of R-15, and increased to R-40. In addition, there was an increase in Y_{RS} from 220 ºC to 260 ºC. Studies on the same theme applied to grass species were developed and similar results were found, where temperatures of 300 ºC and high flow rates resulted in high yields, compared to less extreme conditions. As informed by the authors, this scenario is related to high reaction temperature, thus speeding up the reaction when compared to lower temperatures [25]. Also, for rice straw residues, the yield increased up to 280 ºC, with drastic reduction with the increasing temperature, due to the degradation of sugar into coproducts, such as 2-methyltetrahydrofuran and acetic acid [26]. Increasing the temperature in the SWH procedure results in increased breakdown of water molecules in ionic products, which results in increased $H3O^+$ concentration, once the water reactivity increases and more carbohydrate molecules are converted into sugars [27].

The kinetic behavior of E was similar to the Y_{RS} (Figure 9 (2b)), where for the conditions of higher Y_{RS} (260 °C / R-20), there was an increase in the efficiency of Y_{RS} up to 10 minutes of reaction. After, the conversion rate was minimal and the maximum value of 44.2 ± 2.7 g / 100 g pecan leaves and stalks was reached. Different from the husks biomasses, at 260 ºC / R-40, the E became constant after 6 minutes of reaction, where the lowest value was obtained (21.5 ± 1.8 g / 100 pecan leaves and stalks).

Like the husks and different from the leaves and stalks assays, the shells assays showed the highest Y_{RS} value at the condition of 220 °C / R-15 (27.1 ± 6.9 g / 100 g pecan shells), which did not show significant difference ($p < 0.05$) of the value obtained in the same temperature condition and in R-30 (19.7 ± 1.5 g / 100g pecan shells). No statistical differences were observed for assays 3, 1, 5, 4 and 2. The lowest Y_{RS} value was found in assay 6 (11.7 ± 1.1 g / 100 g pecan shells), which was statistically different from the assays 3 and 1 and did not show a significant difference from the assays 5, 4 and 2.

According to the kinetic profile (Figure 9 (3a)), the reaction rate seems to follow different behaviors for the conditions of higher and lower Y_{RS}. For the conditions of 220 °C / R-20, there was an increase in Y_{RS} until the final reaction time (15 minutes). Up to 10 minutes, this increase was considerable. After, the increase was smaller, but greater than the other biomasses in the same period. In 15 minutes, the maximum value of 27.1 ± 6.9 g / 100 g pecan shells was reached. In the conditions of 260 ºC / R-40, which was the one with the lowest Y_{RS} values, the yield became constant after 8 minutes of reaction, where the lowest value was obtained (11.7 ± 1.1 g / 100 g pecan shells).

The Y_{RS} increased as the temperature increased from 180 °C to 220 °C and decreased under 260 °C for all R conditions. Similar results were obtained from oil palm trunks, in which the authors reported higher yields of reducing sugars at 220 °C, while a reduction was seen at higher temperatures [28]. SWH procedure at high temperatures can cause the degradation of sugars produced by the disruption of cellulose and hemicelluloses, such as furfural and HMF [29].

The kinetic behavior of E was similar to the Y_{RS} (Figure 9 (3b)), where for the conditions of higher Y_{RS} (220 °C/ R-20), there was an increase in Y_{RS} efficiency until the total reaction time (15 minutes). In this condition, the maximum value of 78.7 ± 20.3 g / 100 g pecan shells was reached. At 260 ºC / R-40, efficiency became constant after 8 minutes of reaction, where the lowest value was obtained (33.9 ± 3.3 g / 100 g pecan shells). The SWH process was also applied to hydrolyze palm oil [24]. The authors found a reduction in the efficiency of SWH procedure at temperatures above 240 ºC. As reported by the authors, the main reason is the low dielectric constant of the water at lower temperatures, which results in less degradation of the solutions. In addition, at very high temperatures some thermally treated compounds may be degraded after the release of the sample matrix or may form other compounds [30]. This scenario can be perfectly observed in Figure 2 (3a), where cellulose and hemicelluloses are hydrolyzed into reducing sugars at temperatures higher than 180 ºC and 220 ºC and are reduced when the temperature is 260 °C in different conditions of R.

3.3.4 Hydrolyzed solutions composition

Hydrolyzed solutions were analyzed for the characterization and quantification of sugars and inhibitors for the husks, leaves and stalks and shells biomasses (Table 4, 5 and 6, respectively). Regarding sugars, specifically for pecan husks and leaves and stalks biomasses, glucose was the predominant monosaccharide present in the solutions, followed by xylose. For the husks and leaves and stalks biomasses, the highest concentrations of sugars present in the samples were observed in a total reaction time of up to 3 and 6 minutes, respectively.

Table 4 - Sugars and inhibitors content (g/100 g biomass) obtained by SWH procedure from pecan husks at the highest YRS reaction time of each SWH condition.

Sugar (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Arabinose	1.0	2.8	2.8	0.0	0.3	0.0
Cellobiose	0.5	0.9	1.5	0.0	2.1	0.001
Glucose	2.4	7.8	1.1	0.01	2.2	0.0
Xylose	0.1	3.6	3.5	0.0	4.0	0.0
Total	4.0	15.1	8.9	0.01	8.6	0.001
Reaction time (minutes)	3	0.5	1.5	1.5	0.5	3
Inhibitor (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Furfural	0.007	0.03	0.4	0.02	0.1	0.02
HMF	0.02	0.03	0.1	0.02	0.07	0.02
Total	0.027	0.06	0.5	0.04	0.17	0.04
Reaction time (minutes)	3	0.5	1.5	1.5	0.5	3

Table 5 - Sugars and inhibitors content (g/100 g biomass) obtained by SWH procedure from pecan leaves and stalks at the highest YRS reaction time of each SWH condition.

