UNIVERSIDADE ESTADUAL DE CAMPINAS
FACULDADE DE ENGENHARIA DE ALIMENTOS

DANIEL LACHOS PÉREZ

Subcritical water technology to recover phenolic compounds, sugars and biochar formation from agroindustrial residues: biorefinery concept

Uso da tecnologia da água subcrítica para a recuperação de compostos fenólicos, açúcares e formação de *biochar* a partir dos resíduos da agroindústria: conceito de biorrefinaria

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Orientadora: Profa. Dra. Tânia Forster Carneiro
Co-orientador: Prof. Dr. Julian Martinez

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Resumo

Nos últimos anos, um dos desafios da sociedade baseia-se no conceito de bioeconomia. Este termo refere-se à produção e conversão sustentável de biomassa em uma variedade de compostos benéficos à saúde, produtos industriais e energia. No entanto, para atingir este desafio, novas políticas serão necessárias para produzir bioprodutos de acordo com a disponibilidade de biomassa em cada área, assim como também a pesquisa deve estar focada em alcançar o desenvolvimento de processos ambientalmente corretos, procurando oportunidades em novas matérias-primas e a utilização de solventes limpos.

A palha de cana-de-açúcar é uma excelente fonte de matéria prima, devido a sua grande produção e alto conteúdo de material lignocelulósico, o que a torna uma potencial fonte para produção de biocombustíveis. Além da cana-de-açúcar, outro setor que merece destaque no mercado agroindustrial brasileiro é o da produção de citrus, sendo a laranja a principal representante. A grande quantidade de subprodutos gerados no processamento desta fruta apresenta propriedades bioativas interessantes, que vem sendo utilizadas em inúmeras aplicações nas indústrias de alimentos, saúde, farmacêutica e de cosméticos.

Contudo, novos processos ambientalmente corretos que visem a obtenção de compostos bioativos e conversão para plataformas químicas são necessários, sendo um exemplo o processo hidrotérmico proposto neste trabalho, que visa desenvolver a extração de compostos bioativos e conversão sustentável e eficiente da biomassa em produtos químicos com alto valor agregado para a indústria utilizando água como solvente ou meio de reação. Esta tecnologia é uma alternativa promissora para realizar o fracionamento da biomassa, pois o meio permite a transformação das diferentes frações de biomassa através da alteração de parâmetros apropriados como temperatura, pressão e vazão. Além disso, a água é um solvente limpo, seguro e ambientalmente correto.

Assim, o objetivo deste trabalho foi estudar a palha de cana-de-açúcar e casca de laranja para produção de produtos de maior valor agregado por meio do processo hidrotérmico através dos seguintes métodos: extração com água subcrítica (SWE), hidrólise com água subcrítica (SCW), e processo sequencial extração-hidrólise.

Os resultados obtidos na hidrólise da palha de cana-de-açúcar com água subcrítica mostraram que na temperatura de 200 °C os principais açúcares encontrados nos hidrolisados foram a glicose e açúcares hemicelulósicos, além de subprodutos menores (HMF e furfural), considerados inibidores da fermentação. Os maiores rendimentos foram encontrados para açúcares redutores totais (ART) e conteúdo de glicose, sendo 32,1% (m/m) e 2,1% (m/m) respectivamente. Além disso, análises Termogravimétricas (TGA) e Espectroscopia no infravermelho por transformada de Fourier (FT-IR) evidenciaram informações relevantes sobre a formação de "*biochar*" em temperaturas superiores a 200 °C.

Os resultados obtidos na extração com água subcrítica da casca de laranja desengordurada (resíduo polar pós extração com CO_2 supercrítico) mostraram a recuperação de flavanonas como hesperidina e narirutina. A melhor condição de extração foi obtida a 150 °C e 10 mL/min, resultando em rendimento global de extração igual a 10,63% (m/m), e de flavanonas (hesperidina e narirutina) igual a 210 mg/g de extrato. Os extratos apresentaram alta capacidade antioxidante e a existência de uma correlação elevada e positiva com o conteúdo de fenólicos totais e de hesperidina e narirutina. Quando comparado com técnicas de extração a baixa pressão, o processo com água subcrítica mostrou melhor desempenho.

Por fim, ensaios de aproveitamento integral dos resíduos utilizando um processo sequencial extração-hidrólise em água subcrítica para obter frações concentradas de compostos bioativos e açúcares C5 C6 utilizando casca de laranja foram testados. Os resultados mostraram que foi possível recuperar na temperatura de extração (150 °C) flavanonas e compostos solúveis (açúcares livres) com rendimentos de 24.4 mg/g Orange Peel (OP) e 24 mg/g OP respectivamente, e sequencialmente produzir nas temperaturas de hidrólise (200, 225 e 250 °C) açúcares C5 e C6 com baixa quantidade de inibidores. As análises de TGA e FT-IR providenciaram informações sobre a extração de pectina a temperaturas maiores de 200 ° C.

Palavras chaves**:** *Bioeconomia, Palha de cana-de-açúcar, Casca de laranja, Processo hidrotérmico*

Abstract

In the last years, the challenge is a society based on the concept of bioeconomy. This term refers to the sustainable production and conversion of biomass into a variety of compounds, beneficial to health, or industrial products and energy. In order to accomplish this challenge, new policies will be necessary to develop a decentralized local-scale production to produce bio-products according to the biomass availability in each area, as well as researches must be focused on achieving the development of environmental compatible processes, searching opportunities among new raw materials and by using clean solvents as water or carbon dioxide.

Sugarcane straw is an excellent source of raw material, due to its large production and high content of lignocellulosic material, which makes it a potential source for the production of biofuels. In addition to sugarcane, another sector that deserves to be highlighted in the Brazilian agroindustrial market is citrus production, being orange the main representative. The large amount of byproducts generated in the processing of this fruit shows interesting bioactive properties that have been used in numerous applications in the food, health, pharmaceutical and cosmetic industries.

The hydrothermal process has been proposed to develop sustainable and efficient conversion of biomass into bioactive compounds beneficial to health and chemicals with high value-added for the industry. It is a promising technology to perform the fractionation of biomass because the reaction medium allows the transformation of the different fractions of biomass by choosing the appropriate conditions. Furthermore, water is a clean, safe and environmentally solvent. The use of the semicontinuos reactor has been proposed to study the behaviour of hydrothermal processes being the results obtained “acceptable” compared to the results found in the literature.

This study aimed to study sugarcane straw and orange peel for the production of higher value-added products by hydrothermal process using the following methods: subcritical water extraction (SWE), subcritical water hydrolysis (SCW), and sequential extraction-hydrolysis process.

The results obtained in subcritical water hydrolysis of sugarcane straw showed that the main sugars found in the hydrolysates were glucose, xylose, arabinose, and galactose in addition to 5- hydroxymethylfurfural and furfural as minor

byproducts at the temperature of 200 °C. The highest yields were found for total reducing sugars (ART) and glucose content, being 32,1% (w/w) and 2,1% (w/w), respectively. Fourier transform infrared spectroscopy and thermogravimetric analysis provided additional information on the surface and bulk composition of the residual biomass at temperatures higher than 200 °C.

The results obtained in subcritical water extraction (SWE) of flavanones from defatted orange peel (residue from supercritical CO_2 extraction) showed that the recovery of phenolic compounds as flavanones: hesperidin and narirutine. The maximum yields of hesperidin (188.74 ± 0.51 mg/g extract) and narirutin (21.98 ± 1.39 mg/g extract) were obtained at 150 °C and 10 mL/min. These yields accounted for approximately 21% of the total amount of these flavanones in the extracts, leading to the purest extracts. SWE was compared with three conventional extraction methods and the results demonstrated that, compared to conventional extractions, SWE is a highly efficient method for the recovery bioactive compounds with high antioxidant activity.

Finally, tests using a sequential extraction-hydrolysis process in subcritical water to obtain concentrated fractions of bioactive compounds and C5 and C6 sugars from orange peel was used. The results showed that it was possible to recover at the extraction temperature (150 °C) flavanones and soluble compounds (free sugars) with yields of 24.4 mg / g OP and 24 mg / g OP respectively, and sequentially produce at the hydrolysis temperatures (200, 225 and 250 °C) C5 and C6 sugars with low inhibitors yields. The TGA and FT-IR analyzes provided information on the extraction of pectin at temperatures higher than 200 °C.

Keywords: *Bioeconomy, Sugarcane straw, Orange peel, Hydrothermal process*

SUMÁRIO

1. - CAPÍTULO 1- Introdução geral, objetivos e estrutura da tese

1.1. Introdução geral

O rápido crescimento populacional levou ao aumento da produção de alimentos, especialmente nos países em desenvolvimento. Nesse cenário, grande variedade e quantidade de resíduo são gerados, sendo a biomassa vegetal um exemplo deste. A biomassa refere-se à toda a matéria orgânica de origem animal ou vegetal que pode ser utilizada na produção de diferentes compostos de valor agregado e energia. Dentre os tipos de biomassa existem aquelas de origem vegetal, que representam o maior potencial de aproveitamento energético devido a sua grande disponibilidade (Basu e Mettanant, 2009).

No Brasil, a disposição final dos resíduos orgânicos e de biomassa vegetal ainda não ocorre de forma ambientalmente adequada, sendo que muitos resíduos procedentes das atividades domésticas e da indústria alimentícia são destinados em aterros sanitários, enquanto que as biomassas vegetais das atividades agrícolas permanecem no campo. A cana-de-açúcar e a laranja representam importantes produtos agroindustriais brasileiros com elevadas produções anuais. A produção de cana-de-açúcar na safra 2017/2018 foi de 641 Mton e a quantidade de laranja na safra 2018/2019 foi de 11,15 Mton (FAO, 2019; Unica, 2019). Tais resultados tornam o Brasil o maior produtor mundial desses dois produtos agrícolas, e como resultado, grandes quantidades de resíduos são geradas durante o processamento, constituídos principalmente de palha de cana-de-açúcar e casca de laranja. Por conseguinte, conseguir fazer uma disposição final adequada, assim como valorizar estes resíduos (reciclar e reutilizar) pode tornar a produção mais sustentável e gerar produtos de maior valor agregado.

A palha da cana-de-açúcar é um dos principais resíduos do processamento de cana-de-açúcar. Para cada tonelada de cana processada, são gerados cerca de 140 kg de palha (Vardanega *et al*., 2015; Lachos-Perez *et al*., 2017), o que resultou na produção de 80 milhões de toneladas de palha na safra 2017/2018. A palha de cana-de-açúcar é basicamente composta de material lignocelulósico, isto é, celulose (37%), hemicelulose (36%) e lignina (21%), resultando em potencial fonte de bioenergia devido à sua alta disponibilidade e alto potencial renovável (Szczerbowski *et al.,* 2014; Del Río *et al.,* 2015; Rueda-Ordóñez e Tannous, 2015). A primeira planta de tamanho comercial que converte resíduos de cana para etanol de segunda geração foi lançada em 2013 na Itália. Atualmente no Brasil, a usina GranBio já produz etanol

2G utilizando como matéria prima a palha de cana-de-açúcar. Estes exemplos mostram que o etanol 2G ainda está em fase de desenvolvimento, sendo necessário maior conhecimento sobre a quantificação dos impactos na agricultura, a quantidade de palha disponível após a colheita, as taxas de decomposição, os custos de coleta e, consequentemente, quanto deve ser deixado no campo para otimizar a sustentabilidade do cultivo e processamento da cana.

Além da indústria da cana de açúcar, no Brasil destaca-se a indústria da laranja como uma enorme fonte de resíduos agroindustriais a serem aproveitados. A laranja é uma fruta que pode ser utilizada integralmente, pois, após a extração do suco, gera-se 50% de resíduo constituído de casca, semente e membranas que são secos e comercializados, em forma de "pellets de polpa cítrica", para ração animal (Lohrasbi *et al.,* 2010). Entretanto, a quantidade de proteínas nesse resíduo é baixa, não suprindo as necessidades dos animais. Sua utilização é interessante para outros fins, uma vez que a casca da laranja possui compostos fenólicos como flavanonas de grande interesse medicinal, sendo associados à redução dos riscos de câncer, colesterol e derrames, além de atuar como agente antioxidante, anti-inflamatório, antimicrobiano e antiviral (Chu *et al.,* 2017; Lachos-Perez *et al.,* 2018; Albuquerque *et al.,* 2019). Por outro lado, a casca também possui açúcares solúveis, como glicose, frutose e sacarose, enquanto que a parede celular desta fruta é composta por polissacarídeos como a pectina, celulose e hemicelulose, além de uma pequena quantidade de lignina (Grohmann *et al.,* 1995).

A obtenção de compostos, tanto da palha de cana-de-açúcar como da casca de laranja, podem originar uma gama de produtos comerciais, seja matéria-prima para processos secundários, substitutos para ingredientes ou plataformas químicas para produção de biocombustíveis (Martínez *et al.,* 2012). Entretanto, para explorar estes recursos, estratégias comercialmente viáveis para a extração, reação e disponibilização precisam ser desenvolvidas. O uso da água em condições subcríticas de temperatura e pressão atua como solvente ou meio de reação e vem ao encontro aos interesses por processos limpos de transformação. Devido às suas propriedades, a água subcrítica vem sendo usada para um grande número de aplicações como extração e reações de hidrólise (Moreschi, 2004).

O estado subcrítico da água é definido como o intervalo entre 100 °C e 300 °C (Wagner e Pruß, 2002; Ko *et al.,* 2014) com pressão necessária para mantê-la em

estado líquido, sendo assim um solvente ou meio de reação efetivo para compostos polares e apolares. A extração com água subcrítica é uma técnica emergente, sendo que, o processo geralmente acontece a temperaturas brandas (110 - 180 °C), quando o alvo é a obtenção de compostos bioativos, principalmente porque estes são termossensíveis, e em temperaturas mais altas, os rendimentos de extração frequentemente aumentam, porém, o risco de degradação do extrato também aumenta.

Nos processos de hidrólise com água subcrítica (200-250 °C) a reação ocorre de forma rápida (tempo de reação variando de alguns segundos a poucos minutos), tornando o processo seletivo em função da variação dos parâmetros operacionais (Cantero *et al.,* 2013). A hidrólise de celulose com água subcrítica resulta em composto C6 (6 carbonos) de variados graus de polimerização, com inúmeros usos nas indústrias, como para produção de etanol de segunda geração (2G), quanto ao fracionamento da hemicelulose, resultando na obtenção de compostos C5 (5 carbonos) e C6. Entretanto, as condições operacionais necessárias para decompor a matriz lignocelulósica são severas, sendo que a degradação de açúcares simultaneamente com o processo hidrolítico é comum. Isso leva à formação de ácidos orgânicos, furfural e 5-hidroximetil-furfural (5-HMF), entre outros aldeídos furânicos, que são tóxicos para os microrganismos fermentadores em uma possível produção de etanol 2G (Prado *et al.,* 2016; Cocero *et al.,* 2018). Assim, o processo de hidrólise deve ser otimizado para que os rendimentos de açúcares fermentáveis sejam maximizados, enquanto a formação de produtos de degradação seja minimizada.

Foram encontrados poucos trabalhos na literatura tratando da extração-hidrólise usando água subcrítica na forma sequencial. Além disso, foram encontrados poucos registros de trabalhos que tenham feito o aproveitamento integral dos resíduos utilizando um processo sequencial para obter frações concentradas em compostos bioativos e ricas em açúcares fermentáveis, e com baixo conteúdo de aldeídos furânicos. Baseando-se nisto, este trabalho apresenta alternativas para a extração, hidrólise e processo sequencial extração-hidrólise de dois resíduos agroindustriais dando ênfase ao uso do conceito de biorrefinaria.

1.2. Objetivos

1.2.1. Geral

O objetivo principal deste trabalho foi valorizar os resíduos procedentes da agroindústria (palha de cana-de-açúcar e casca de laranja) mediante processos hidrotérmicos através de extração e hidrólise e o processo sequencial em água subcrítica, visando a obtenção de produtos com maior valor agregado (compostos bioativos, açúcares e *biochar*) usando um conceito de biorrefinaria.

1.2.2. Específicos

- Estudar a hidrólise de água subcrítica a partir da palha de cana-de-açúcar:
  - Quantificar o rendimento dos açúcares redutores totais;
  - Avaliar a influência da pressão e temperatura no processo;
  - Identificar e quantificar quimicamente os principais monômeros formados e inibidores;
  - Examinar a estrutura macromolecular do resíduo sólido e composição superficial remanescente no reator;
- Estudar a extração com água subcrítica de compostos fenólicos e flavonoides a partir da casca de laranja desengordurada:
  - Quantificar o rendimento global;
  - Quantificar fenólicos totais;
  - Identificar e quantificar as flavanonas predominantes contidos nos extratos (hesperidina e narirutina);
  - Quantificar a capacidade antioxidante dos extratos.
- Realizar o aproveitamento integral dos resíduos utilizando um processo sequencial extração-hidrólise em água subcrítica para obter frações concentradas de compostos bioativos e outros produtos de interesse como açúcares e aldeídos furânicos:
  - Quantificar o rendimento dos compostos solúveis (açúcares livres);
  - Quantificar compostos fenólicos totais;
  - Quantificar a capacidade antioxidante dos extratos;
  - Uso da tecnologia da água subcrítica para a recuperação de compostos fenólicos, açúcares e formação de biochar a partir dos resíduos da agroindústria: conceito de biorrefinaria;

- Quantificar o rendimento dos açúcares redutores;
- Identificar e quantificar os principais monômeros formados e inibidores;
- Examinar a estrutura macromolecular do resíduo sólido e composição superficial remanescente no reator.

1.3. Estrutura da tese

Esta tese se encontra dividida em capítulos. Os capítulos que apresentam a revisão bibliográfica e os resultados experimentais correspondem a artigos que estão publicados ou estão sendo revisados em revistas científicas da Área de Engenharia de Alimentos.

O **Capítulo 1** é composto pela introdução, onde se insere ao leitor o tema central desta tese, colocando, de forma sucinta, os pontos mais relevantes, os objetivos e estrutura da tese. Sendo o Brasil o maior produtor mundial de cana-de-açúcar e laranja, primeiramente foi contextualizada a importância da quantidade e variedade de resíduos orgânicos gerados e biomassa vegetal. Por conseguinte, detalhou-se de que forma valorizar estes resíduos (reciclar e reutilizar) podem tornar a produção sustentável e gerar produtos de maior valor agregado. Em seguida, foi explicado o uso da tecnologia da água subcrítica, uma técnica emergente e bastante promissora, baseada no uso de água como solvente em alta pressão e tempratura e meio de reação para obtenção de novos compostos químicos com inúmeras aplicações na indústria farmacêutica e/ou de cosméticos, assim como para produção de biocombustíveis.

O **Capítulo 2** apresenta a revisão bibliográfica, onde justificou-se o uso da água sub/supercrítica como solvente para obtenção de composto bioativos e como meio de reação para fracionamento da biomassa e produção de hidrogênio, assim como também a valorização dos resíduos sólidos remanescentes do processo hidrotérmico (*biochar)*. A revisão visa resumir os desenvolvimentos recentes e aspectos essenciais do uso da água sub/supercrítica nos processos de extração, hidrólise, gaseificação e carbonização da biomassa, sendo os compostos bioativos, açúcares, hidrogênio e *biochar* os produtos finais destes processos. Tipos de reatores, parâmetros de processo e as diferentes biomassas usadas com água sub/supercrítica são apresentados resumidamente. Os benefícios da adição de catalisador para melhorar a eficiência do processo são também abordados.

Este capítulo deu origem a um artigo de revisão que foi publicado na revista *Biofuel Research Journal* no ano de 2017 intitulado "*Applications of subcritical and supercritical water conditions for extraction, hydrolysis, gasification, and carbonization of biomass: a critical review*".

O **Capítulo 3** relata o processo de hidrólise da palha da cana-de-açúcar, em um reator semi-contínuo a temperaturas de reação entre 190 a 260 °C e pressões de operação entre 9 e 16 MPa. Os maiores rendimentos dos principais produtos da hidrólise da palha de cana-de-açúcar foram glicose, xilose, arabinose e galactose, além de 5-hidroximetilfurfural e furfural como subprodutos em menores quantidades na temperatura de 200 °C. A formação do *biochar* esteve presente em amostras tratadas a temperaturas iguais e superiores a 190 °C. As amostras tratadas a 260 °C continham aproximadamente 20% em peso de *biochar,* mas mantinham conteúdo substancial de hemicelulose e celulose. A espectroscopia de infravermelho por transformada de Fourier e a análise termogravimétrica providenciaram informações adicionais sobre a formação de "biochar" e permitiram visualizar grande aplicação como adsorvente altamente seletivo.

Este capítulo consiste em um artigo que foi publicado na revista Bioresource Technology no ano de 2017 intitulado "*Sugars and char formation on subcritical water hydrolysis of sugarcane straw*". Os autores Geoffrey A. Tompsett, Patricia Guerra, e Michael T. Timko contribuíram na realização das análises dos resíduos sólidos remanescentes (FTIR, TGA). O autor Mauricio A. Rostagno contribuiu na realização das análises de identificação e quantificação dos inibidores de fermentação.

Os resultados obtidos do *biochar* permitiram que um posterior trabalho no grupo de pesquisa fosse publicado confirmando a hipótese de que a composição diferenciada dentro das partículas do *biochar* ainda contêm celulose e hemicelulose. Desta forma, decidimos finalizar os ensaios com palha de cana-de-açúcar e iniciar os ensaios com uma nova matéria prima.

Deste modo, decidiu-se usar outra matéria-prima (casca de laranja) para continuar dando ênfase no conceito de biorrefinaria. Este material vinha sendo utilizado por outros grupos de pesquisa da faculdade. No entanto, o resíduo era comumente descartado após processos de extração com CO_2 supercrítico. Sendo assim, surgiu o interesse desse resíduo rico em carboidratos e compostos fenólicos polares. Neste contexto, para o melhor aproveitamento do resíduo após o processo de extração com dióxido de carbono supercrítico, a casca de laranja desengordura foi a nova matéria prima usada neste trabalho.

O **capítulo 4** apresenta os resultados provenientes da extração com água subcrítica para extrair flavanonas, variando a constante dielétrica dependente da temperatura. Flavanonas, incluindo hesperidina e narirutina, constituem a maioria dos flavonoides que ocorrem naturalmente em frutas cítricas. Neste capítulo avaliaram-se os efeitos dos parâmetros operacionais de temperatura (110-150 °C) e vazão de água (10-30 mL/min). Os rendimentos máximos de hesperidina (188,74 ± 0,51 mg/g extrato) e narirutina (21,98 ± 1,39 mg/g extrato) foram obtidos a 150 °C e 10 mL/min. Os resultados mostram que, os rendimentos foram responsáveis por aproximadamente 21% da quantidade total das flavanonas nos extratos.

Adicionalmente, esta tecnologia foi comparada com outros três métodos convencionais de extração à baixa pressão e os resultados demonstraram que, em comparação com extrações convencionais, a extração com água subcrítica é um método altamente eficiente para a recuperação de compostos bioativos com alta capacidade antioxidante.

Este capítulo consiste em um artigo que foi publicado na revista *The Journal of Supercritical Fluids* no ano de 2018 intitulado "*Subcritical water extraction of flavanones from defatted orange peel*". Os autores Andressa M. Baseggio e Mário R. Maróstica Junior contribuíram na realização das análises de capacidade antioxidante. O autor Mauricio A. Rostagno contribuiu na realização das análises de identificação e quantificação dos flavonoides (hesperidina e narirutina).

O **capítulo 5** apresenta um estudo visando à obtenção de frações de extrato rico em flavanonas e frações com hidrolisados ricos em açúcares C5 e C6, de forma sequencial a partir da casca de laranja, usando água subcrítica em dois níveis de temperatura em um processo de extração-hidrólise.

Usando o conceito de biorrefinaria, planejou-se ensaios de extração seguido de hidrólise com água subcrítica: ou seja, tecnologia de extração-fracionamento sequencial em duas etapas para a produção simultânea de flavanonas e açúcares. Neste caso o resíduo de casca de laranja utilizado foi o subproduto do processamento de suco, fornecido pela empresa CPKelco, Limeira, SP-Brasil. Os experimentos hidrotérmicos de extração-hidrólise de casca de laranja foram conduzidos em um reator de fluxo semi-contínuo. O primeiro passo envolveu a extração subcrítica das flavanonas e compostos solúveis (açúcares livres) a 150 °C. Após a recuperação dos extratos ricos em flavanonas, o reator foi aquecido em três

temperaturas diferentes em processo sequencial. O primeiro foi operado a 200 °C, o segundo a 225 °C e o último a 250 °C. As taxas de fluxo de água para todas as etapas foram de 10, 20 e 30 mL/min. Então, os hidrolisados coletados foram analisados para quantificar as concentrações de açúcares, compostos bioativos, capacidade antioxidante e produtos principais de degradação. Além disso, os resíduos sólidos remanescentes do processo foram analisados usando espectroscopia FT-IR e TGA.

Este capítulo trata de um artigo que será submetido (2019) na revista *Bioresource Technology*. Os autores Geoffrey A. Tompsett, e Michael T. Timko contribuíram na realização das análises dos resíduos sólidos remanescentes (FTIR, TGA). Os autores Andressa M. Baseggio e Mário R. Maróstica Junior contribuíram na realização das análises de capacidade antioxidante. O autor Mauricio A. Rostagno contribuiu na realização das análises de identificação e quantificação dos flavonoides (hesperidina e narirutina) e dos inibidores de fermentação. Os autores Patrícia F. Ávila e Rosana Goldbeck contribuíram na realização das análises de açúcares por HPLC.

O **Capítulo 6** apresenta uma discussão dos principais resultados obtidos neste trabalho, enquanto o **capítulo 7** apresenta as conclusões gerais e sugestões para trabalhos futuros, onde são resumidos os principais resultados oriundos do desenvolvimento do projeto apresentado nessa tese e ainda são apresentadas algumas sugestões de pesquisas futuras.

No **Capítulo 8**, é apresentada a memória do período de doutorado com todos os trabalhos acadêmicos realizados paralelamente ao desenvolvimento desta tese.

Por fim, o **capítulo 9** contém uma lista com todas as referências utilizadas nesta tese. No Apêndice são apresentadas informações suplementares dos artigos desenvolvidos nesta pesquisa.

Finalmente, o Anexo apresenta as licenças para utilização dos artigos publicados neste trabalho.

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2. - CAPÍTULO 2 - Revisão de Literatura

Applications of subcritical and supercritical water conditions for extraction, hydrolysis, gasification, and carbonization of biomass: a critical review

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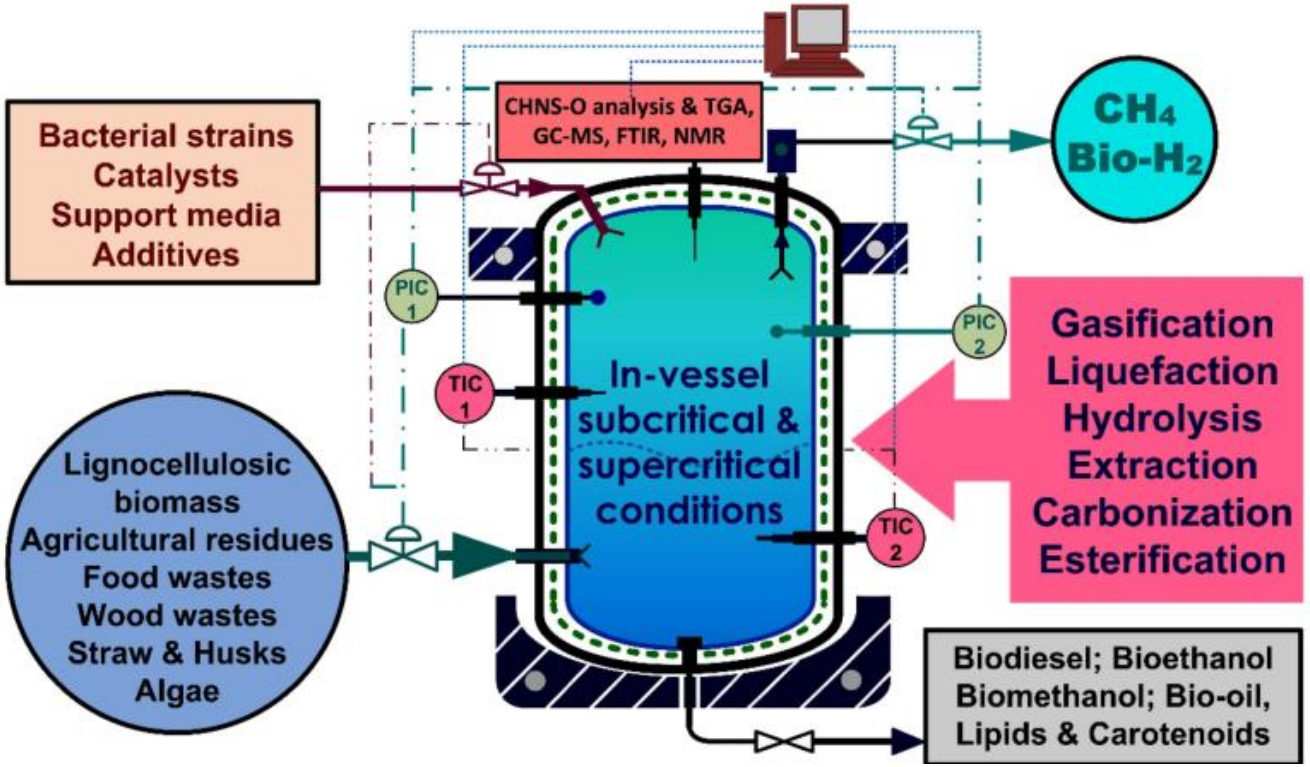
Graphical Abstract



Abstract

This review summarizes the recent developments and essential aspects of the use of subcritical and supercritical conditions in water extraction, hydrolysis, carbonization and gasification processing of biomass. Bioactive compounds, reducing sugars, hydrogen, biodiesel, and hydrothermal char are the final products of subcritical and supercritical water processes. Subcritical and supercritical conditions present a set of clean and fast conditions which eliminate the need for pretreatment, require less reaction time, generate less corrosion and residues, do not use toxic solvents and reduce the formation of degradation byproducts. The type of reactor, process parameters, and types of biomass used for subcritical and supercritical water process are also briefly presented. The benefits of catalyst addition to improve process efficiency are addressed. The present review also revisits advances of the research trends in the development of subcritical and supercritical water process technologies.

Keywords: Biomass, Subcritical water, Supercritical water, Waste-to-Energy.

2.1. Introduction

Currently, our society is partially based on the concept of bioeconomy. Here, the term “bioeconomy” refers to the “sustainable production and conversion of plants into food, fibers, health and industrial products, and energy” (Yamamoto et al., 2014). Biomass-derived fuels have potential as viable alternatives to petroleum-based fuels in the short to medium term (Prado et al., 2016). Several techniques have been designed and evaluated for the recovery of bioactive compounds, sugars from natural feedstocks and to produce biogas, biohythane, or valuable carbonized solids from different types of biomass. However, comprehensive experiments and simulations are needed to optimize process parameters before the economic viability may be achieved at industrial scales. For liquid biofuel production, the most pressing challenge is more effective and benign bioconversion of biopolymers into sugars, since this step requires breaking down the lignocellulosic complex via energy-intensive processing steps.

Conversion of wastes into bioenergy products is especially promising as a method to increase value and minimize the environmental and ecological footprints of existing industrial processes. However, the utilization of renewable or even waste feedstocks does not guarantee that a process is either sustainable or green. To be both sustainable and green, processes must use benign catalysts, solvents and auxiliary chemicals. Due to the quantities used, the selection of green solvents is especially important for achieving process sustainability. Here, benign solvents include especially those identified as Generally Regarded As Safe (GRAS), a category that includes water, ethanol, CO_2, and combinations (Clark & Pfaltzgraff, 2012; Timko et al., 2016b; Vardanega et al., 2015). Different techniques have been developed to streamline and enhance the solvation intensity, power and effectiveness of these solvents, including the use of high pressures and (sometimes) high temperatures (Vardanega et al., 2015).

Solvent selection is important for sustainable extraction and reaction processes. Subcritical water, supercritical fluid, and ultrasound-assisted processing are some of the emerging green extraction techniques receiving renewed and sustained research interest among many research groups worldwide. For recovery of sugars from biomass feeds, subcritical and supercritical water hydrolysis have been studied as alternatives that reduce the cost and chemical use of enzymatic, acid, and alkaline processing (Rostagno et al., 2015). The objective of supercritical water

gasification is to transform wet biomass to a hydrogen-rich biogas. Supercritical water gasification process is effective at temperatures above its critical point, often around 600 °C (Lachos-Perez et al., 2015) and the introduction of a catalyst permits operation at reduced temperatures.

Extraction, hydrolysis, and gasification often co-generate substantial quantities of a carbonaceous char material. Valorizing this material as a co-product is necessary to achieve favorable economic performance for the overall process. In fact, recent works have shown that processes designed to maximize the yield of solid carbon products (processes that are collectively termed "*hydrothermal carbonization*" (HTC)) may have economic benefits as integrated technologies. Unlike pyrolysis, HTC is suitable for both wet and dry feedstocks and HTC of the former can result in superior energy balance compared to pyrolysis. The hydrothermal char product of HTC has shown promise in many applications (Libra et al., 2011), including power generation as a "renewable coal" (Mumme et al., 2011), water purification (Regmi et al., 2012) electrochemistry (Wei et al., 2011), and catalysis (Karagöz et al., 2005). This review emphasizes in a fresh perspective the application of subcritical and supercritical water conditions as an environmentally benign method to extract, hydrolyze, gasify, and carbonize biomass to produce bioactive compounds, sugars, biogas and other valuable solids.

2.2. Biomass

The term "biomass" can be defined as the total mass of living or recently dead (unfossilized) organic matter within a given environment. More appropriately, biomass attributes to all forms of organic matter potential recoverable from a variety of renewable sources such as dedicated energy crops and trees, agricultural crops, animal wastes, crop wastes from agricultural activities, wood and municipal wastes, among others (Olanrewaju, 2012). Most of the biomass used comes from agro-industrial residues, because these are renewable and have a low-cost or even no cost at all when the raw material is a residue. Main residue types are, for example, molasses, bagasse, and maize milling by-products (Pedras, 2015).