Sugar (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Arabinose	2.0	2.3	0.6	1.5	0.02	2.0
Cellobiose	0.7	0.9	0.3	1.0	1.6	0.8
Glucose	3.4	4.3	0.7	3.7	0.0	0.08
Xylose	2.0	2.7	0.7	5.0	0.0	2.6
Total	8.1	10.2	2.3	11.2	1.62	5.48
Reaction time (minutes)	2	1	1.5	0.5	6	0.5
Inhibitor (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Furfural	0.03	0.01	1.2	1.1	0.01	0.5
HMF	0.08	0.09	0.6	0.6	0.01	0.3
Total	0.11	0.1	1.8	1.7	0.02	0.8
Reaction time (minutes)	2	1	1.5	0.5	6	0.5

Table 6 - Sugars and inhibitors content (g/100 g biomass) obtained by SWH procedure from pecan shells at the highest Y_{RS} reaction time of each SWH condition; accumulated samples obtained by SWH procedure at the highest Y_{RS} condition of 220 ºC / R-15 for 15 minutes.

Sugar (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Arabinose	1.0	0.6	**5.6**	14.0	0.0	0.0
Cellobiose	0.4	0.003	**1.1**	3.1	0.6	0.7
Glucose	0.0	0.1	**3.3**	3.3	0.1	0.07
Xylose	0.0	0.0	**59.7**	0.0	0.0	0.0
Total	1.4	0.703	**69.7**	20.4	0.7	0.77
Reaction time (minutes)	1	1	**-**	0.5	4	3
Inhibitor (g/100 g biomass)	**T-180 ºC / R-15**	**T-180 ºC / R-30**	**T-220 ºC / R-15**	**T-220 ºC / R-30**	**T-260 ºC / R-15**	**T-260 ºC / R-30**
Furfural	0.008	0.0	**13.0**	1.9	1.6	1.2
HMF	0.03	0.05	**3.8**	0.4	1.5	1.6
Total	0.038	0.05	**16.8**	2.3	3.1	2.8
Reaction time (minutes)	1	1	**-**	0.5	4	3

In general, in the conditions where temperatures were 180 °C and 220 °C, the highest sugars concentrations were obtained. The literature reports that these inhibitors are the result of cellulose degradation during extraction processes [31, 32]. The scenario of high process optimizations at these conditions was also observed for palm oil trunks [28] and bamboo [33]. In high temperatures, sugars and other elements suffer a large degradation process, which leads to their loss, not remaining in the hydrolyzed solution [34]. This degradation is related to time and temperatures increase [35].

Considering that the samples from the pecan shells biomass at 220 ºC and R-15 obtained the highest sugar content compared to all biomasses under all SWH process conditions, an accumulated evaluation of total reaction time of 15 minutes can be observed in Table 5 for sugars and inhibitors. Regarding sugars, arabinose was the predominant monosaccharide present in hydrolyzed solutions, followed by glucose. With an exception of the condition of 220 ºC / R-15, the highest concentrations of sugars in the samples were observed in a total reaction time of up to 4 minutes.

As for husks and leaves and stalks biomasses, under conditions where the temperature was 220 °C, the highest sugars concentrations were obtained. This scenario may be related to the fact that this temperature leads to the lowest sugar content. In high temperatures, sugars and other compounds suffer a large degradation process, which leads to their loss, thus not remaining in the hydrolyzed solution [34]. Considering the condition of 220 ºC / R-15, which is represented by accumulated samples of a total reaction time of 15 minutes, arabinose was the predominant monosaccharide, followed by glucose (Table 5). The behavior of reducing sugars can be seen in Figure 10 (a)), where there was a large decrease in concentrations with increasing total reaction time. The same can be observed for furfural and HMF inhibitors for the 220 ºC / R-15 condition, which presented the high content of furfural (Figure 10 (b)). Also, it was observed a slight increase in short reaction times and then a large decrease in concentrations with increasing total reaction time, as noted for sugars content.

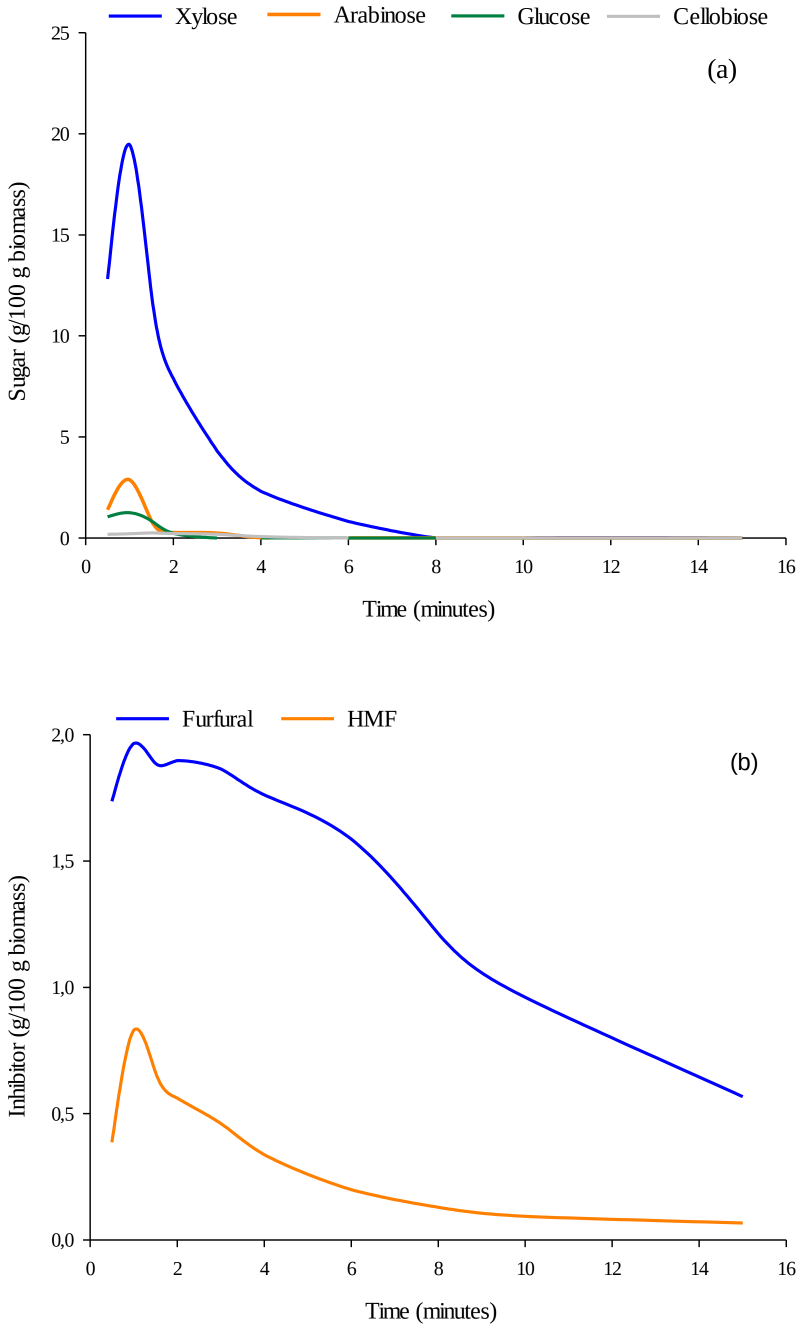


Figure 10. Reducing sugars (a) and inhibitors (b) (non-accumulated samples) in hydrolyzed assay from pecan shell in the conditions of highest Y_{RS}; Y_{RS}: reducing sugars yield (g/100 g of biomass), R: water/ solids mass ratio (g water/g biomass).

3.3.5 Morphology of solid biomasses

The morphological structure of pecan biomasses was influenced by the SWH procedure. The surface of fresh husks were visibly broken granules due to the milling performed for sample preparation. Under the hydrolysis conditions which resulted in the highest Y_{RS}, where the reactor temperature was 220 °C, a disruption of the lignocellulosic structure and the reduction of granule size was clearly observed, which is in agreement with obtaining the concentrations of sugars and inhibitors by disaggregating the cellulose and hemicelluloses components (Table 1).

The same scenario was observed for the fresh leaves and stalks biomass, where the surface of large granules where the lignocellulosic matrix of biomass is clearly present before the SWH procedure. Under the hydrolysis conditions which resulted in the highest Y_{RS}, where the reactor temperature was 260 °C, a disruption of the lignocellulosic structure was clearly observed by reducing the size of the granules and the number of these aggregates.

Finally, for the shell biomass, the behavior of the lignocellulosic structure of the fresh mass and after the SWH procedure is similar to the other biomasses. The Figure 11 shows the profile of large lignocellulose aggregates present before the SWH procedure. Under the hydrolysis conditions that resulted in the highest Y_{RS}, which can be the highest Y_{RS} among the different biomasses, where the reactor temperature was 220 °C, the disruption of this matrix can be observed by reducing the granule size and increasing the number of aggregates. The disruption of the lignocellulosic matrix and the remarkable removal of sugars from its structure in high temperature hydrolysis procedures were also observed in rice husks [12], coconut husks [37] and in sugarcane bagasse under a subcritical CO_2-water condition, where it was possible to verify the rupture and detachment of the material after the SWH procedure [38].