Cellulose, hemicellulose and lignin are the components comprising lignocellulosic biomass. Cellulose is a regular, linear, homopolymer consisting of D-glucose monomers linked by β-(1,4) glycosidic bonds. Cellulose is the dominant structural polysaccharide. Plant cellulose is composed of two parts: a crystalline

structure (organized) and a non-organized amorphous structure, also called *para-crystalline structure*. Individual cellulose polymers are "bundled" together as cellulose fibrils, which are usually independent and weakly connected by hydrogen bonds (Hendriks & Zeeman, 2009). Hemicellulose is a polysaccharide consisting of various sugar monomer units such as xylose, galactose, mannose, arabinose, and also glucose; unlike cellulose, hemicellulose is branched and amorphous. The function of hemicellulose is to bind cellulose and lignin. Lignin is a random, three-dimensional polymer consisting of phenyl-propanoic sub units. Lignin is naturally made of coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol, arranged in an irregular structure that provides strength and resistance to enzymatic degradation (Pedras, 2015).

For production of biofuels, the most economic and technological significant barrier is conversion of biomass into sugars readily available for microbial action, a process that requires cleaving and dismantling the lignocellulosic complex. Biopolymer breakdown is usually performed via energy intensive processing of the cellulose and hemicellulose fractions contained in the biomass into sugars; subsequent fermentation processes convert the simple sugars into fuels and/or chemicals. The complex polymer composition of biomass, including cellulose, hemicellulose, and lignin polymers, makes direct and efficient conversion to bioenergy particularly difficult (Zhu et al., 2016). The combination of elevated temperatures and favorable solvent properties makes subcritical/supercritical processing a promising alternative to conventional biological and chemical processes for decomposition of the lignocellulosic complex (Rostagno et al., 2015).

In addition to the aforementioned biopolymers (cellulose, hemicellulose, and lignin), biomass may also contain proteins, simple sugars, pectins, phenolics, glycosides, saponins, fats, waxes, alkaloids, gums, resins, terpenes, starches, essential oils potassium, sodium and calcium (Yu et al., 2008). These minor components have potential as flavors, fragrances, pharmaceuticals, biomaterials, and nutraceuticals, all of which are more valuable than liquid fuels. Valorization of these minor components can therefore be an important strategy for improving overall process economics of an integrated biorefinery.

Lignocellulosic biomass is abundant and inexpensive; however, commercial-scale conversion of lignocellulosic biomass into fuels requires regular delivery of a consistent raw material, a difficult logistic and supply challenge. In fact,

overall economics of bio-ethanol production depend heavily on the cost of the feedstock (Davis et al., 2015). Thus, economically viable production of bioethanol requires careful process logistics and supply-chain consideration.

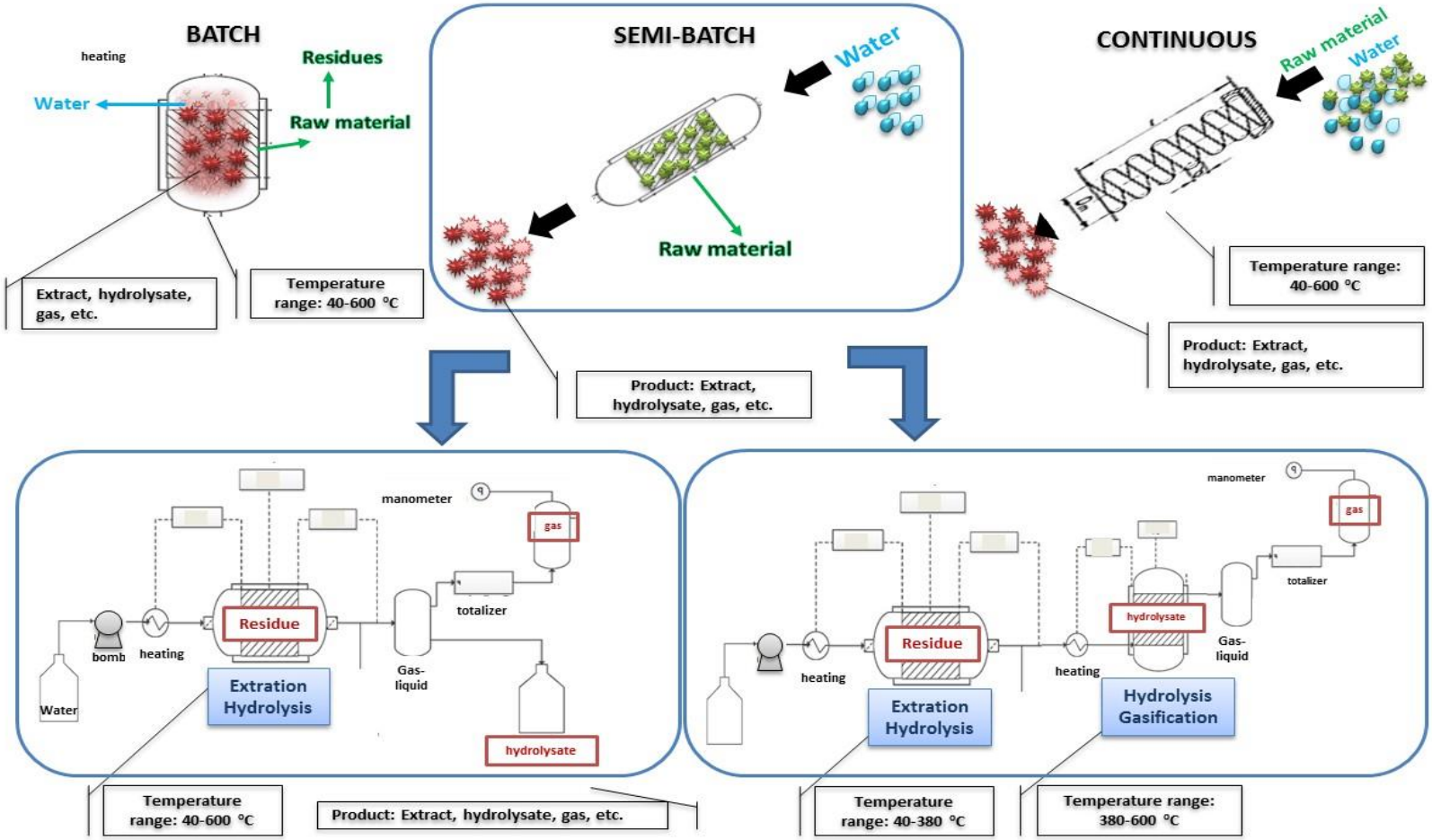
2.3. Subcritical and supercritical water conditions for biomass processing

The properties of any pure substance are determined by temperature and pressure. A pure substance enters the supercritical state when it is heated and pressurized to temperatures and pressures greater than its critical point. For water, the critical temperature is 374 °C and the critical pressure is 22.1 MPa (Taylor et al. 2001; Elliott et al. 2015). Industrial applications that use water at the critical temperature and critical pressure may have a very high economic cost due to the high pressure equipment and the energy to be applied; for this reason, careful engineering experiments, design, and development are required to optimize processes based on supercritical water and reduce capital and operating costs. The motivation to study subcritical and supercritical conditions steams from the fact that such biomass processing conditions afford some of the advantages embodied by the Green Chemistry and Green Chemical Engineering concepts, namely, better energy efficiency and energy savings, minimization of wastes generation and improved atom economy and better interphase mass transfer coefficients.

Subcritical/supercritical water extraction, hydrolysis, gasification, and carbonization can be carried out in batch, semi-batch and continuous systems (Figure 1). When the raw material(s) (biomass) and reaction solvent (water) are placed inside a close the reactor, the process is known as a batch. On the other hand, when biomass is brought into contact with a continuous flow of the reaction medium the process is known as a semi-batch. An example here is flow hydrolysis of a packed bed consisting of the raw biomass. In continuous process, both the biomass feed and the solvent are continuously entering and exiting the reactor. Rapid reaction rates afforded by operation at high temperature can be conducive to continuous processing (Williams & Onwudili, 2005). For example, Elliott et al. (2015) reported observation of yield benefits for conversion of a batch process to continuing operation. Since the carbon and energy recovery efficiency can be favorable, considerable scope exists for commercial application of supercritical water technologies at the continuous scale. On the other hand, the technical difficulties associated with pumping biomass slurries has made most studies focus on subcritical and supercritical processes that are performed using

batch or semi batch systems. As result, many technical hurdles need to be addressed to determine the optimal scale of continuous systems. Furthermore, integration of several semi-batch processes for a simulated continuous operation at the industrial level may be preferred over batch or continuous operation.

Figure 1. Sub/supercritical water hydrolysis performed in batch, semi-batch and continuous systems.



In addition to the type of reactor (batch, continuous, or semi-continuous), several factors influence the performance of subcritical and supercritical water hydrolysis, chiefly: feedstock properties, solvent properties, reactor configurations, time-temperature behavior of reacting particles, and the use of catalysts and other reagents. Some of these factors are discussed later.

2.4. Subcritical water extraction technology

Plant materials contain many compounds useful as flavors, fragrances, pharmaceuticals, and dietary supplements. To use the compounds present in the biomass they must first be separated from the rest of the raw material. The typical extraction process consists in using a solvent (liquid or gas) to selectively remove and/or dissolve target compounds from the raw material matrix (i.e. the biomass). The process can be performed using different types of extraction systems and several variables will affect the efficiency and selectivity of the process, including raw material and target compounds characteristics, temperature, extraction solvent and solvent to feed ratio, among others.

Solvent characteristics play a major role in the selectivity of the process affecting both target compound selectively and – to a lesser extent – mass transfer rates. Water alone or as part of a mixture of miscible solvents is primarily used for extracting polar to moderately polar compounds. Water is used as a solvent for several extraction processes focusing on the recovery of useful and potentially valuable compounds from diverse biomass types. Due to their polarity, antioxidants, phenolic compounds and carbohydrates are among the most common compounds extracted using water as solvent (Table 1). In general, an increase in the extraction temperature increases extraction rate by increasing diffusion constants, increasing solubility, and swelling the biomass matrix. The last stage of the extraction process is controlled by diffusion and stands to be improved the most by increasing extraction temperature (Rostagno & Prado, 2013). Solubility of compounds in the solvent is also affected by temperature. Illustratively, the solubility of gallic acid, cathechin and protocatechuic acid in water increases more than 200 times when the temperature is increased from 25 °C to 142 °C (Srinivas et al., 2010).

When using water as solvent for extraction processes performed at ambient pressure, extraction temperature is limited to the normal boiling point of water (100 °C). In contrast, in pressurized systems, the process can be performed above the boiling

point of the solvent. Usually high pressure extraction processes using water are performed using temperatures up to 150 °C. Increasing extraction temperature greater than 100 °C affects the characteristic of water as a solvent, modifying its dielectric constant and viscosity. As a result, the water solubility of mid-polar compounds increases with increasing temperature, allowing water to replace or reduce the amount of organic solvent such as methanol and ethanol used for extraction (Çam & Hışıl, 2010).

Table 1. Highlights of results of biomass for the production of bioactive compounds under subcritical water extraction (SWE).

Raw material	Target compounds	Extraction technique	Highlights of results	Reference
Blackberry residues	Polyphenols and antioxidants - Anthocyanins	Solvent: water, acidified water pH = 2.5, ethanol and ethanol + water 50% v:v). Temperature: 60, 80 and 100 °C Pressure: 7.5 MPa	Recovery of phenolic was significantly enhanced at higher temperatures. Higher extraction yields recorded for anthocyanins with acidified water at 60 and 80 °C.	Machado et al. (2015)
Pomegranate peels	Polyphenols and antioxidants - Punicalagin and ellagic acid derivatives	Solvent: Water Temperature: 40,65,90 °C Extraction time (static): 5,15,30 Pressure: 102.1 atm Flush volume: 5-100 mL	Temperatures higher than 40 °C, longer extraction times and larger particles reduced extraction yield. Pressurized water had augmented the yield in comparison to methanol, ethanol and acetone.	Çam and Hışıl (2010)
Potato peel	Phenolic compounds Gallic acid, Chlorogenic acid, Caffeic acid, Protocatechuic acid, Syringic acid, p-hydroxyl benzoic acid, Ferulic acid, and Coumaric acid	Solvent: Water Temperature: 100 to 240 °C Extraction time Pressure: 6 MPa Flow-rate: 2 mL/min Residence time: 30-120 min.	Best extraction yields at 160 to 180 °C, 6 MPa and 60 min. Chlorogenic acid and gallic acid were essential conponents extracted at 180 °C.	Singh and Saldaña (2011)

Sugar cane bagasse	Hemicellulose components (arabinoxylans)	Solvent: Water Temperature: 170, 180, 190, and 200 °C Extraction time: 15 min Pressure: not specified	Increasing temperatures increased release of polymeric hemicellulose but decreased lignin extraction.	Banerjee et al. (2014)
Pomegranate seed residues	Total Phenolic compounds antioxidant capacity	Solvent: Water (high pressure); Water methanol, ethanol and acetone (low pressure). Extraction time: 15–120 min. Temperature: 80–280 ◦C; Solid to water ratio: 1:10–1:50, m/v) Pressure: 6.0 MPa	Increasing extraction temperatures increased the total phenolic content in extracts. Optimum extraction occurred at 220 °C for water to solids ratio of40.	He et al. (2012)
Citrus peel	Phenolic compounds - flavanones hesperidin and narirutin	Temperature: 110–200 °C Extraction time: 5–20 min Pressure: 100 atm.	Peak extraction yield at 160 °C for extraction time of 10 min.	Cheigh et al. (2012)
Onion skin	Phenolic compounds - flavonol quercetin	Solvent: Water (high pressure); Water methanol and ethanol (low pressure. Temperature: 100–190 °C. Extraction time: 5–30 min. Ratio of the mixture sample and diatomaceous earth: 0.5:3.5–2:2. Pressure: 90–131 bar.	Peak extraction yield for quercetin obtained at 165 °C, and for 15 min of extraction time. Extraction yield with water was significantly greater that those recorded with methanol, ethanol and water-at-boiling-point	Ko et al. (2011)

Flaxseed meal	SDG lignan, total phenolics, and total flavonoids	Solvent: Water Temperature: 160, 170, and 180 °C Extraction time: 5, 15, 30, and 60 min Pressure:	Higher extraction temperatures of 170 and 180 °C decreased yields by less than 10% but impacted on extraction time reductions much more significantly. Total phenolics and total flavonoids were best extracted at 180 °C for 15 min.	Kanmaz (2014)
Winery wastes	Total polyphenols and flavonoids	Solvent: Water Temperature: 100, 120 and 140 ◦C Pressure: 8 MPa, 11.5 MPa and 15 MPa	Extraction yield potentially to reach its maximum at 140 ◦C and 11.6 MPa. Subcritical water gave much higher yields that ethanol and water under atmospheric conditions.	Aliakbarian et al. (2012)
Grape Pomace	Phenolic compounds-tannins, anthocyanins, croanthocyanidin	Solvent: Water Temperature: 50−200 °C Extraction time: 5-30 min	Optimum extraction for anthocyanins obtained at 100 °C. Higher temperatures and longer extraction times considerably lowered extraction yields of phenolics. Proanthocyanidin was extracted only below 100°C.	Vergara-Salinas et al. (2013)
Apple pomace and citrus peel	Pectin	Solvent: Water. Solid to liquid ratio of 1:30. Temperature. Apple pomace: 130 -170 °C for Citrus peel 100 - 140 °C Extraction time: 5 min	Optimum extraction temperature was 120 °C for citrus peel. With apple pomace substrate, optimum extraction was obtained at 150 °C.	Wang et al. (2014)

The scope for increasing process temperature to improve extraction efficiency depends on the thermal stability of target compounds. Polyphenols, a class of compounds with high antioxidant capacity and biological effects, provide an example of water extraction of temperature sensitive natural products. For recovery of phenolics from pomegranate peels, extraction temperature should not be greater than 40 °C, as this temperature optimizes solubility and extraction rates while minimizing thermal degradation (Çam & Hışıl, 2010). Sugarcane bagasse provides a second example. Sugarcane bagasse contains many compounds of potential value, including polyphenols which must be extracted at conditions which minimize thermal degradation (Zhao et al., 2015). In contrast, temperatures as great as 190 °C can used for the extraction of non-cellulosic heteropolysaccharides composed of xylose, glucose, galactose, mannose, arabinose and smaller amounts of 4-O-methylglucuronic acid from sugarcane. The interest in the recovery of these compounds is to use them as water-soluble polymers to replace synthetic polymers in food packaging, wound dressings, and drug capsules (Banerjee et al., 2014; Jayapal et al., 2013).