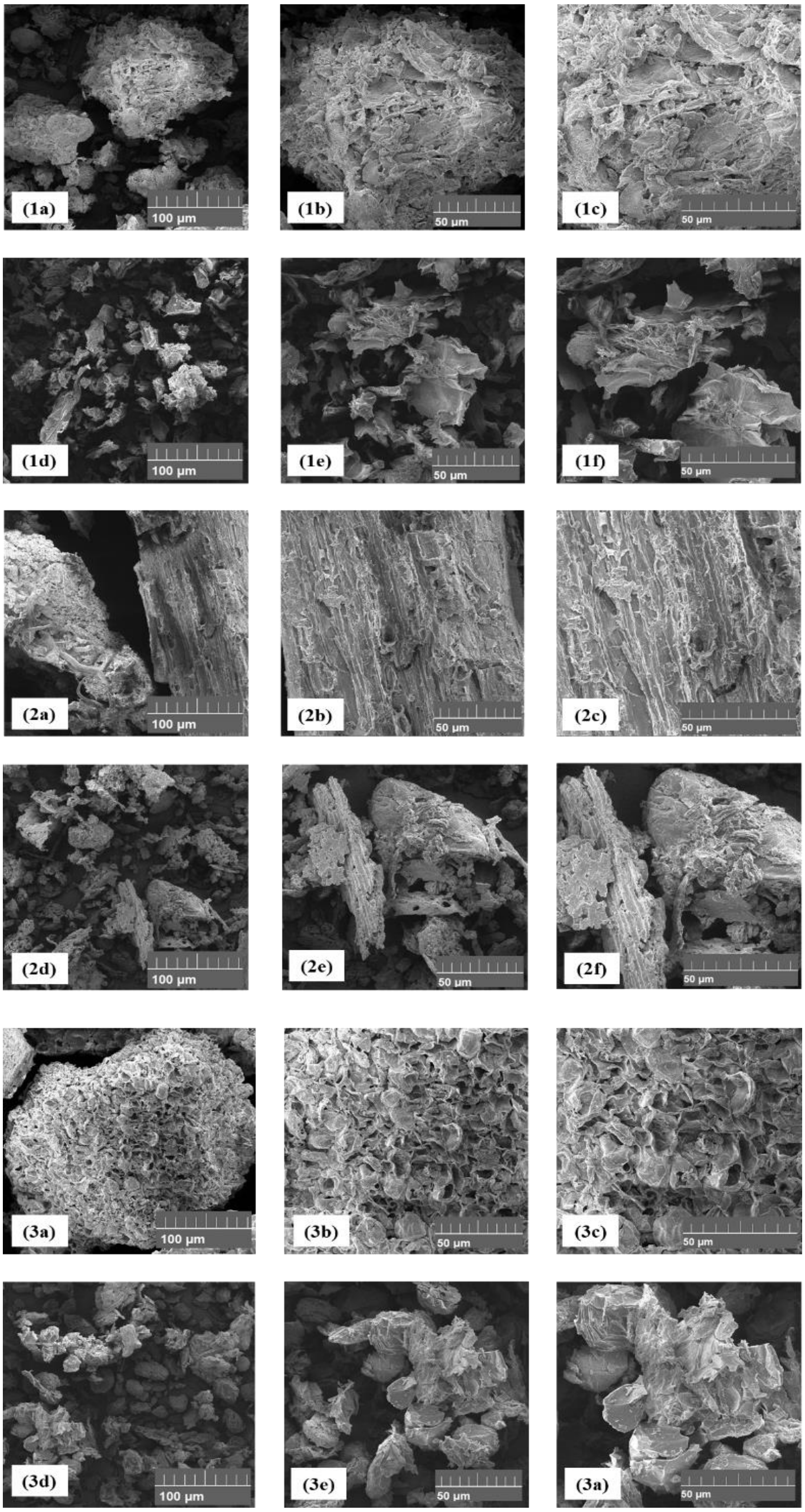


Figure 11. SEM micrograph of the structural surface of fresh pecan husks (1a, 1b and 1c – fresh biomasses; 1d, 1e and 1f - solid coproducts after SWH), leaves and stalks (2a, 2b and 2c – fresh biomasses; 2d, 2e and 2f - solid coproducts after SWH) and shells (3a, 3b and 3c – fresh biomasses; 3d, 3e and 3f – solid coproducts after SWH) in the highest sugars content condition in the magnifications of 500× (1a-3a, 1d-3d), 1000× (1b-3b, 1e-3e) and 1500× (1c-3c, 1f-3f).

3.3.6 Thermogravimetric Analysis

Pecan biomasses and SWH solid coproducts were analyzed by TGA to verify the degradation of these materials as a function of temperature increase (Figure 12). Thereafter, a thermogravimetric derived analysis (DTG) was developed based on the recommendations in the literature to determine the percentage composition of cellulose, hemicelluloses, lignin and charcoal masses [7]. The determination of these components individually was performed by integration and graphically normalized. Average temperatures were assigned to each of the components in the DTG curves. For cellulose, hemicelluloses, lignin, and char, the peak base temperature range by the DTG is specified in the literature.

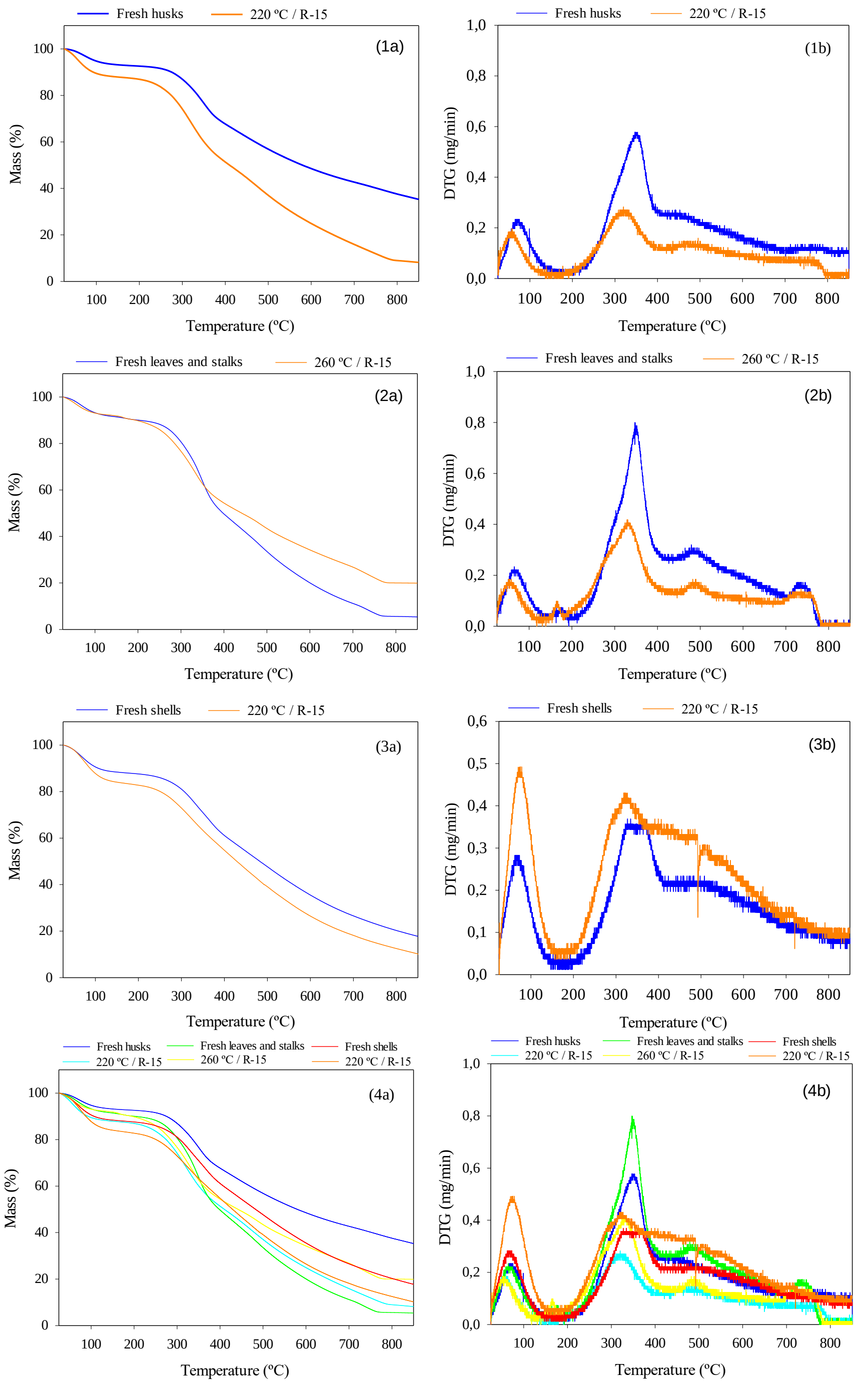


Figure 12. TGA of fresh pecan biomasses and solid coproducts after SWH procedure for husks (1a), leaves and stalks (2a), shells (3a), and all biomasses (4a) and DTG for husks (1b), leaves and stalks (2b), shells (3b), and all biomasses (4b); Y_{RS}: reducing sugars yield (g/100 g of biomass), R: water/ solid mass ratio (g water/g biomass).

For the thermal decomposition of cellulose, the temperature ranges were those recommended by the current literature [7], where, for the determination of cellulose, the range of 330-370 °C was used. For the determination of hemicelluloses, the temperature range was 175-350 °C. For the determination of lignin, the range of temperature used was 370-550 °C. Finally, for char determination, the temperature range was 550-770 °C. After heating the samples to 850 °C under a nitrogen chamber, only approximately 10 wt. % of pecan husks remained.

For husks, considering the solid coproduct generated from the SWH process in the conditions of 220 ºC and R-15, this value was approximately 8wt. %. The peak observed in the range between approximately 200 °C and 400 °C refers to the presence of hemicelluloses and cellulose [36, 7]. Higher peak attenuation was observed after the SWH process conditions, which shows the dissociation of cellulose and hemicelluloses after this procedure and is shown in Table 6. As shown in Table 7, there was a higher decoupling of cellulose at a temperature of 220 °C, which was approximately 26%. The lignin content was higher after the SWH process. Considering the largest dissociations of cellulose and hemicelluloses, the remaining solid presents a higher composition of lignin and char.

Table 7 - Composition (dry mass basis) of pecan biomasses obtained by the areas of peaks in the DTG analysis referring to cellulose, hemicelluloses, lignin, and char.

	Biomass	**Cellulose**	**Hemicelluloses**	**Lignin**	**Char**
Composition (wt.%)	**Husks**	13.1	19.2	38.4	29.1
	Leaves and stalks	14.2	31.7	28.5	25.5
	Shells	10.5	23.4	39.5	26.4

3.3.7 Fourier-transform infrared spectroscopy

The chemical constitution of the fresh residue of pecan biomasses and the solid coproduct obtained after the SWH procedure was performed by FT-IR (Figure 13).

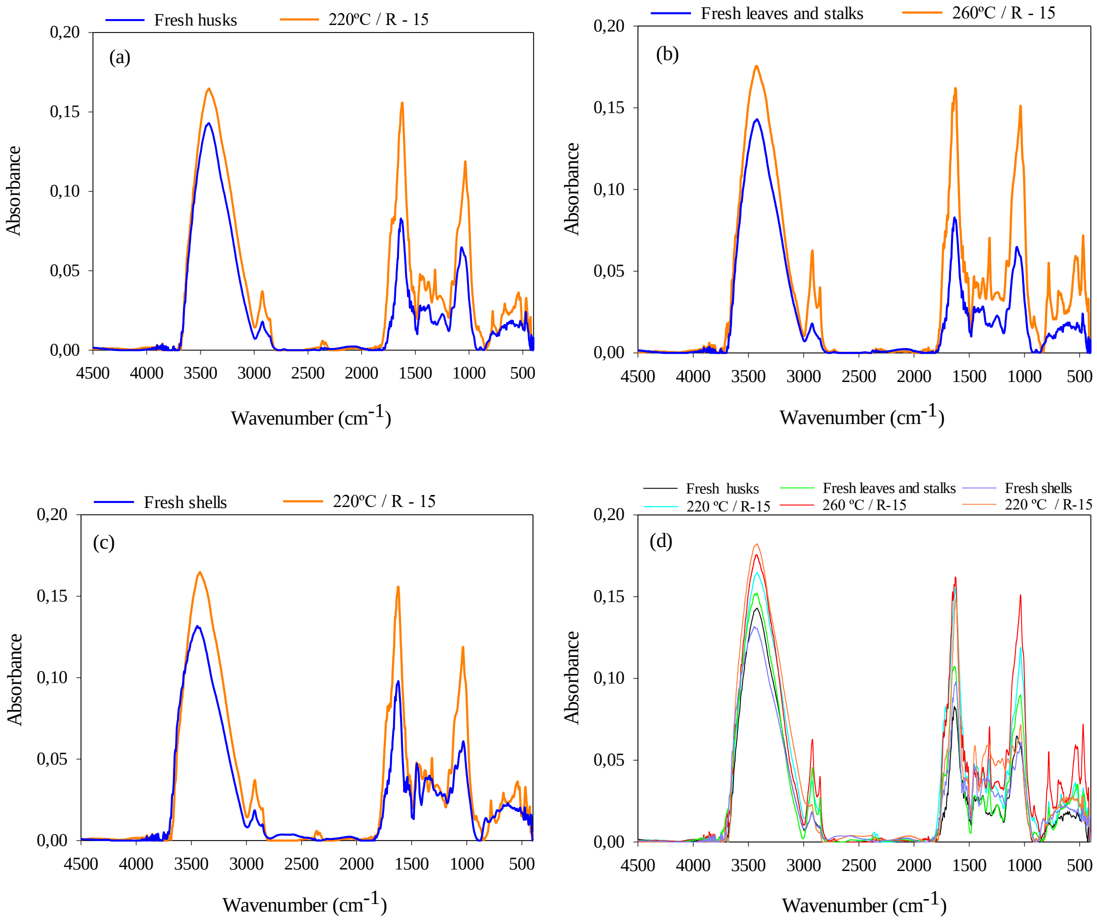


Figure 13. FT-IR spectroscopy analysis of fresh pecan husks and solid coproducts after SWH procedure for husks (a), leaves and stalks (b), shells (c), and all biomasses (d) in the conditions of the highest Y_{RS}.

For all biomasses, the FT-IR spectra of fresh material and solid coproducts after the SWH process showed similar behavior, but with different peak absorption intensities, indicating the different cellulose, hemicelluloses and lignin contents in the samples. The results obtained were similar to those found in the literature [7, 22]. SWH has removed certain components in different amounts if considered the different biomasses and conditions of the SWH procedure. The region of the bands near 3420 cm^{-1}, 3430 cm^{-1} and 3445 cm^{-1} for husks, leaves and stalks, and shells, respectively, reflects the –OH stretch, which is widely present in lignin structures [7, 39]. The bands' approach of 1034 cm^{-1}, 1035 cm^{-1} and 1031 cm^{-1} for husks, leaves and stalks, and shells, respectively, indicate the –CH stretch of cellulose sugar units [40].

Considering the materials resulting from the SWH process, the high-temperature conditions resulted in a peak increase corresponding to a range of approximately 4000 to 3000 cm^{-1}. This result is based on the lignin contents in the samples after the SWH process. In addition, there is a reduction in the peak corresponding to the range from 3500 to 3000 cm^{-1}. Clearly, the peak increase for the coproduct after the SWH procedure in the range between 4000 and 3000 cm^{-1} is noteworthy, as the temperature for the SWH process for leaves and stalks biomass was higher than for other biomasses.