For thermally stable compounds, the scope for increasing extraction temperature to improve extraction efficiency and reduce extraction time is greatly increased compared to thermally labile compounds. In fact, subcritical water is employed in the extraction of several classes of phenolics from different biomass, including citrus peel, pomegranate seed residues, flaxseed meal sticks, sour cherry pomace, and onion skin among other examples (Adil et al., 2008; Cheigh et al., 2012; Chienthavorn & Insuan, 2004; Kanmaz, 2014; Ko et al., 2011). Subcritical water has also been used for the extraction of antioxidants from eucalyptus biomass, canola meal, onion peel, winery wastes, grape pomace spent coffee grounds and silver skin, just to name a few examples (Aliakbarian et al., 2012; Hassas-Roudsari et al., 2009; Kulkarni et al., 2008; Lee et al., 2014; Narita & Inouye, 2012; Vergara-Salinas et al., 2013; Xu et al., 2015; Zeković et al., 2014). For many compounds and raw materials, subcritical water extraction efficiencies and yields are usually greater than can be obtained with organic solvent using conventional techniques.

In some applications, acids have been used to modify water to improve extraction efficiency for some compounds. For example, anthocyanins, a valuable class of compounds present in blackberry residues, are extracted most efficiently using

acidified water and temperatures between 60 and 80 °C. The remaining phenolic of the blackberry residues could then be extracted by increasing the temperature and a using alcohol/water mixture as the extraction solvent (Machado et al., 2015). This example points to the optimization of acidity for recovery of a specific target compound.

2.5. Subcritical and Supercritical water hydrolysis technology

Decomposition of cellulose and hemicellulose into pure sugar streams is the major technical and economic bottleneck limiting commercialization of biofuels. Conventional technologies to convert biomass into sugars, including dilute acid treatment, steam explosion, and enzymatic hydrolysis, have been extensively studied in recent years (Agudelo et al., 2016; Jiang et al., 2016; Kapoor et al., 2017; Li et al., 2016b; Qin et al., 2017; Romero-García et al., 2016). Currently, acid and enzymatic hydrolysis processes are used in the synthesis of second-generation bioethanol. However, acid hydrolysis requires neutralization of the medium after, and the use of enzymes is restricted due to their high cost and the operational processing steps (Li et al., 2016a). Simple sugars are products of reducing sugars, such as glucose, fructose, galactose, and xylose. Compared to dilute acid pretreatment, hydrothermal technologies, especially those based on subcritical and supercritical water, have potential for decomposition of biomass into simple sugars with high yields (Shitu et al., 2015). Due to their environmentally benign characteristics and abundance, water and CO_2 are mostly used in reactions at subcritical and supercritical conditions for agricultural biomass residue processing.

Hydrothermal processing can be divided into two categories – those that are performed at subcritical conditions and those that are performed at supercritical conditions. Subcritical water hydrolysis is usually conducted in a temperature range of 100 to 374 °C under sufficient pressure to keep water in the liquid state (Lachos-Perez et al., 2016; Yoshida et al., 2015). Subcritical water treatment aims to utilize the waste biomass to generate raw materials for new products and a concomitant reduction in waste streams volumes. Supercritical water processing is performed at temperatures greater than 374 °C and typically at pressures greater than 25 MPa. At these conditions, water behaves as a single non-condensable phase, with a density close to a liquid and transport properties similar to a gas (Marrone & Hong, 2009).

Hydrothermal treatment offers several advantages, including rapid reaction rates and replacement of acids/bases with a more environmentally acceptable solvent.

In addition, many feeds of interest are moist and the water contained in the raw material and/or organic residue may be used as the reaction medium; compatibility with moist feeds eliminates the need of a drying step used in conventional methods.

Despite potential, the application of supercritical fluid technology to agricultural waste is still under development. A particular challenge is that hydrolysis rates and sugar yields depend on the characteristics of the residues, composition and structure of the cell wall, and the types monosaccharides present in the feed. As a result, each raw material must be studied individually, each new feed representing a new set of technological challenges (Prado et al., 2014).

The 3 main components of biomass respond differently to hydrothermal treatment. Hemicellulose hydrolyzes the most readily. Kim et al. (2014) found that 60-70% of the pentose content of hardwood could be recovered at mild conditions (<200 °C), but that recovery of the remaining pentose content required more severe treatment. Pińkowska et al. (2011) studied hydrothermal decomposition of xylan as a model compound for hemicellulose. Pińkowska et al. (2011) reported the maximum soluble sugar yield at 220-235 °C and for the shortest residence time studied (0 min, i.e., heating of the reactor to reaction temperature followed by immediate cooling). Increasing the temperature or residence time decreased sugar yields, as sugar decomposition and re-combination became increasingly important.

Cellulose is generally more recalcitrant to hydrolysis than hemicellulose. Sasaki et al. (2000) studied dissolution and hydrolysis of cellulose in supercritical water, finding that at 400 °C cellulose mainly decomposed to form hydrolysis products but that at temperatures from 320 to 350 °C primary hydrolysis products decomposed. The same authors studied cellulose dissolution using a diamond anvil cell, finding that individual cellulose particles became gradually smaller with increasing reaction time at T < 280 °C but rapidly disappeared at T > 320 °C. Sakaki et al. (2002) reported nearly 100% cellulose decomposition after 12 min at 295 °C, with the product consisting of a water soluble fraction (81 wt %) and a solid deposit (18 wt %). Sasaki et al. (2004) later studied cellulose decomposition in a continuous flow microreactor and successfully reproduced their data using an empirical kinetic model. Ehara and Saka (2002) studied supercritical water hydrolysis of microcrystalline cellulose in batch and flow reactors, finding that the flow system decreased sugar degradation but that glucose yield was maximized in the batch reactor. Later, Ehara and Saka (2005) suggested sequential

supercritical and subcritical water treatment to maximize cellulose hydrolysis and minimize sugar degradation. More recently, Cantero et al. (2013) studied ultra-fast reaction conditions (< 0.1 s) for cellulose hydrolysis, reporting >96% yield of total mono/oligo saccharides at 400 °C; with minimal (5 ppm) production of 5-hydroxymethylfurfural degradation product.

Lignin is the most recalcitrant of the 3 main biomass polymers and its hydrothermal decomposition has been studied mainly at temperatures greater than 300 °C (Ma et al., 2016). For example, Yong and Matsumura (2012) studied decomposition of lignin in a flow reactor over the temperature range from 390 to 480 °C and at residence times from 0.5 to 40 s, finding complete decomposition within 5 s. Pińkowska et al. (2012) studied hydrothermal treatment of alkali lignin over the temperature range from 280 to 390 °C. The authors found the greatest yields of stable phenol and cresol products at 280 °C (11 23 wt%).Barbier et al. (2012) performed a detail analysis of the products of lignin decomposition in sub- and supercritical water (370-390 °C) and concluded that the mechanism consisted of a complex network of parallel and sequential fragmentation and re-condensation reactions. In their studies of model lignin compound decomposition, Kanetake et al. (2007) found that guaiacol completely decomposed within 100 minutes (at 380 to 400 °C), producing catechol as the main product. Yong and Yukihiko (2013) studied guaiacol decomposition at short residence times (0.5 to 40 s) and under conditions of rapid heating; these authors confirmed rapid guaiacol decomposition, with char, gas, phenolic, and benzene products. At temperatures greater than the critical point, Yong and Yukihiko (2013) observed formation of polycyclic aromatic hydrocarbons.

The majority of studies of sub- and supercritical hydrolysis have focused on different types of whole biomass. Most studies on hydrolysis suggest (1,4)-glycosidic linkages contained in cellulose break most rapidly under supercritical conditions, producing higher yields of mono- and oligosaccharides than under subcritical conditions. The main hydrolysis products are water soluble oligomers (*celohexose, celopentose, celotetraose, cellotriose, and cellobiose*), monomers (*glucose and fructose*), and decomposition products of these monomers (1*,6-anhydroglucose, glyceraldehyde, erythrose, glycolaldehyde, dihydroxyacetone, piruvaldehido 5-hydroxymethyl-furaldehyde (5-HMF) furaldehyde, and organic acids*). The generation of soluble sugars from rice bran was reported by Pourali et al. (2010), who applied

hydrothermal process conditions to decompose rice bran at different reaction temperatures and times in a batch reactor. They observed the greatest yields of water-soluble sugars at 220 °C, and these sugars were primarily oligomers and monomers. Likewise, Shimanouchi et al. (2014) recovered reducing sugars from *Carya cathayensis* Sarg Peel (CCSP) under subcritical water at different reaction temperatures, and also reported that the optimal temperature for formation of reducing sugars was 190 °C. Mohan et al. (2015) studied the conversion of bamboo to total reducing sugars by hydrolysis in subcritical water using a batch reactor at temperatures of 170 to 200 °C for 40 min, obtaining a maximum yield of 42.21% at 180 °C after 25 min of reaction. Prado et al. (2014) studied the conversion of several agro-industrial residues in a semi-continuous reactor (50 mL) by hydrolysis with subcritical water (208 and 257 ° C) for 30 min at a flow rate of 33 mL/min and pressure of 20 MPa. The results from Prado et al. (2014) indicated that for palm fiber hydrolysis increasing the temperature reduced the yield of rafinose (0.1%) and increased the yield of glucose (0.7%) and 5-HMF (0.8%). However, the yield of sugars from coconut husk in this work did not change with temperature, and in the case of grape seed the yield of sugars was calculated to be about 1.0%. All of these studies indicate that subcritical/supercritical water hydrolysis processes should be evaluated individually for each raw material.

Selecting reactor conditions to optimize sugar yield must balance biopolymer hydrolysis rates and sugar degradation rates, both of which increase with increasing temperature. For example, Lin et al. (2015) studied the competitive reactions involved in sugar production and degradation from rice straw substrates at concentrations of 2.5 and 10 wt% in a batch reactor containing subcritical water at temperatures from 250 to 300 °C, at pressures ranging from 12 to 20 MPa, and stirring speeds between 100 rpm and 300 rpm. In the latter study, the greatest yield was 0.346 g/g of rice straw and least sugar breakdown was obtained at 280 °C, 5% w/w, 20 MPa and 200 rpm. In addition, increasing the temperature to 300 °C decreased the yield, which the authors attributed to the degradation of primary sugars to form acetic acid and 2-methyltetrahydrofuran (Lin et al., 2015). Zhu et al. (2016) studied the conversion of corn ear to reducing sugars by hydrothermal treatment at 190-320 °C. Their results showed complete degradation of hemicellulose and cellulose, with yields of sugars varying between 5.15% and 13.31%. These results indicate that hemicellulose hydrolyzed most readily, and once hemicellulose was depleted the hydrolysis of the

cellulose started; however, degradation of the produced reducing sugars was faster than the degradation of the cellulose. The combination of a first stage held at supercritical conditions and a second subcritical stage showed better results than those obtained in separate sub- or supercritical treatments and greater control of product degradation (Ehara & Saka, 2005; Li et al., 2016a).

Another strategy to tune reaction rates independently of temperature is to adjust the solution phase pH. Carbon dioxide (CO_2) can be added to acidify subcritical and supercritical water to increase reaction rates. CO_2 reacts with water to form carbonic acid, releases protons to acts as a catalyst for hydrolysis reactions (Rogalinski et al., 2008), as shown in Equation 1:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-} \qquad \textit{Equation 1}$$

The addition of CO_2 as acid catalyst has the advantage that the acid is released during de-pressurization and does not require a neutralization step which generates waste. Investigations with the addition of CO_2 showed that it increases hydrolysis rates, increases the yield of monomers, decreases the molecular weight distribution of the product, and apparently decreases the formation of degradation products (Liang et al., 2016; Miyazawa & Funazukuri, 2005; Prado et al., 2017; Schacht et al., 2008).

2.6. Supercritical water gasification technology

Gasification with supercritical water can break large biomass molecules into smaller molecules such as carbon monoxide (CO), methane (CH_4), hydrogen (H_2) and carbon dioxide (CO_2) because supercritical water is an adequate reaction medium for the hydrolysis reaction and subsequent gasification. The overall reaction is endothermic at temperatures greater than 680 °C and slightly exothermic at temperatures less than 680 °C (Castello & Fiori, 2011). Hydrogen is generally the target product of biomass gasification. Hydrogen boasts the merits of being entirely clean, given that its combustion produces water. Hydrogen production from steam gasification is highly economic and effective with low environmental impacts.

Supercritical water gasification is a relatively new process. Treatment of a variety of agricultural wastes at temperatures near 600 ◦C and in the presence of supercritical water produces a gas rich in hydrogen (recently termed as ‘biohythane’)

(Peterson et al., 2008). One of the main characteristics of supercritical water gasification is the reduction of coal and tar, formation compared with conventional technologies, and this observation aroused initial interest in supercritical water gasification. In addition, supercritical water gasification boasts relatively higher reaction efficiencies and yields as compared to conventional gasification methods, mainly with respect to hydrogen production due to water in the medium, without the need for a biomass drying step. Therefore, the conversion of humid biomass containing 90% of water in the gasification process seems to be a sustainable technological option (Calzavara et al., 2005).

Some of the vital reactions that take place in supercritical water biomass gasification are summarized in Equation 2 (Guo et al., 2010; Reddy et al., 2014)

$$CH_xO_y + (2-y)H_2O \rightarrow \ CO_2 + (2 - y + {}^{x}/_{2})H_2 \qquad \text{Equation 2}$$

where *x* and *y* are the elemental molar ratio of H/C and O/C in the biomass, respectively. The product of the reaction is synthesis gas, whose quality depends on *x* and *y* (Guo et al., 2010). In addition to *Equation 2*, other intermediate reactions may occur during gasification of biomass in supercritical water:

- Steam Reforming

$$CH_xO_y + (1-y)H_2O \rightarrow CO + (1 - y + {}^{x}/_{2})H_2 \qquad \text{Equation 3}$$

- Cellullose Hydrolysis

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad \text{Equation 4}$$

- Glucose reaction

$$C_6H_{12}O_6 \rightarrow 6CO + 6H_2 \qquad \text{Equation 5}$$

- Lignin hydrolysis

$$(C_{10}H_{10}O_3)_n + nH_2O \rightarrow nC_{10}H_{12}O_4 \rightarrow \text{phenolic} \qquad \text{Equation 6}$$

- Reaction of steam reforming (phenolic)

$$\text{phenolic} + H_2O \rightarrow CO + CO_2 + H_2 \qquad \text{Equation 7}$$

- Reaction of steam change

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \text{Equation 8}$$

- CO Methanation Reaction

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \text{Equation 9}$$

- CO_2 Methane Reaction

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \text{Equation 10}$$

- Hydrogenation Reaction

$$CO + 2H_2 \leftrightarrow CH_4 + 0.5O_2 \qquad \text{Equation 11}$$

Reducing the biomass particle size, increasing the reaction temperature, or increasing the steam-to-biomass ratio promote H_2 yield and increases gasification rates. Many experimental studies have shown that temperatures from 500 to 700 °C have a significant bearing on yields and compositions of gases evolved, but pressures above the critical have significantly much less influence on these gas compositions. Pressure and residence time are other important control parameters of the supercritical gasification process. With increasing pressure, the ionic product of the water increases, so that the rate of hydrolysis also increases. In addition, high pressure improves the reaction of the vapor change, but reduces the rate of decomposition reactions (Guo & Faghri, 2007). The optimization of H_2 generation from processes conducted under supercritical gasification regimes using water and corncob biomass was investigated using the orthogonal experimental design technique by Lu et al. (2012). They found that temperature yielded greater influence than pressure, concentration of feedstock and addition of an oxidizer on the process. Acid hydrolysis of the feedstock increased H_2 yield in contrast to addition of an oxidizer, which increased the carbon gasification efficiency but not hydrogen yield.

Temperature is a very important parameter and has significant effect on the biomass gasification in supercritical water, particularly when there is no use of catalysts. Lee et al. (2002) studied the gasification of glucose in supercritical water conditions and observed increasing H_2 and CO_2 yields with increasing temperature. In another work, a 30% increasing the reaction temperature to 650 ° C increased the carbon efficiency and gasification efficiency of 167% and 300%, respectively (Hao et al., 2003).

Lu et al. (2006) studied the production of hydrogen as a function of increasing pressure to 30 MPa, and the results obtained had shown that carbon and

gasification efficiency were independent of pressure. Williams and Onwudili (2005) have studied glucose gasification in supercritical water, and reported that it reached 90% conversion after 120 min. On the other hand, Basu and Mettanant (2009) demonstrated that increasing residence time of supercritical water gasification (650 ° C and 30 MPa) of rice husks increased hydrogen yield from 7 to 14 mol kg^{-1}. Lee et al. (2002) studied the influence of residence time on the gas yield from gasification of 0.6 M glucose at 28 MPa and 700 °C, showing high yield of hydrogen regardless of the residence time, provided that residence time was greater than 10.4 s. Safari et al. (2016) gasified almond shell, wheat straw and walnut shell in supercritical water for hydrogen production, and observed that increasing the reaction time up to 30 min increased the hydrogen yield and gasification efficiency.

Subcritical and/or supercritical processing conditions can also enable the formation and potentially recovery of monomers and high-value chemicals from the gasification of agricultural residues (Table 2). Near the critical temperature, catalysts are required and gas containing methane is generated. At critical and higher temperatures, the generated gas will be rich in hydrogen if the concentration of the agricultural wastes feedstock is low and if the concentration of the biomass in water does not decrease. At these conditions, the product tends to contain more hydrocarbons and become less amenable for biomass conversion (Yusman, 2007).