3.4 CONCLUSIONS

Pecan biomasses were processed by SWH, in a semi-continuous mode. The husks and the shells obtained the highest yields (26.5 ± 7.1 wt.% and 27.1 ± 6.9 wt.%, respectively) at 220 ºC and R-15. For leaves and stalks, the highest yields (26.3 ± 1.6 wt.%) were obtained at 260 ºC and R-15. HPLC analysis showed the presence of arabinose, cellobiose, glucose, xylose, furfural and hydroxymethylfurfural. TGA, SEM and FT-IR analyses indicated modifications of solid structures and compositions. SWH is an important technology for the waste recycling context within a sustainable and clean way.

E-supplementary data for this work can be found in e-version of this paper online.

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CAPÍTULO 4

ESTRUTURA, CONTRIBUIÇÃO TEÓRICA, CONCLUSÕES E RECOMENDAÇÕES PARA TRABALHOS FUTUROS

4.1 ESTRUTURA

O objetivo desta Dissertação foi explorar o tópico acerca da obtenção de açúcares redutores em biomassas residuais da cultura da nogueira-pecã. Em particular, procurou-se explorar, ainda, quatro pontos de pesquisa: 1) análise e caracterização físico-química e morfológica das diferentes biomassas em condição *in natura;* 2) parametrização das condições ótimas do processo de hidrólise para as diferentes biomassas; 3) caracterização do meio hidrolisado; e 4) análise e caracterização das diferentes biomassas após os procedimentos das hidrólises.

Ao empregar as análises, descritas detalhadamente no Capítulo 3, este estudo contribui principalmente para a dinâmica do processo de hidrólise em água subcrítica para a obtenção de açúcares redutores e a literatura sobre a valorização de material remanescente de processos agrícolas e industriais. Para isso, foram considerados os seguintes segmentos: 1) uma inserção acerca da cultura da nogueira-pecã, espécie de grande importância regional e nacional, em uma literatura carente do tema; 2) uma revisão da literatura detalhada a respeito da identificação da espécie da nogueira-pecã e a aplicabilidade de seus resíduos e temas relacionados às principais tecnologias empregadas para o processo de caracterização físico-química destes materiais; e 3) uma descrição dos procedimentos referentes à aplicação da tecnologia subcrítica, importante ferramenta no meio científico.

De maneira geral, este estudo gerou, também, um conjunto de proposições relacionadas à agregação de valor de coprodutos de espécies vegetais frente ao desperdício destes materiais em uma esfera agrícola e industrial, em âmbito global. Do mesmo modo, proporcionou uma análise relativa ao desempenho destes materiais quanto à: 1) abundância de componentes de extrema importância científica e industrial em sua composição; 2) interesse em uma tecnologia ambientalmente correta e cientificamente aceita; 3) possibilidade de inovação e inserção socioeconômica, uma vez que viabilizam fontes de diversificação e desenvolvimento das regiões produtoras; e 4) perspectivas e potencialidades do uso destes materiais em um cenário de restrições de recursos.

Ainda, ressalta-se que este capítulo aborda as questões de pesquisa levantadas anteriormente, sintetizando os principais resultados derivados da análise de dados, minunciosamente relatados no **Capítulo 3**. Este estudo inclui dados coletados de diferentes biomassas de nogueira-pecã e uma análise sucinta de todos os procedimentos aplicados para a obtenção dos resultados, além de dados adicionais de várias outras fontes.

Este Capítulo final prossegue, a partir da descrição da contribuição teórica que esta

Dissertação proporciona, seguida das principais conclusões do estudo e recomendações para futuras pesquisas.

4.2 CONTRIBUIÇÃO TEÓRICA

O objetivo dessa Dissertação foi explorar a obtenção de açúcares redutores provenientes de biomassas residuais da nogueira-pecã. A análise e discussão conduzidas culminaram em um conjunto de proposições que contribuem principalmente para a literatura relacionada ao tema, mas também fornecem algumas ideias para a literatura a respeito do emprego da tecnologia subcrítica nesses materiais.

Como mencionado na Seção 1.3, a literatura acadêmica sobre a aplicação da tecnologia subcrítica em coprodutos de nogueira-pecã, especificamente, é fragmentada. Entretanto, alguns autores argumentam, de forma singular, a notoriedade do reaproveitamento de resíduos, mostrando a dinâmica das perspectivas desta pesquisa, bem como das alternativas da tecnologia subcrítica frente a outras técnicas designadas como nocivas. No entanto, existe uma tendência emergente no meio científico que reconhece a natureza da reciclagem de materiais potencialmente viáveis por meio de estratégias favoráveis ao ambiente, resultando em perspectivas otimistas para este cenário.

Como resultado da adoção deste desenho de pesquisa, que pode ser considerado uma contribuição metodológica para o campo, surgiram, naturalmente, contribuições teóricas para diferentes domínios. Portanto, este estudo contribui para o emprego da tecnologia subcrítica, bem como ressalta a importância do panorama acerca da reciclagem de resíduos e suas viabilidades. Esses direcionadores e temas foram importantes para orientar este estudo exploratório e para orientar também estudos futuros a respeito do assunto. Esta Dissertação, também, introduziu novas relações entre a cultura da nogueira-pecã, exclusivamente, e a aplicação de tecnologias reconhecidas como ‘limpas’, explorando a riqueza dos materiais remanescentes e a magnitude de suas aplicabilidades.

Como apontado anteriormente, vários estudiosos abordam a importância da reciclagem de resíduos e a dinâmica do seu contexto, o que é especialmente promissor. Neste mesmo sentido, a exploração acerca a tecnologia subcrítica, corrobora as assertivas levantadas por esta pesquisa. Além disso, inúmeros pesquisadores do assunto têm abordado a necessidade de ampliação da pesquisa acerca dessa técnica, o que resultaria em uma melhor compreensão do desempenho do processo. Com isso, este estudo contribui para a literatura sobre esse método, desenvolvendo uma avaliação abrangente de seu desempenho (Seção 2.6). Ainda, salienta-se que este estudo possibilitou a compreensão das melhores condições para os processos das hidrólises, considerando-se o uso de diferentes biomassas. Tal abordagem é excepcionalmente relevante, uma vez indicadas as variáveis observadas e o emprego de diferentes matérias-primas, o que propicia a este trabalho servir como um modelo instrutivo a outros trabalhos a serem realizados a respeito do tema.