Table 2. Selected agricultural waste biomass used to generate biofuel(s) under supercritical water gasification conditions.

Feedstocks	Temperature (°C)	Pressure (MPa)	Reference
Corn starch, Potato starch and waste	600	22-34.5	Peterson et al. (2008)
Oily waste water	500-650	25-41	Zhiyong and Xiuyi (2015)
Timothy grass	450–650	23-25	Nanda et al. (2016a)
Eucalyptus grandis	450	27	Louw et al. (2016)
Rice straw	less than 600	25	Yoshida et al. (2004)

Beet residues	450-600	30	Ondze et al. (2015)
Peanut shell	600-800	25	Lu et al. (2007)
Corn cob	600-800	25	Lu et al. (2007)
Fruit pulp	400-600	25	Elif and Nezihe (2016)
Chicken manure	620	30	Cao et al. (2016)
Sugarcane bagasse	400	-	Barati et al. (2014)
Sewage sludge	400-600	24,6-49,6	Acelas et al. (2014)
Wheat straw	650	26	Kang et al. (2016c)
Empty fruit bunches from oil palm	380	24	Sivasangar et al. (2015)
Sewage sludge	600	23	Sawai et al. (2014)
Food waste	400	22,1	Amuzu-Sefordzi et al. (2014)

Composition of the feed plays a role in H_2 yields from gasification. Safari et al. (2016) found that wheat straw yielded more H_2 than walnut or almond shell on account of its high lignin content; the corresponding H_2 yields from wheat straw, almond shell and walnut were 7.25, 4.10 and 4.63 mmol g^{-1} at 10, 15 and 20 mins, respectively. Yoshida et al. (2009) pre-treated sewage sludge using sub-critical water hydrolysis and reported a two-fold increase in methane yield (after 3 days incubation) for the pre-treated sludge.

Table 3 listed studies on SCWG of model compounds for biogas production in recent years. Reddy et al. (2014) investigated the decomposition routes of cellulose and lignin under quasi supercritical conditions and found that temperature, pressure, reaction time, catalysts, feed concentration and reactor configuration all influenced H_2 production. These authors also indicated that around supercritical temperatures and pressures, hydrolysis rates could be enhanced based on ionic mechanisms and that reactors for supercritical water gasification still had much scope for optimization.

Demirbas (2010) found the generation of hydrogen under supercritical gasification with water highly attractive, although its cost of production was greater that hydrogen production from steam methane reforming. In this same work, increasing the temperature from 600-800 °C at residence times of 2-6 s increased the H_2 yield from 53 to 73% by volume, while the effect of pressure was negligible beyond the critical pressure of water. Guo et al. (2012) investigated hydrogen evolution from supercritical water gasification of glycerol at 445-600 °C, 25 MPa and 3.9-9.0 s in continuous flow, and indicated that increasing the temperature greater than 487 °C and/or increasing the glycerol concentration in the feed improved the gasification efficiency.

Supercritical biomass gasification can benefit from innovative reactor engineering approaches. Liao et al. (2013) studied supercritical water gasification of glucose and corncob to produce hydrogen using a novel solar thermal reactor. In this work, an increase in direct normal solar irradiation (DNI) caused an increase in the reactor temperature. Moreover, the elevated DNI and low feed concentrations had increased H_2 yield, indicating the effectiveness of solar energy in supercritical water gasification systems. Later et al. (2013) evaluated the potential of pre-treating sawdust using sub-critical water prior to supercritical water gasification and revealed an increase in gas yields from 24.6 mol kg^{-1} for untreated sawdust to 47.7 mol kg^{-1} for pre-treated sawdust (neutral conditions).

Table 3. Summary of supercritical water gasification of model compounds for biogas production.

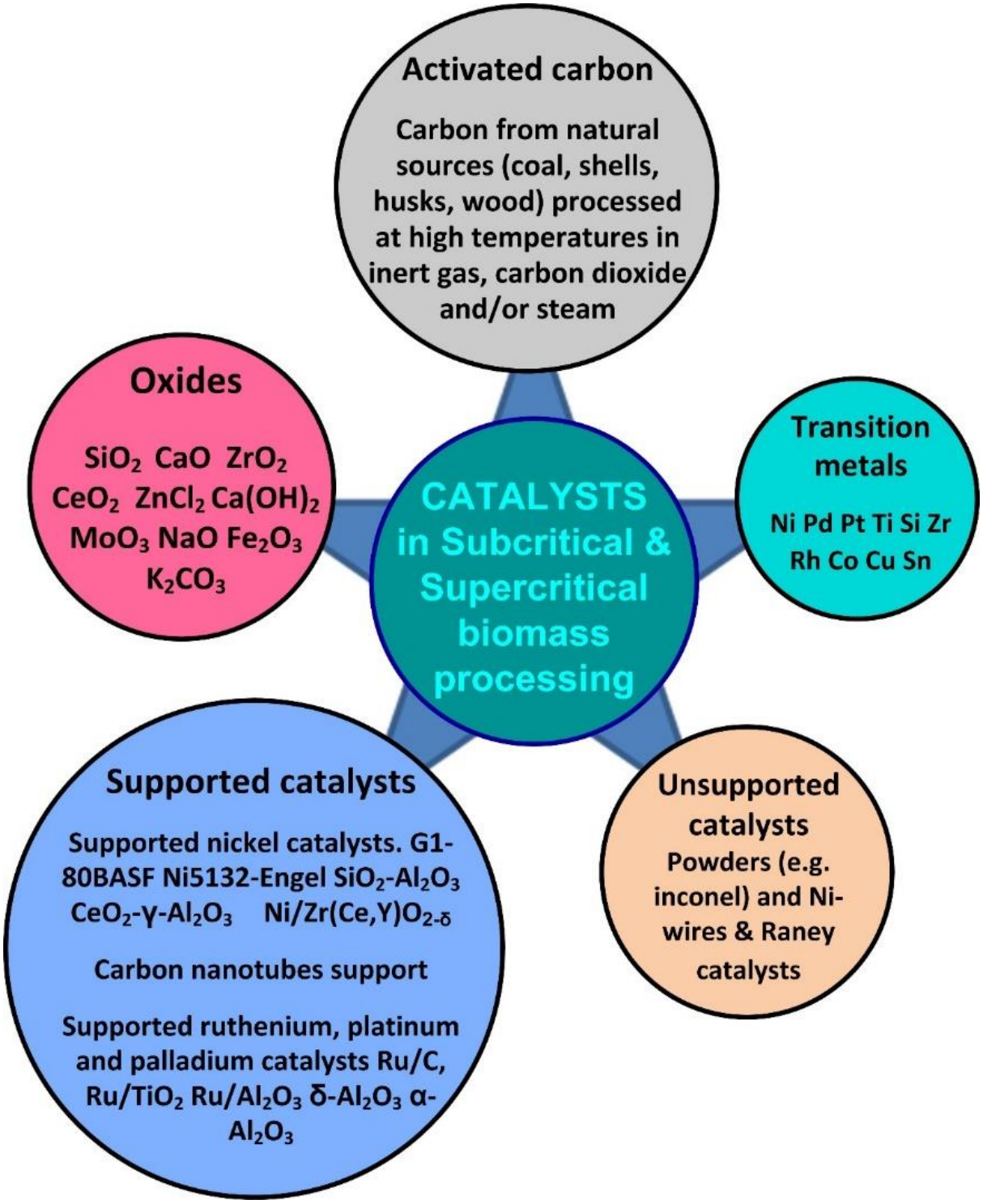
Model compounds	Catalyst	Experimental Condition	Experimental results	Reference
Glucose	Homogeneous organometallic catalyst and Raney nickel	Temperature: 310–350 °C Pressure: 10–21 MPa	homogeneous catalysts less effective than Raney nickel	Azadi et al. (2009)
Cellulose	Ru/C, Pd/C, CeO_2 particles, nano-CeO_2, nano-(CeZr)xO_2	Temperature: 500 °C Pressure: 27 MPa	Catalyst used was Ru/C_4Pd/C_4nano-(CeZr)xO_{24}nano-$CeO_{24}CeO_2$ particles. With sodium carboxymethylcellulose, cellulose or sawdust can be completely gasified	Hao et al. (2005)
Xylan (Hemicellulose)	Ru/a-Al_2O_3/CaO	Temperature: 550 °C Pressure: 36 MPa	Hydrogen yield was of 10.7 mol kg–1	Onwudili and Williams (2013)
Glycerol	Ru/Al_2O_3	Temperature: 700 – 800 °C	Ruthenium had high activity for C–C bond cleavage; H_2 synthesis decreased when CH_4 increased when glycerol levels were augmented to 40%.	Byrd et al. (2008)
Humic acid	-	Temperatures: 325–600 °C Feed concentration: 10–25 wt% Reaction time: 30–90 min	High H_2 yield of 0.79 mol kg^{-1} at 600 °C, 15 wt% humic acid and 75 min without catalyst.	Gong et al. (2017)

Phenols	Ru/CeO_2	Temperatures: 450 - 500 °C Feed concentration: 5 wt% phenol	Carbon utilization efficiency rose to 90% in supercritical water gasification of phenol with Ru/CeO_2 and 5 wt% loading of phenol Gaseous yields had risen from 60% (no catalysis) 150% at 500 °C with catalyst.	Guan et al. (2016)
Methanol	Ni catalyst	Temperature: 500-550 °C. Feed concentration: 10 wt.% methanol	Conversion rates significantly enhanced with Ni catalyst.	DiLeo and Savage (2006)
Oleic acid	Ru/Al_2O_3, Ru/AC, Pt/AC, Pd/AC, $Ni/SiO_2–Al_2O_3$	Temperature: 400–500 °C, Pressure: 28 MPa. Reaction time: 30 min	Higher temperatures and catalyst considerably improved yields.	Youssef et al. (2011)
Lignin	Ni/MgO	Temperature: 250–400 °C.	Higher nickel loadings on magnesium oxide augmented synthesis of gases. Highest yield was 78% with 20 wt % Ni/MgO catalyst (400 °C).	Sato et al. (2006)
Cellulose and lignin alkali	alkali catalyst (K_2CO_3) and absence of catalyst	Temperature: 300 -600 °C. Pressure: 9-41 MPa. Reaction time 1 h	K_2CO_3 favouredgasification rates and restricted char generation.	Güngören Madenoğlu et al. (2016)
Fructose	KOH and NaOH catalyst	Temperature: 550 – 700 °C. Residence time: 30 - 75 s. Feed concentration: 4 - 10 %. Catalyst concentration: 0,2 – 0,8 %. Pressure: 25 MPa	Gas synthesis yields, carbon gasification efficiency and hydrogen yields much improved at optimum conditions (700 °C, 60 s residence feed concentration of 4 wt%).	Nanda et al. (2015)

Glucose	-	Temperature: 550 °C Pressure: 25 MPa Flow rate water: 1 -10 mL/min Conc. Solution: 50, 100, 150, 250 g/L	Biogas generation fluctuated from 100-200 L kg^{-1} glucoseBiogas composition (vol./vol.) was: CO 40-50%, H_2 10-15%, CH_4 10-20%, C_{2+} 2-8%, with finally CO_2 20-30%.	Molino et al. (2016)

The role of catalysis has also been regularly studied in biomass processing for biofuel production under subcritical and supercritical conditions using different liquids (namely ethanol, methanol and water). Although the exact mechanistic pathways involved remain unclear, many studies have shown that the overall process performance and yield have been enhanced when using specific types of metal-based (Azadi & Farnood, 2011) and/or zeolite-type catalysts (Figure 2), while a few have demonstrated that adequately satisfactory process metrics could be reached in catalyst-free reactions. Guo et al. (2010) provided an overview on the physicochemical characteristics of supercritical water gasification and confirmed that alkali metal catalysts enhance water-gas-shift reactions, but cause fouling and corrosion of equipment. Still according to Guo et al. (2010), transition metal catalysts promote methanation reactions, catalyze steam reforming reactions and bond breakage. Yet, many catalysts are instable followed by damage of their support.

Figure 2. Broad classification of the main types of homogeneous and heterogeneous catalysts used in biomass processing for biofuel production under subcritical and supercritical conditions with highlights of main effects of catalysts.



Process conditions influence gasification efficiency and H_2 yields. Kang et al. (2016a) conducted a process optimization study on the catalytic gasification of lignin and cellulose under supercritical condition with water using K_2CO_3 and 20 Ni-0.36 Ce/Al_2O_3 using Taguchi experimental design for process optimization. Kang et al. (2016a) found that temperature wielded the highest impact on the process followed by catalyst type and loading, and finally the type of biomass used. They also found that H_2 yield was enhanced at high temperatures of 650 °C and high catalyst loading. Nanda et al. (2016b) have probed the influence of nickel-laden feedstocks gasified in sub- and supercritical water conditions at varying temperatures, water-to-biomass ratios, pressures and residence times, and thence found that nickel-laden biomasses yielded more hydrogen that non-catalytic ones with the optimal conditions for gasification observed at 500 °C, a water-to-biomass ratio of 10 at 45 min at 23-25 MPa. Susanti et al. (2012) assessed the supercritical water gasification of glucose in an updraft gasifier reactor under different temperatures, reaction time, feed concentration and without a catalyst, and showed that the total gas and hydrogen yields increased with increasing temperatures. Moreover, the highest yields were achieved at 740 °C and 1.8 wt% of feed for 60 s, and carbon efficiency of 91% was recorded.

Catalysts enhance H_2 yields by favoring the reactions of the water gas shift process according to Parthasarathy and Narayanan (2014). Seif et al. (2016) studied the hydrothermal gasification of various industrial waste streams using different catalysts, temperatures and reaction times, and reported that Co_3O_4 was the most effective catalyst that could enhance the gasification efficiency and H_2 yields. Seif et al. (2016) also argued that temperatures over 375 °C and residence time of 45 min promoted H_2 generation, although catalysts were more effective at lower temperatures and longer residence time.

Gasification of fruit pulp in supercritical water catalyzed by Ru/C was investigated at varying temperatures, residence times, biomass and catalyst ratios by Elif and Nezihe (2016), who demonstrated that H_2 yield increased 400% at temperatures greater than 500 °C. Huang et al. (2017) studied the catalytic supercritical water gasification of glucose over $Ni/Zr(Ce,Y)O_2$-δ catalysts at 500 °C, 23-24 MPa and feed concentration of 10 wt%, and reported that carbon gasification efficiency was improved as Ni concentration had been increased from 0.1 to 0.7. In this same work, hydrogen yields of 22 mol kg^{-1} were obtained using $Ni_{0.5}Zr_{0.8}Y_{0.2}O_{2.8}$

(NZY582) catalysts and were 10 times greater than without catalysis. Addition of Ni/CeO_2-γ Al_2O_3 catalysts to supercritical water gasification of biomass at 400 °C, 24,5 MPa and 9.09 wt% glucose greatly boosted H_2 yield and selectivity according to Lu et al. (2010). Lu et al. (2010) also deduced that coking and carbon deposits caused deactivation of catalysts and the presence of Ce in the catalysts inhibited this effect.

Catalyst selection is an important consideration, both for activity and stability. Yamaguchi et al. (2009) investigated the generation of hydrogen under supercritical water gasification regimes of woody biomass with catalyst and observed that H_2 yield was heightened at shorter residence time and elevated temperatures. Palladium > ruthenium > platinum > rhodium > nickel catalyst's over activated carbon and titanium favored lignin gasification. Amuzu-Sefordzi et al. (2014) demonstrated that nickel catalysts promoted steam reforming reactions (at 400 °C and 22.1 MPa for 10 min) with minimum impacts on the water gas shift reaction compared to alkali catalysts (NaOH), which favored H_2 yield. Behnia et al. (2016). probed the influence of nickel and ruthenium metallic catalysts on CH_4 and H_2 generation from glucose subjected to supercritical water gasification at 500 °C and reported the greatest H_2 yields and complete carbon conversion in glucose were achieved using Ni20% Ru 2%/γ-Al_2O_3 catalyst. Tar formation was inhibited and CH_4 formation was improved. Kang et al. (2016b) screened of 29 catalysts generated using 5 supports for the generation of hydrogen by the water gasification of lignin under supercritical, and finally ranked Ni-based catalysts in order of reactivity as follows Al_2O_3 > TiO_2 > AC > ZrO_2 > MgO. Kang et al. (2016b) also showed that Ce had improved H_2 selectivity by favoring dispersion of Ni and inhibiting Ni-Al_2O_3 interactions. Here, the 20Ni–0.36Ce/Al_2O_3 catalyst exhibited a peak H_2 yield of 2.15 mmol g^{-1}. Li et al. (2011) observed that Cu improved the catalytic performance of Ni in reforming reactions to generate H_2, and that Cu also mitigated sintering of alumina whilst Co promoted Ni-based catalysis with respect to hydrogen selectivity. Madenoğlu et al. (2012) studied the sub- and supercritical gasification behavior of cotton and tobacco stalks with water as supercritical fluid at 300-600 °C with addition of 10 wt% of natural mineral catalysts, and found that Trona was most effective while Dolomite was least efficient. Madenoğlu et al. (2012) determined H_2 yields as high as 42.9% and 39.9% from tobacco and cotton stalks using Trona as catalyst at 600 °C. The generation of hydrogen using subcritical water gasification of food wastes, glucose and glutamic acid was studied by

Muangrat et al. (2010) who examined the effects of adding NaOH, Ni/Al_2O_3 and Ni/SiO_2 catalysts. Muangrat et al. (2010) found that glutamic acid yielded less hydrogen than glucose and the addition of NaOH increased H_2 production while the combined use of the different catalyst with NaOH resulted in a marginal increase in H_2 yield. An interesting feature of the work of Muangrat et al. (2010) was that NaOH also prevented carbon deposition on the active sites of the catalysts.

2.7. Hydrothermal carbonization

2.7.1. Hydrothermal Reaction Mechanism

HTC comprises a complex network of reactions, and kinetics and details of each reaction are governed by feedstock, temperature and pressure. A large number of chemical occur during the biomass conversion to hydrothermal char, and the full reaction network is not yet established. However, the conversion of biomass to biochar is believed to involve parallel and sequential hydrolysis, dehydration, condensation, and polymerization reactions (Funke & Ziegler, 2010). For example, Brunner (2009) suggested that the network consists of hydrolysis of glycosidic bonds to convert biomass polymers into sugars, followed by hydrolytic degradation of the simple sugars to produce compounds that act as building blocks to form hydrothermal chars. Similarly, Titirici et al. (2008) found that hexoses (six carbon sugars) like glucose react to form HMF as an intermediate, while pentoses like xylose instead form furfural. Subsequent to biopolymer breakdown, the resulting simple carbohydrates and degradation products condense to form larger molecules (Titirici et al., 2007). Aromatization reactions convert the carbohydrate and furanic molecules into fully and partially aromatic structures in the hydrothermal char (Baccile et al., 2009; Sevilla & Fuertes, 2009a). Falco et al. (2011) report that the aromaticity of the product char depends on the molecular structure of the carbohydrate feed; for example, xylose carbonization results in a more arenic product than does carbonization of glucose. Throughout the process, decarboxylation and decarbonylation reactions removed carbonyl groups from the hydrothermal char, resulting in production of carbon dioxide and carbon monoxide and reducing the oxygen content of the hydrothermal char (Li et al., 2011). Interestingly, Timko et al. (2016a) reported a ball milling treatment that simultaneously decreased the oxygen content of a hydrothermal char and increased its aromaticity; the authors attributed their finding to formation and recombination of carbon radicals during ball milling.

2.7.2. The Hydrothermal Carbonization Process

Valorization of solid byproducts formed during gasification or hydrolysis of biomass feeds is key for improving overall process economics and maximizing environmental benefits of using biorenewable feeds. In fact, the solids themselves may have sufficient value to justify HTC as a stand-alone process and in recent years the technology has been the subject of several reviews (Funke & Ziegler, 2010; Libra et al., 2011; Titirici & Antonietti, 2010). As a thermal process which is conducted in the presence of a liquid water phase, HTC affords a favorable energy balance compared to pyrolysis or torrefaction for wet feeds. Moreover, the performance of the HTC process can be tuned by adjusting many operating parameters including: the design of the reactor; the reaction thermal history (including the set point temperature, ramp rate, and cooling rate) pressure and time; and the feedstock itself.

In terms of reactor designs, HTC is usually performed in sealed batch reactors, with only a limited number of studies reported under flow conditions (Elliott et al., 2013; Jazrawi et al., 2013) Large-scale batch HTC reactors have reportedly been built in industry and design and operation flow reactors are on-going topics of university and industrial research. In terms of pressure, most HTC processes are performed at the saturation pressure of water, though several studies have measured the pressure changes that occur during the HTC process (Heilmann et al., 2010). The effects of operating HTC at pressures greater than the saturation pressure of water are unknown, but likely modest given the body of work on HTL.

Hydrothermal carbonization is typically performed at temperatures ranging from 150 to 300 °C, as these temperatures maximize the char yield (Sevilla & Fuertes, 2009b). Reaction temperatures must be selected to optimize the overall energy balance (Funke et al., 2013) as well as to tune the char yield and/or composition. Gao et al. (2012) and (Sevilla & Fuertes, 2009a) showed that properties, such as particle size and yield of the hydrothermal char product are dependent on the reaction temperature. Furthermore, using NMR spectroscopy, Falco et al. (2011) reported that increasing reaction temperature of hydrothermal carbonization increased the arene content relative to furan of the hydrothermal chars and decreased the carbonyl content in the same chars (Falco et al., 2011).

Reaction time has been reported to have small effect on the yield of hydrothermal char (Sevilla & Fuertes, 2009a; Sevilla & Fuertes, 2009b). However, the

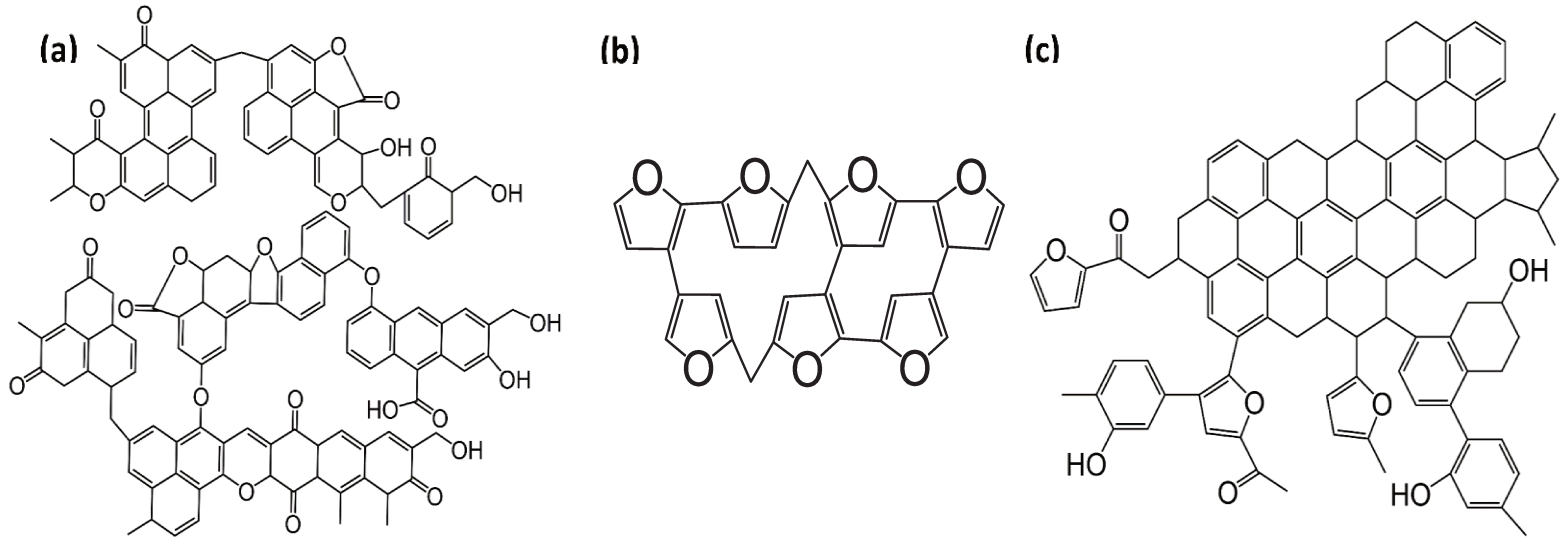
composition and properties of the material has been found to vary with time. Gao et al. (2012) examined the effect of residence time on the properties of hydrothermal chars made from water hyacinth, reporting found the oxygen content decreased from 20 wt% to 13 wt% after 4 hours of reaction time. Thermal analysis indicated that chars recovered after 6 and 24 hours of reaction time showed nearly identical DTG graphs (Gao et al., 2012). Similarly, Falco et al. (2011) used NMR analysis to show that structure of hydrothermal char changes rapidly over the first several hours of reaction, and then stays mostly constant.

As mentioned previously, HTC is suited to processing a wide range of wet and dry biomass feedstocks, including agricultural waste biomass (Sevilla et al., 2011; Xue et al., 2012) and municipal wastewater sludge (Berge et al., 2011). Wiedner et al. (2013) reported that carbonization of different whole biomass feedstocks produce hydrothermal chars with different properties; however, establishing a predictive link between hydrothermal char composition and the composition of the feed is a current knowledge gap (Kang et al., 2012). Despite the challenge, progress is being made to tailor char composition. For example, Demir-Cakan et al. (2009) co-carbonized glucose and acrylic acid to produce hydrothermal char enriched in carboxylic acids. Latham et al. (2014) used a nitrogen enriched algal feed solution to produce a nitrogen rich char. Likewise, Yang et al. (2012) carbonized chitosan, a acetyl functionalized polymer of d-glucosamine, to obtain a nitrogen-rich material that was easily made highly fluorescent (Zhao & Wu, 2006).

2.7.3. Hydrothermal char characterization

The variety of feedstocks and reaction conditions make hydrothermal carbonization a highly variable process, the result of which is a complex, heterogeneous molecule. Figure 3 shows three hydrochar model compounds proposed by Sevilla and Fuertes (2009a), Chuntanapum and Matsumura (2009), and Latham et al. (2017). Many different techniques have been deployed in attempts to better understand the structure and properties of hydrothermal char. Most commonly elemental analysis has been used to understand how it compares to more common thermal residues, such as pyrolysis char or soot. Hydrothermal chars generally show higher carbon contents, and lower oxygen contents than their feeds (Sevilla & Fuertes, 2009a; Sevilla & Fuertes, 2009b), but also tend to have higher oxygen contents than pyrolysis chars (Bridgwater et al., 1999).

Figure 3. Hydrothermal char model compounds proposed in the literature.



Structure (a) Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. Structure (b) Hydrothermal carbon from biomass: structural differences between hydrothermal and pyrolyzed carbons via ^{13}C solid state NMR. Structure (c). Formation of tarry material from 5-HMF in subcritical and supercritical water.

Vibrational spectroscopy, both infrared and Raman, is often used to characterize hydrothermal chars. Infrared spectroscopy indicates that the hydrothermal char surface consists of many different oxygen-bearing functional groups (Liu et al., 2013; Sevilla & Fuertes, 2009a). Because of apparent similarities with the spectra of graphitic materials (Ferrari et al., 2006; Graf et al., 2007; Sadezky et al., 2005), Raman micro-spectroscopy of hydrothermal char suggests a defect-rich carbonaceous structure, consisting of polycyclic aromatic hydrocarbon (PAH) sub-units with 8-10 rings (Chuntanapum & Matsumura, 2009). However, Raman spectra of furan and furan derived molecules (Kim et al., 2011) suggest that interpretation of hydrothermal char spectra may not be straightforward and that the presence of oxygen functional groups may shift band locations and intensities. Efforts to improve the interpretation of hydrothermal char Raman spectra are underway and may follow similar work performed for analysis of pyrolysis chars (Smith et al., 2016). In contrast with Raman micro-spectroscopy, NMR spectroscopy suggests that hydrothermal char is a highly furanic material (Baccile et al., 2009), consisting of PAH sub-units possessing approximately 1-5 rings on average. C-XANES (Latham et al., 2017) spectra of hydrothermal char is also consistent with a furanic material, consisting of small PAH sub-units.

2.7.4. Hydrothermal Char Applications

As previously stated hydrothermal chars are being investigated for a variety of applications that benefit from high surface areas (which can be achieved by post-reaction activation), the high oxygen content of the hydrothermal char surface, or the ability of hydrothermal chars to be modified to include various heteroatoms or functional groups (e.g., carboxylic acids, amines, and sulfonic acids). Reported surface areas of hydrothermal chars range from approximately 10 $m^2 g^{-1}$ for chars synthesized from simple carbohydrates up to approximately 100 $m^2 g^{-1}$ for some biomass-derived chars (Liu et al., 2010; Sevilla & Fuertes, 2009a). Base treatments can increase the meaured surface area of hydrothermal chars. For example, Li et al. (2011) and Sevilla et al. (2011) pyrolyzed hydrochar in the presence of KOH to increase the surface area of the hydrochars from approximately 10 $m^2 g^{-1}$to greater than 1200 $m^2 g^{-1}$. The increased surface area obtained after base treatment may be due to removal of acidic side chains that block pore access (Li et al., 2011), as well as partial gasification and expansion of lattice structure of the aromatic islands that form as a result of

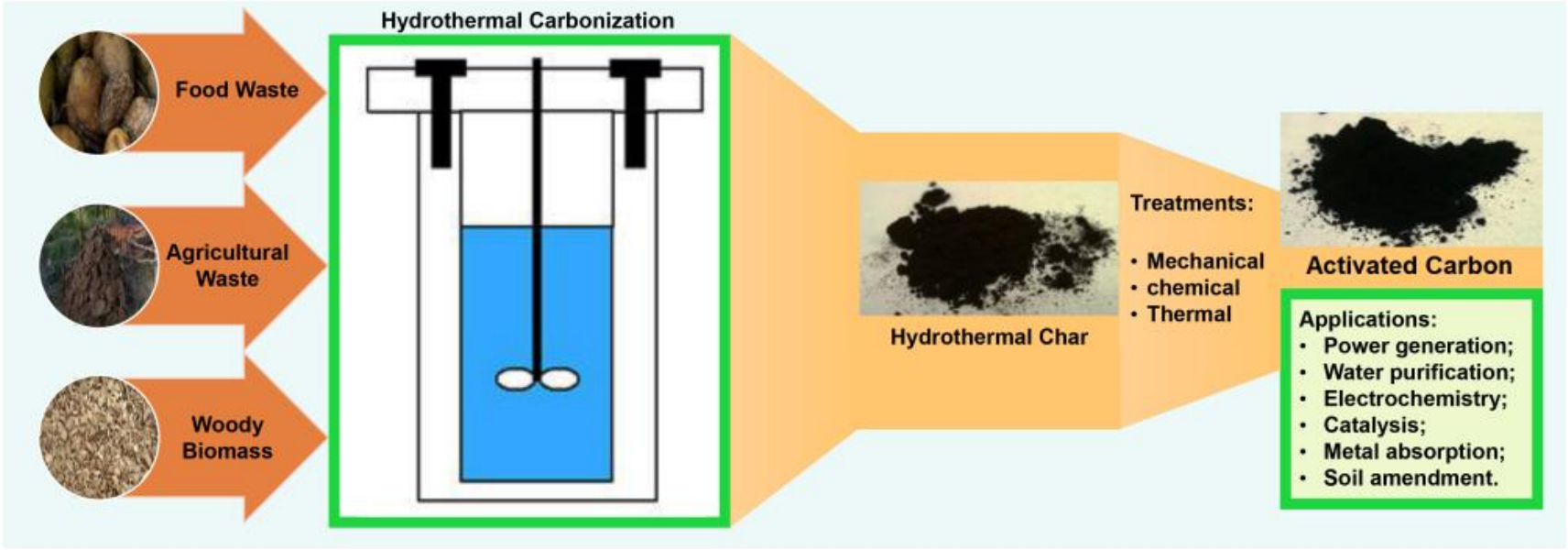
temperature treatment (Yoon et al., 2004). These increased surface areas were used by Sevilla et al. (2011) to produce high capacitance carbon electrodes with a specific capacitance of 236 F g^{-1} (100 F cm^{-3}) measured at a sweep rate of 1 mV s^{-1}. Sevilla et al. (2011) also showed that that these high surface area materials (Li et al., 2011) could be used for hydrogen storage; in fact, the 5 wt% hydrogen storage capacity of hydrothermal char was very similar to the reported hydrogen capacity of carbon nanotubes (Cheng et al., 2001).

Given the success of pyrolysis chars for many soil amendment and remediation applications (Sohi et al., 2010), soil amendment is an obvious application for hydrothermal chars. However, the behavior of hydrochars and pyrolysis chars are distinct from one another, and the two materials cannot be used interchangeably; for example, Eibisch et al. (2015) reported that pyrolysis char reduced the in situ availability of a model pesticide (isoproturon) by a factor of 10–2283 compared to 3–13 observed for hydrochar treatments. On the other hand, Ro et al. (2016) report that the nutrient retention of hydrothermal char amended soils was greater than observed for pyrolysis char amended soils, though the mechanism of soil retention could not be clarified. Malghani et al. (2013) showed that hydrothermal chars are less stable than pyrolysis chars in soil, as the carbon content of soils mixed decreased by 60% after 105 days, while the carbon content reduction of soils mixed with pyrolysis chars was only 10%. Moreover, Busch et al. (2012) reported potential toxicity concerns with using hydrothermal char in soils, potentially a consequence of using raw hydrothermal chars that were not rinsed prior to use.