A revisão de literatura (**Capítulo 2**) contribui para um conjunto de conhecimentos com uma revisão estruturada da literatura sobre a cultura da nogueira-pecã. Neste item, são levantadas informações acerca do panorama atual, a caracterização dos materiais remanescentes da cultura, a abordagem contemporânea da aplicabilidade desses remanescentes, tecnologias recentemente adotadas para a agregação de valor destes componentes, um contexto histórico e as principais expectativas relativas a essa temática. Com isso, esta Dissertação adiciona percepções informativas e apropriadas no contexto específico da cultura abordada e das metodologias adotadas.

Seguindo a estrutura geral do trabalho, o artigo realizado (**Capítulo 3**) refere-se aos dados coletados envolvendo a caracterização dos materiais *in natura* e das soluções resultadas dos processos de hidrólise. Este trabalho promove uma melhor compreensão acerca dos rendimentos e da caracterização dos açúcares nas diferentes biomassas da nogueira-pecã, mediante a aplicação de múltiplas técnicas reportadas na literatura. Ainda, é importante destacar que a obra exibe a caracterização das estruturas dos materiais remanescentes em dois momentos: previamente e posteriormente às hidrólises. Esta análise permite uma avaliação precisa do comportamento dos componentes destes materiais. Por fim, evidencia-se que todos os pontos aqui abordados são fundamentais, uma vez que a literatura científica sobre o tema ainda é limitada.

De modo geral, este estudo apresenta certas características que a distinguem de trabalhos anteriores no campo, o que pode ser observado, sobretudo, em função da carência de informações relacionada ao tema e às metodologias aplicadas. Portanto, esta Dissertação contribui para essa literatura, primeiramente, introduzindo a noção da importância da cultura da nogueira-pecã na produção de remanescentes ricos em compostos específicos e potencialmente viáveis às mais diversas finalidades, ao mesmo tempo que emprega uma tecnologia rápida e limpa, amplamente retratada em função de sua eficácia. Paralelamente, este estudo lança mais luz sobre o reaproveitamento de resíduos lançados no ambiente e sobre os gatilhos que essa problemática acarreta ao longo do tempo.

Para resumir, este trabalho contribui, principalmente, para a literatura acerca da tecnologia subcrítica e sua aplicabilidade em materiais reaproveitados, em particular para biomassas vegetais de nogueira-pecã. Estritamente, examinou a quantificação dos teores de açúcares redutores, a partir da investigação e caracterização de soluções resultadas dos processos de hidrólises, fornecendo uma ampliação da abordagem acerca de uma cultura de grande importância no cenário agrícola e econômico da região. O estudo também demonstrou a relevância do reaproveitamento de resíduos dos processamentos agrícolas e industriais, de modo a desenvolver um entendimento mais preciso de como o processo se desenrola e múltiplas aplicabilidades destes componentes.

4.3 CONCLUSÕES

A revisão da literatura, apresentada no **Capítulo 2**, traz uma gama de informações relacionadas ao panorama atual da cultura da nogueira-pecã em um âmbito nacional e internacional. Também, descreve as principais características das biomassas residuais desta cultura e suas diversas aplicabilidades relatadas na literatura. Ainda, foi possível compreender as principais tecnologias dos processos de extração de compostos de interesse desses materiais e a tecnologia envolvendo água em condição subcrítica, fundamental para o desenvolvimento deste estudo. Por fim, o **Capítulo 3** demonstra a prática desta ferramenta nos materiais vegetais da nogueira-pecã e suas respostas para as variáveis consideradas, objetivando a otimização das melhores condições do processo de hidrólise. Ainda, a seção aborda as análises e caracterizações físico-química e morfológica dos materiais in natura e após as diferentes condições da hidrólise subcrítica. Ainda, objetivou-se analisar a quantificação de açúcares redutores determinada por espectrofotometria e caracterizada por cromatografia líquida de alta eficiência.

Com o objetivo de se determinar o rendimento dos açúcares redutores presentes nas diferentes biomassas da nogueira-pecã, verificou-se que para os resíduos de pericarpo, a melhor condição da hidrólise com água subcrítica foi aquela com temperatura de 220 ºC e razão líquido/ sólido de 15 g água/ g biomassa (26.5 ± 7.1 g/ 100g biomassa). Já para as biomassas de folhas e talos, o maior rendimento de açúcares foi obtido na condição de temperatura de 260 ºC e razão líquido/ sólido de 15 g água/ g biomassa (26.3 ± 1.6 g/ 100g biomassa). Por fim, para os materiais de cascas, o maior rendimento de açúcares foi na condição de 220 ºC e razão líquido/ sólido de 15 g água/ g biomassa (27.1 ± 6.9 g/ 100g biomassa). Ainda, por meio do método da CLAE foi possível constatar a presença dos inibidores furfural e HMF e a quantificação destes elementos nas soluções de maiores rendimentos de açúcares.

O detalhamento da estrutura superficial das diferentes biomassas evidenciou as alterações resultadas em função dos procedimentos de hidrólise. Esta determinação foi confirmada pelas análises em MEV, que apontaram a ruptura da estrutura dos materiais *in natura* e o aumento da presença de microestruturas superficiais, o que corrobora a tecnologia subcrítica como uma importante ferramenta a ser aplicada para o rompimento da estrutura lignocelulósica com o objetivo de se obter açúcares redutores.

O comportamento das diferentes biomassas em função da temperatura por meio das análises de TGA e DTG possibilitou compreender as alterações que as condições térmicas podem provocar na massa dos resíduos, estabelecendo as faixas de temperatura de determinação da composição química desses materiais.

De maneira geral, o desenvolvimento deste estudo proporciona o surgimento de importantes informações relacionadas à caracterização das biomassas da nogueira-pecã e à aplicação da tecnologia subcrítica e as melhores condições de extração de compostos em materiais residuais da espécie, sustentando as inúmeras aplicabilidades destes resíduos em diversas áreas de estudo.