Hydrothermal chars have shown promise for adsorption of metal cations from aqueous solutions Figure 4. Regmi et al. (2012) reported that the copper and cadmium adsorption capacities of switchgrass hydrothermal chars were comparable to those measured for Calgon WPH activated carbon. Furthermore, an aqueous KOH post-treatment increased adsorption capacity by nearly 100% (Regmi et al., 2012). Similarly, Demir-Cakan et al. (2009) showed that hydrothermal chars co-carbonized with acrylic acid produced materials with lead and cadmium high capacities (approximately 350 mg g^{-1} for lead and 988 mg g^{-1} for cadmium). These extremely high adsorption capacities compared favorably with that measured for HNO_3 oxidized carbon nanotubes; the lead and cadmium capacities of oxidized nanotubes have been reported as 97 and 10.9 mg g^{-1}, respectively. Xue et al. (2012) found that H_2O_2

treatment increased the lead adsorption capacity of a peanut shell hydrothermal char from 0.88 mg g^{-1} to 22.82 mg g^{-1}, performance similar to an activated carbon.

Figure 4. Hydrothermal char applications from agricultural waste, woody biomass and food waste.



2.8. Conclusions

Renewable energy is an area of active research which includes solar energy, wind power systems, geothermal power, and bioenergy. Renewable energy derived from biomass processing systems holds substantial promise and prospect for scale-up towards mass production of different types of bioenergy, namely, bio-ethanol and other liquid fuels, biogas, (or biohydrogen, biomethane, or biohythane), and hydrothermal chars. However, utilization of a renewable resource does not ensure an environmentally sustainable process. For this reason, the principles of green chemistry and green engineering must be married with the utilization of renewable resources to yield environmentally sustainable production of bioenergy. The application of subcritical and/or supercritical conditions for water extraction, water hydrolysis, water and hydrothermal carbonization using a variety of biomass embodies many principles of green chemical engineering. The core green engineering principles encompassed by subcritical and/or supercritical processing for bioenergy generation are designing less hazardous and low-toxicity chemical synthetic routes which may additionally be catalytically assisted, using benign/safer solvents, and designing chemical schemes which are more energy efficient using renewable feedstocks.

The above discourse highlighted three main areas of research avenues. The first aspect is related to the significant impact and influence of the process fluid temperature(s) on the kinetics of the processes and on the thermal stability of the moieties involved. Conversely, the impact of pressure is less substantial than temperature, provided that the pressure is sufficient to maintain a liquid water phase. The second aspect pertains to the substrate-specific dependence of feed properties that make development and optimization of sub- and supercritical water processes highly feedstock dependent. As a result, the need is urgent to understand fundamentals sufficiently that reactors might be designed for processing a wide range of feeds, rather than be optimized for a single feed. The last aspect concerns the minimum throughput of feedstock needed to ensure a sustained supply-chain relationship in the overall network configuration and logistics which become relevant when upscaling bench-scale subcritical/supercritical biomass processing schemes.

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3. CAPÍTULO 3 – Palha de cana-de-açúcar

Sugars and char formation on subcritical water hydrolysis of sugarcane straw

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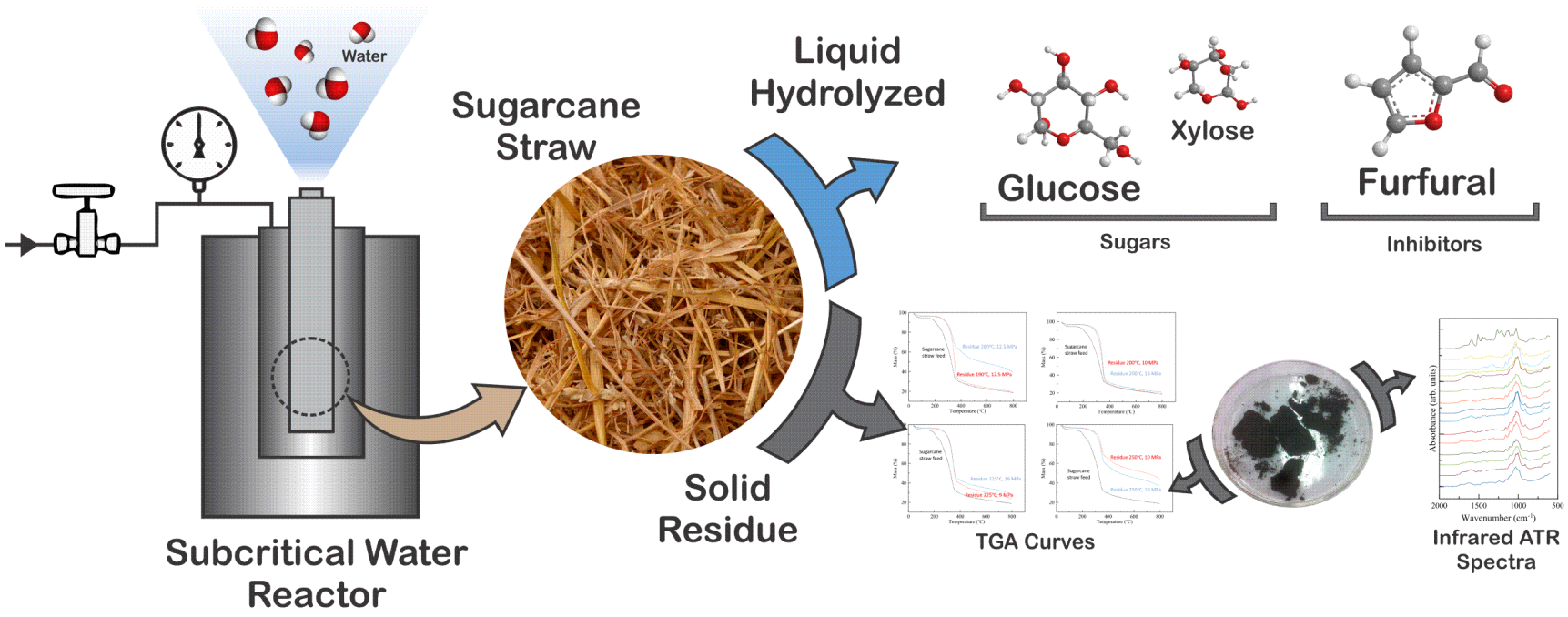
Graphical Abstract



Abstract

Subcritical water has potential as an environmentally friendly solvent for applications including hydrolysis, liquefaction, extraction, and carbonization. Here, we report hydrolysis of sugarcane straw, an abundant byproduct of sugar production, in a semi-continuous reactor at reaction temperatures ranging from 190 to 260 °C and at operating pressures of 9 and 16 MPa. The target hydrolysis products were total reducing sugars. The main products of sugarcane straw hydrolysis were glucose, xylose, arabinose, and galactose in addition to 5- hydroxymethylfurfural and furfural as minor byproducts. Fourier transform infrared spectroscopy and thermogravimetric analysis provided additional information on the surface and bulk composition of the residual biomass. Char was present on samples treated at temperatures equal to and greater than 190 °C. Samples treated at 260 °C contained approximately 20 wt% char, yet retained substantial hemicellulose and cellulose content. Hydrolysis temperature of 200 °C provided the greatest TRS yield while minimizing char formation.

Keywords: *Sugarcane Straw, Subcritical Water Hydrolysis, Sugars, TGA, FT-IR*

3.1. Introduction

One of the major challenges facing society is adoption of a bioeconomy, that is, conversion from an economic system based primarily on non-renewable resources to one based on renewable ones. The term bioeconomy is further associated with sustainable production and conversion of biomass to provide food, health, fiber, industrial products and energy (Venkata Mohan et al., 2016; Yamamoto et al., 2014). The advantages of the bioeconomy relative to the current status include decreased pollution and independence from finite resources, including especially petroleum. In particular, the vast amount of available biomass represents an attractive potential feedstock for many energy and chemicals processes. From an economic standpoint, some evidence suggests that energy production from renewable carbon sources may be competitive with production from non-renewable carbon sources. Industry must play a decisive role in the transition to a bioeconomy, and research is needed to develop cost competitive biomass based processes.

Agriculture is a significant activity globally and particularly in Brazil, producing a massive amount of lignocellulosic residues that can be used a feedstock in fractionation/hydrolysis processes to produce fermentable sugars. Sugarcane straw is one of the main residues of sugarcane processing. For each ton of sugarcane processed, an estimated 140 kg of straw are generated (Oliveira et al., 2013; Vardanega et al., 2015). According to UNICA (Sugarcane Industry Union), the south central region of Brazil alone produced 666 million tons of sugarcane in the 2015/2016 harvest, resulting in the production of 80 million tons of straw (dry basis). The straw is either burned to permit manual harvest of sugarcane or left on the field after mechanical harvest as a soil treatment (da Silva et al., 2010). The traditional practice of burning is gradually being reduced due to new regulations (Brazilian Federal Law 2661/98 and State of São Paulo Law 11241/02), and mechanized harvesting now accounts for 93.6% of the total harvest. Rising ethanol production benefits the sugarcane agroindustry, and the increased reliance on mechanical harvesting has increased the production of sugarcane straw that is available for electricity generation, chemical production, or production of second generation ethanol (Candido & Gonçalves, 2016).

Subcritical water (SCW) extraction and fractionation of valuable components from lignocellulosic biomass has been actively studied in recent decades

(Allen et al., 1996; Cantero et al., 2015; Lachos-Perez et al., 2016; Mayanga-Torres et al., 2017; Prado et al., 2014). SCW is defined as liquid water at a temperature between 100 °C (the normal boiling point) and 374 °C (the critical temperature) and at pressures greater than the saturation pressure. The physicochemical properties of SCW can be tuned by varying the temperature and pressure. As the temperature is increased from 100 °C to the critical point, the dielectric constant, viscosity and surface tension decrease while the diffusion rate increases (Lachos-Perez et al., 2017; Prado et al., 2016). As a result of the temperature dependence of the dielectric constant, water extracts polar molecules most efficiently at temperatures less than about 150 °C, while extraction of less polar molecules benefits from increasing the extraction temperature. Moreover, when extraction is performed at temperatures above 150 °C, the natural biopolymers present in biomass – namely hemicellulose and cellulose – undergo hydrolysis reactions to yield simple sugars and sugar oligomers. These valuable products can be extracted for use in fermentation and other applications (Carr et al., 2011).

SCW hydrolysis and extraction of valuable compounds from many different biomass types has been reported in the literature (Ciftci & Saldaña, 2015; Liang et al., 2016; Lin et al., 2015; Mohan et al., 2015). Recently our group published two works reporting SCW hydrolysis/extraction from sugarcane bagasse and coffee residues (Lachos-Perez et al., 2016; Mayanga-Torres et al., 2017; Prado et al., 2016). Although the majority of SCW studies have been performed in batch reactors (Hongdan et al., 2013; Lin et al., 2015; Lü & Saka, 2010), some recent work has investigated hydrolysis in semi-batch reactors consisting of a packed bed of biomass treated under flow conditions by SCW (Ciftci & Saldaña, 2015; Lü & Saka, 2010). Flow conditions have the potential to reduce sugar degradation and char yields that limit sugar yield (Cantero et al., 2013) and recent studies have indicated that careful process design of flow processes can result in aqueous products with sugar concentrations similar to those obtained in batch processes (Lü & Saka, 2010; Machmudah et al., 2016). However, the physical properties, composition, and impurities present in biomass vary with biomass type and growing condition. Due to the lack of a predictive theories, Lachos-Perez et al. (2016) suggested that each biomass must be studied individually to quantify the yields of valuable compounds that can be obtained using SCW extraction and hydrolysis.

Despite the amount of sugarcane straw available for energy and chemicals production, we are not aware of previously published reports on SCW hydrolysis of sugarcane straw. Therefore, this study aimed to determine the potential of SCW hydrolysis to obtain valuable energy products, chiefly simple sugars, and other valuable compounds, from sugarcane straw. To understand the bulk and surface composition of the residual straw and identify opportunities for future improvements, the residue was analyzed using Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The results presented here establish the potential of SCW hydrolysis for recovery of sugars and char from sugarcane straw.

3.2. Material and Methods

3.2.1. Raw material and chemicals

Sugarcane straw (*Saccharum officinarum Linnnaeus*) was supplied by the sugar and ethanol plant Ester located in Cosmópolis, SP, São Paulo, Brazil. Sugarcane straw was ground (batches of 10 g in 20 s) in a knife mill (Marconi, model MA 340, Brazil) coupled to an induction motor of 3800 rpm, and separated by sieving using granutest sieves with a mesh of 16, 24, 32, 48, 80 and 100 Tyler series and then obtained the mean diameter between sieves of 303 µm.

Chemical standards used to calibrate the high performance liquid chromatograph (HPLC) were: glucose (>99%), arabinose (>99%), xylose (>99%) and galactose (>99%). All standards were purchased from Sigma and used without further modification. Type I water was obtained from an Elga Purelab Flex 3 sytem (Veolia Water, Marlow, UK). HPLC grade acetonitrile was obtained from J.P. Baker (Darmstadt, Germany) and phosphoric acid (85% P.A.) was obtained from Ecibra (São Paulo, Brazil). Acetone (96%) supplied by Sigma was used for the determination of extractives. Sulfuric acid (96%), acetic acid, HPLC grade sodium chlorite (99%), and sodium hydroxide were purchased from Wako Pure Chem. Ind., Ltd., Osaka, Japan and used for quantification of holocellulose, α-cellulose and lignin content in the straw. Distilled water was used as the reaction medium in the experiments, and Milli-Q water was used in the HPLC analysis.

3.2.1.1. Sample characterization

Moisture, ash, and total extractives contents were determined directly on unextracted samples. Protein was determined from the mass fraction of atomic

nitrogen obtained by CHN elemental analysis using an Elemental Analyzer Flash model 2000 (Thermo Fisher Scientific Inc, Delft, Holanda) and applying a calibration factor (6.25) recommended by Gnaiger and Bitterlich (1984). Moisture and ash content were determined using the methodologies recommended by the National Renewable Energy Laboratory described in the technical report (LAP TP-5100-60956, 510-42618). The acetone extractives content in sugarcane straw was determined by Soxhlet extraction with acetone for 16 h (del Río et al., 2015b). In all cases, the composition of sugarcane straw was measured in three independent experiments; average values and standard deviations are reported here.

3.2.1.2. Chemical composition of sugarcane straw

Holocellulose, α-cellulose, and lignin contents were measured in extractive-free sugarcane straw. The holocellulose content was determined as the mass remaining after $NaClO_2$ delignification (Wise et al., 1946). Initially, 2.5 g of biomass was heated with 150 mL water at 75 °C. Then 0.2 mL acetic acid and 2.0 g $NaClO_2$ were added to the slurry. After 1 h, 0.2 mL acetic acid and 1.0 g $NaClO_2$ were added every hour for 3 h. The slurry was filtered and washed with distilled water and acetone. The delignified residue (holocellulose) was weighed after drying for 24 h in an oven at 105 °C. Holocellulose (1 g) was then transferred to a flask with 25 mL of 17.5% NaOH aqueous solution and stirred for 40 min at 20 °C. After 5 min, the residue was filtered, and 40 mL of a 10% acetic acid aqueous solution was added to the residue. The residue was filtered again and washed with 1 L of boiling water. The α-cellulose residue was filtered, dried at 105 °C for 48 h in vacuum, and weighed. The lignin content in the sample was determined by Klason's method based on acid hydrolysis. This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. The lignin fractionates into acid insoluble material and acid soluble material. The acid soluble lignin content was measured using a UV-Vis spectrophotometer at 240 nm (Hach, modelo DR/4000U, São Paulo, Brazil).

3.2.2. Experimental procedure

Hydrothermal liquefaction experiments of sugarcane straw were conducted in a semi-continuous flow reactor (i.e. batch for the solid and continuous for the liquid) described previously (Lachos-Perez et al., 2016) (Figure 3). In each experiment, 5.0 grams of sugarcane straw were loaded into the reactor. Hydrolysis experiments were performed using a factorial design with two variables and two levels in duplicate,

resulting in 10 separate experiments. The independent variables were temperature (°C) and pressure (MPa), with values presented on Table 4. Temperature levels were selected to be greater than the normal boiling point and less than the critical temperature of water (374 °C) and pressure levels were selected to be greater than the saturation pressure water at the process temperature. The volumetric water flow rate was maintained at 10 mL/min. Solvent to feed mass ratio (S/F) was 60 kg water/kg feed, which is similar to previous studies (Ciftci & Saldaña, 2015). The S/F ratio was selected after preliminary measurements of total reducing sugars yields at 170 °C and 7 MPa showed that all of the easily accessible carbohydrate had been hydrolyzed when this condition had been reached.

The liquid product was collected after reaction and analyzed to quantify concentrations of sugars and several major degradation products. The collected biomass was dried at 105 °C for 24 h. Solid products were analyzed using FT-IR spectroscopy and TGA (details below).

The severity factor (R_0), has been useful for modeling the combined influence of temperature and residence time on biomass hydrolysis yields.

$$R_0 = t \exp\left(\frac{T - 100}{14.75}\right) \qquad \text{Equation 1}$$

where t is the resident time (min), T is temperature (°C), 100 is the reference temperature, and 14.74 is an empirical parameter related to activation energy, assuming pseudo first order kinetics. Hydrolysis results are typically represented as functions of the natural log of the severity factor (i.e., ln(R_0)).