4.4 RECOMENDAÇÕES PARA TRABALHOS FUTUROS

Este estudo sugere a importância da prerrogativa acerca do aproveitamento e aplicabilidade de materiais vegetais residuais, optando por alternativas sustentáveis e benéficas ao meio ambiente. A maior parte dos referenciais levantados neste trabalho focaram suas obras no propósito de exploração destes materiais e todas as vantagens decorrentes de seu desenvolvimento. Portanto, salienta-se a necessidade de continuidade destas pesquisas, não somente relacionadas à cultura da nogueira-pecã, compreendendo alcançar agregação de valor a esses coprodutos, o que possibilita sua aplicação para inúmeros propósitos.

Ainda, este trabalho gerou proposições a respeito do emprego da tecnologia subcrítica em materiais remanescentes de nogueira-pecã. Entretanto, é notável que mais pesquisas, utilizando tal abordagem, são necessárias para corroborar essas proposições. De fato, é de suma importância que os pesquisadores e a literatura científica moderna abordem as perspectivas levantadas, de modo a explorar as ideias geradas por esta Dissertação. Ainda, salienta-se que esta pesquisa viabiliza estender suas descobertas para avaliar condições ótimas para o processo da hidrólise em água subcrítica, considerando-se as variáveis observadas, como temperatura e vazão. Além disso, uma vez que este estudo se concentrou em investigar a potencialidade de biomassas residuais provenientes dos processamentos industriais e dos processos de colheita, como fontes de açúcares redutores e compostos de interesse, pesquisas mais representativas, preferencialmente, relacionadas à obtenção de biocombustíveis como uma alternativa sustentável para a geração de energia, também poderiam trazer mais *insights* sobre a importância e magnitude de destinos mais adequados a estes materiais.

A partir das asserções abordadas no item 2.6, uma distinção entre as diversas metodologias utilizadas para os processos de hidrólise, e que têm sido reportadas na literatura, pode ser ressaltado como um ponto interessante. Pesquisas futuras se beneficiariam de reconhecer as melhores condições, o que pode proporcionar a formulação de metodologias de pesquisa de uma maneira que potencialize a dinâmica das técnicas adotadas. Como é de total interesse dos pesquisadores um aprofundamento e particularidades de suas pesquisas, as proposições geradas neste estudo podem ser desenvolvidas com outros métodos de pesquisa complementares.

O estudo identificou as características mais relevantes no que se refere ao material da nogueira-pecã, tanto em condição *in natura*, como em solução hidrolisada. No entanto, considerando-se a ampla abordagem anteriormente descrita no que se refere ao conceito de biorrefinarias, os resultados evidenciam que as soluções originadas das hidrólises podem ser, facilmente, submetidas a processos de fermentação, integrando técnicas de conversão destes materiais em biocombustíveis, que podem ser detalhadamente caracterizados conforme sua composição e poder calorífico. Portanto, é de grande interesse investigar e caracterizar esses materiais, de modo a explorar seus impactos em cada um dos elementos do modelo de negócios.

Ainda, salienta-se a importância de uma avaliação sucinta da cristalização das diferentes biomassas, especificamente no decorrer do processo da hidrólise, visando uma investigação acerca da digestibilidade destes materiais ao longo desta fase. Pesquisas futuras podem tentar desenvolver uma concepção relacionada a este tópico, refletindo com mais precisão o amplo espectro de adversidades prováveis no procedimento, uma vez que estes materiais são agentes propícios à obstrução das tubulações.

Este estudo sugeriu as melhores condições dos procedimentos de hidrólise por meio de uma tecnologia que consome água em seu processamento. Assim, a utilização deste recurso tem um impacto impressionante no progresso do processo ao longo do tempo. Entretanto, ressalta-se que a conjuntura do consumo de água no processo não tem sido explorada em detalhes na literatura. Portanto, pesquisas adicionais podem investigar um levantamento acerca do consumo de água no processo das hidrólises e sua influência no sistema ao longo do tempo.

Outros importantes tópicos a serem considerados são um estudo cinético e a capacidade e determinação da adsorção do material ao longo do processo da hidrólise. Esta questão precisa de mais detalhes de investigação e as informações potenciais geradas contribuiriam para a literatura acerca do tema.

Considerando-se a carência de estudos que se aprofundam na determinação de açúcares redutores em resíduos de nogueira-pecã, exclusivamente, destaca-se a necessidade do emprego de metodologias que oportunizem esse contexto. Esta tese propôs exatamente esta conjuntura, a partir de metodologias específicas presentes na literatura aplicadas em diversas outras espécies vegetais. Este quadro serve como uma perspectiva alternativa para examinar esses processos em uma cultura pouco abordada. Entretanto, aponta-se que muitos outros estudos podem ser desenvolvidos para avaliar as concentrações dos açúcares redutores em biomassas vegetais, por meio de inúmeros outros procedimentos presentes na literatura. Pesquisas futuras também poderiam desenvolver ainda mais essa abordagem, considerando-se, ainda, a comparação e eficácia de diferentes métodos de determinação destes componentes.

Este estudo averiguou a potencialidade de diferentes biomassas de nogueira-pecã a partir de uma metodologia específica, amplamente abordada anteriormente. Entretanto, seria pertinente a adoção de sugestões de diversas outras práticas quanto ao aproveitamento dos resíduos gerados nas fases iniciais dos preparos das amostras e dos processos das hidrólises. Pesquisas adicionais podem desenvolver maiores diretrizes no que se refere a estes materiais e compreender o seu comportamento e desempenho podem ser relevantes para o desenvolvimento de pesquisas futuras que utilizam não somente material remanescente de nogueira-pecã, mas, também, de outras espécies.

Conforme evidenciado acima, o campo do aproveitamento e caracterização de biomassas vegetais apresenta uma variedade de caminhos de pesquisa estimulantes e desafiadores. Um paradigma mais dinâmico que captura a valorização de materiais tem sido reportado na bibliografia científica atual. Desta forma, o presente estudo tentou fornecer uma compreensão mais rica desse contexto e, simultaneamente, uma base para investigações mais rigorosas e produtivas sobre esse tópico. Assim, este trabalho almeja, também, inspirar pesquisas futuras, não apenas no contexto de aproveitamento e aplicação de biomassas descartadas de nogueira-pecã, mas, também, em outros contextos que envolvem esta cultura.

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