Table 4 Influence of parameters (Temperature and pressure) on the TRS yield (X_0)

Real variable		Codified variables		Water density (kg/m^3)	Residence time (min)	TRS (%)
(°C)	P (MPa)	X_1	X_2			x_0
200	10	-1	-1	870.94	8.87	32 ± 1
250	10	1	-1	805.7	8.21	17 ± 0.4
200	15	-1	1	874.51	8.91	28.0 ± 0.7
250	15	1	1	811.02	8.26	17.6 ± 0.5
225	12.5	0	0	842.6	8.58	18.5 ± 0.3
225	12,5	0	0	842.6	8.58	18.5 ± 0.6
190	12.5	-1.4	0	883.85	9.00	23 ± 1
225	16	0	1.4	845.55	8.61	21 ± 2
260	12.5	1.4	0	793.29	8.08	14.06 ± 0.02
225	9	0	-1.4	839.57	8.55	25.7 ± 0.4

3.2.3. Total reducing sugar determination

The total reducing sugar (TRS) content of the hydrolyzate was determined using the colorimetric method proposed by Somogyi and modified by Nelson (SN) (Miller, 1959; Nelson, 1944). The hydrolyzate was subjected to acid hydrolysis to decompose sugar oligomers into monomers prior to detection as TRS. After the coloring reaction, sample absorbance at 540 nm was measured using a spectrophotometer (Hach, model DR/4000U, São Paulo, Brazil). The concentration of TRS was calculated using an external calibration curve based on glucose standard solutions and expressed as glucose equivalents. When necessary, hydrolysis product mixtures were diluted with distilled water before the absorbance measurement to ensure that the concentration fitted within the instrumental calibration range.

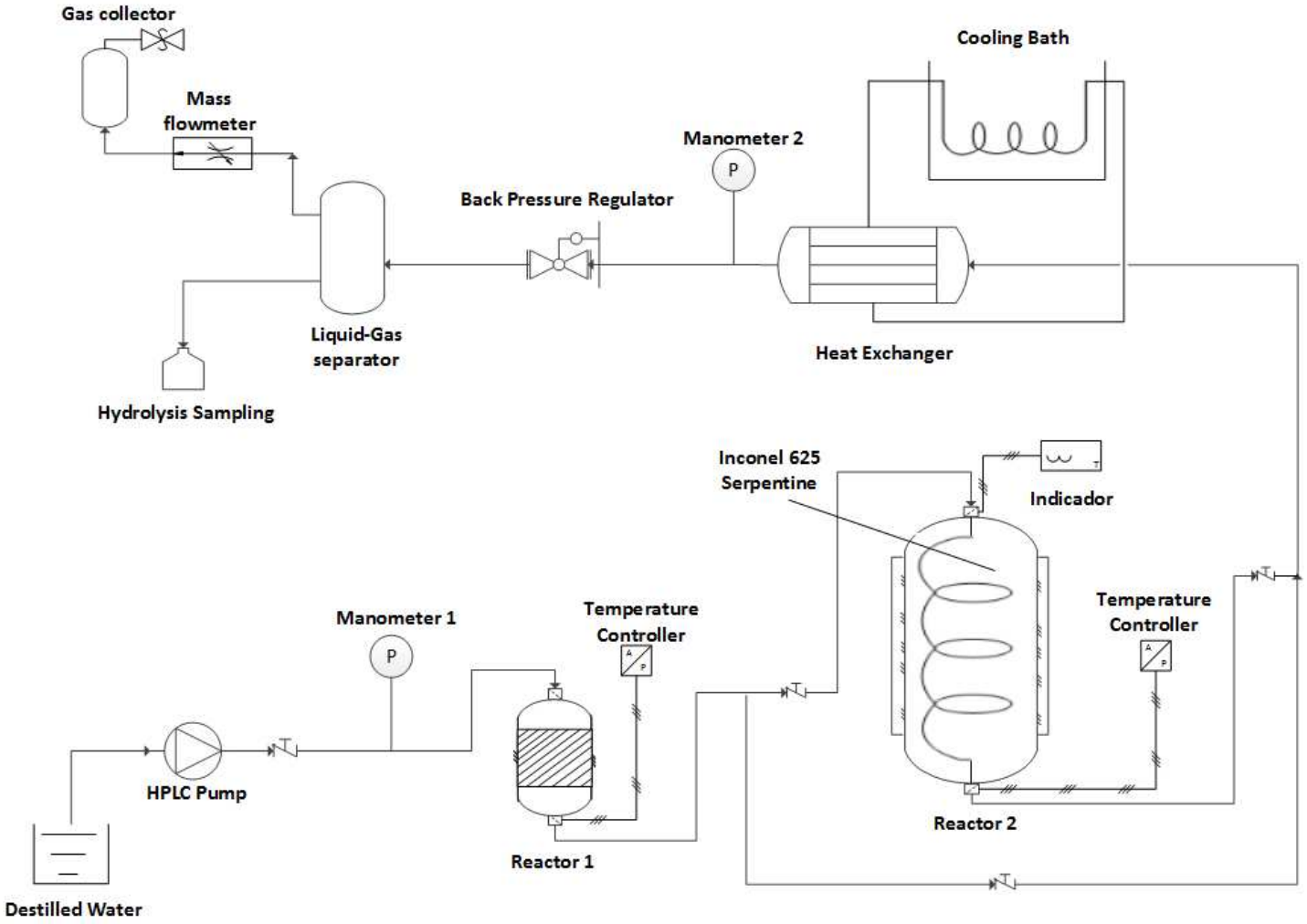


Figure 3. Schematic diagram of experimental apparatus.

3.2.4. Determination of saccharides by chromatography

Total hemicellulose (xylose, galactose, arabinose, and mannose) and cellulose (glucose) sugars in the hydrolyzate were determined by HPLC. The HPLC column used for the separation of the compounds was SUPELCOGEL Pb (Supelco), Crosslinked HPLC Column. 9 µm particle size, L × I.D. 30 cm × 7.8 mm and pre column SUPELCOGEL™ Pb Guard Column. 9 µm particle size, L × I.D. 5 cm × 4.6 mm. The column temperature was set to 85 °C and Milli-Q® grade water was used as the mobile phase at a flow rate of 0.5 mL/min. Sugar identification was based on retention time matching relative to times measured for known standards. A Waters IR detector (2414) was used to quantify the sugars and their derivatives. The detector response was calibrated using solutions with known concentrations.

3.2.5. Determination of inhibitors by high-performance liquid chromatography (HPLC)

Inhibitor concentrations present in the hydrolyzate were measured using HPLC in the EXTRACT-US system (FAPESP 2013/04304-4 – Patent pending). The EXTRACT-US system is composed of a HPLC liquid pump (PU-2080, Jasco, Japan), ternary gradient unit (LG 2080-2, Jasco), 3 line degasser (DG 2080-55, Jasco), and UV-Vis detector (UV-7075, Jasco). The sample was filtered through a nylon syringe filter (0.20 µm, Analítica, São Paulo, Brazil) before analysis.

Compounds were identified by comparing matching measured retention times in with retention times measured for standards. The detector response was calibrated using standard solutions. All analyses were performed in duplicate and the results expressed as mg of compound/L of sample.

3.2.6. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of sugarcane straw and carbonized products was performed using a Netzsch TG 209 F1 Libra. Samples were placed in an alumina crucible and held under a nitrogen flow rate of 20 mL/min. The samples were heated from 35 °C to 800 °C (5 °C/min). Raw thermogravimetric data were converted into derivative thermograms (DTG) using the vendor software.

3.2.7. Fourier-Transform Infrared (FT-IR) spectroscopy

Infrared spectra were obtained using a Bruker Vertex 70 FT-IR spectrometer with a La-DTGS detector. Dry powder samples were placed on a Specac diamond ATR cell and spectra collected at 4 cm^{-1} resolution, with 512 scans taken over the 600-4000 cm^{-1} spectral range and then averaged to obtain representative spectra. MagicPlot software was used for peak fitting infrared spectra. Fitted peak areas of bands at ca. 1730, 1512, 912 and 1600 cm^{-1} were used to estimate the relative content of hemicelluloses, lignin, cellulose and char respectively. These bands correspond to the carbonyl C=O stretch for hemicelluloses, C=C stretching vibration for lignin, skeletal C-H for cellulose and C=C stretch for amorphous carbon (char), respectively. The peak areas were normalized to the area of the lignin band at 1512 cm^{-1}. The estimated uncertainty is ±3%.

3.2.8. Statistical analysis

Temperature (X_1) and pressure (X_2) were used as independent variables and TRS yield (X_0) as a dependent variable for the statistical analysis of the SCW treatment. For statistical analysis, 20 experimental values were used (10 tests × 2 for duplicates). ANOVA and multiple regression of these results were performed using the software SAS 9.0. A second-order model was tested via multiple regression analysis, as shown by Eq. (1):

$$X_0 = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1 X_1 + \beta_{22} X_2 X_2 \quad \text{Equation 2}$$

where X_0 is the response variable; $\beta_0, \beta_1, \beta_2, \beta_{12}, \beta_{11}, \beta_{22}$are fitting parameters; and X_1, X_2 are the independent variables.

3.3. Results and Discussion

3.3.1. Sugarcane straw characterization

Table 2 provides composition data describing the main constituents of the sugarcane straw; results obtained by Rueda-Ordóñez and Tannous (2015), Szczerbowski et al. (2014) and del Río et al. (2015a) are shown for comparison. Beginning with the proximate analysis, the measured moisture content did not differ much from published data and ranged between 6.5 and 8.4%. The measured ash content was around 6.8%, greater than the values reported by del Río et al. (2015a) and Rueda-Ordóñez and Tannous (2015). Inter-comparison of ash content reported in

different studies requires caution because observed differences may be due either to actual differences in composition or to differences in sample preparation and handling (Szczerbowski et al., 2014).

The measured acetone extracted lipid content of the sugarcane straw was 3.5%. The extractives content reported in the other studies varied widely. For example, some authors reported extractives content in the range from 6.2-7.5 wt% (Oliveira et al., 2013), whereas others reported extractives content in the range from 5.28-10.6 (Rueda-Ordóñez & Tannous, 2015). Differences may be due in part to different procedures. In particular, the greatest values were measured using ethanol (95%), a solvent that extracts greater amounts of low-molecular-weight carbohydrates, salts, polyphenols and other water-soluble compounds (del Río et al., 2015b) than the acetone used in this study.

3.3.2. Chemical composition

Table 2 shows good agreement between the various data sets on holocellulose, α-cellulose, and Klason lignin content, while the reported values of acid-soluble lignin content varied more substantially. The measured chemical composition data agree reasonably well with literature values (del Río et al., 2015a; Rueda-Ordóñez & Tannous, 2015; Szczerbowski et al., 2014), with some minor discrepancies as noted. Discrepancies may arise due to differences of the ages of the plants that were analyzed, storage times and temperatures, types of plant tissue analyzed, and cultivation and harvesting conditions. However, a great deal of the data scattering is also due to differences in the characterization methods, including (a) the use of extractives-free samples for lignin and holocellulose analysis, and (b) the extent of extractives removal during treatment with different solvents (Szczerbowski et al., 2014).

Table 5 - The main constituents of the sugarcane straw.

	This Work	(del Río et al., 2015a)	(Szczerbowski et al., 2014)	(Rueda-Ordóñez & Tannous, 2015)
Proximate analysis (wt%)				
Moisture	6.5±0.2	-	-	8.4±0.3
Ash	6.8±0.8	4.7±0.5	6.2±0.2	3.9±0.2
Protein	2.31±0.04	-	3.7±0.1	-
Acetone extractible	3.5±0.1	1.4±0.1	3.50±0.06[a]	5.28[b]
Chemical composition (wt%)				
Klason lignin	21±3	17±0.2	20.6±0.2	
Acid-soluble lignin	5.7±0.1	1.9±0.2	0.71±0.03	21.63[c]
Holocellulose	73±1	72.9±0.7	77.7±0.3	73.09[d]
α-cellulose	37±3	37.9±0.3	37±1	39.81

[a] Extractives in organic solvents

[b] Extractives in water and ethanol

[c] Lignin total

[d] Cellulose+Hemicellulose

3.3.3. TRS Yields

Table 1 shows the experimental design with the results of TRS yield (Zhu et al., 2013). The ANOVA indicated that TRS yield depends strongly on hydrolysis temperature ($p < 0.05$). The polynomial model of Eq. 2 represents statistically the behavior of the TRS global yield as a function of the fit parameters, with a confidence level of 95%:

$$Y = 19.04 - 5.23X_1 - 1.30\,X_2 + 2.94\,X_{22} \qquad \text{Eq. 2}$$

where Y is the predicted TRS yield, X_1 the hydrolysis temperature, and X_2 the pressure. The TRS model contains hydrolysis temperature and pressure as linear and cross correlation terms. Interestingly, the effect of increasing temperature is to

decrease TRS yields, suggesting that increasing the temperature increases the rates of degradation and charring more than it increases the hydrolysis rate – consistent with recent studies on green coffee powder hydrolysis in SCW (Mayanga-Torres et al., 2017), while the solid residue at the end of the process showed a reduction of the content with the increase in temperature as expected based on the hydrolysate measurements (Figure 2).

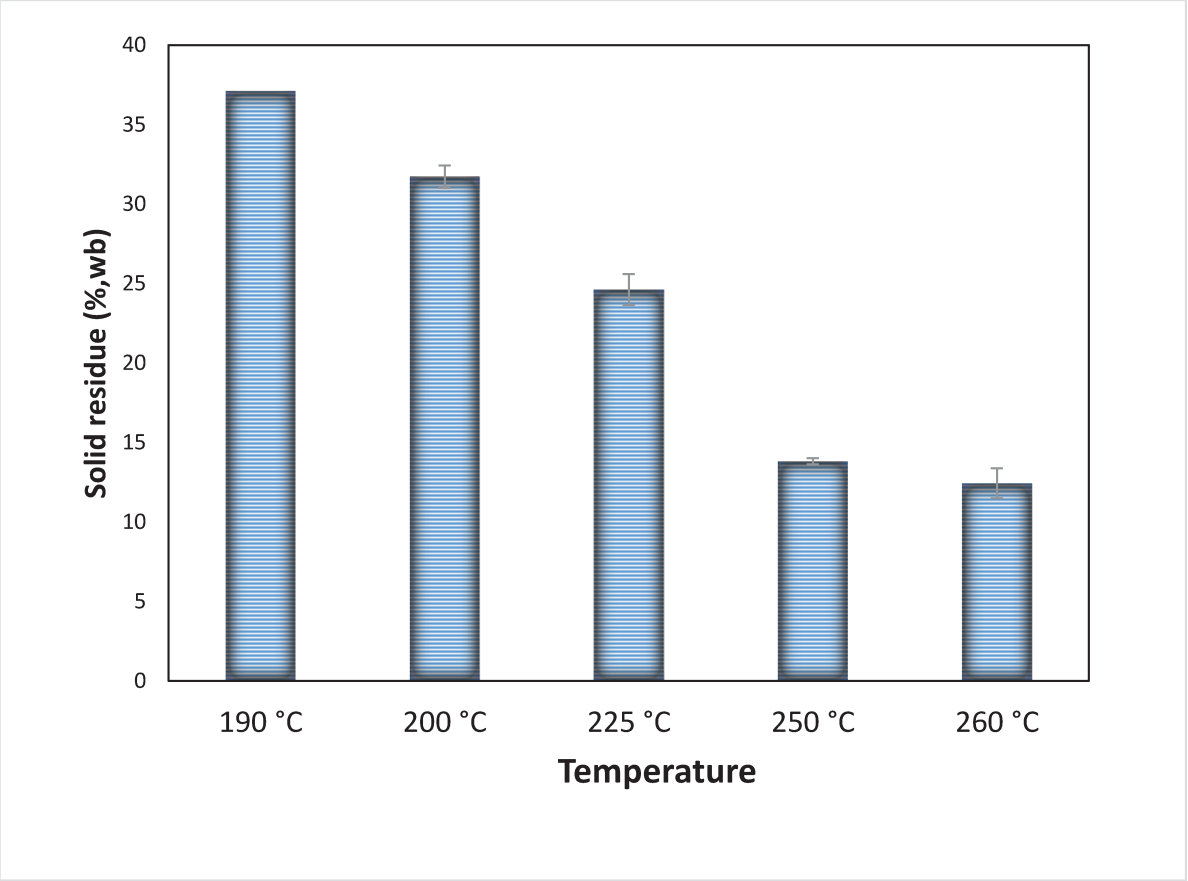


Figure 4. Solid residue remaining inside the reactor after the subcritical water hydrolysis of sugarcane bagasse.

The maximum yield was obtained at 200 °C, consistent with TRS yields reported in the literature and obtained from SCW hydrolysis of different types of biomass (Klinchongkon et al., 2015; Prado et al., 2014). For example, Mlyuka et al. (2016) reported optimal sugar extraction from *Eriobotrya japonica* leaves at 200 °C. The maximum TRS yields were 32.03% and 28.02%, observed at 15 and 10 MPa, respectively. The fact that increasing reaction temperature greater than 200 °C did not improve TRS yields indicates that hydrolysis rate acceleration due to thermal, Arrhenius effects and catalysis by hydronium and hydroxide ions is balanced by increasing rates of degradation and charring that depend on the same factors. At 200 °C, an optimal condition exists where thermal effects and hydroxide and hydronium

released by water (and determined by its auto-ionization constant, K_w) are balanced between hydrolysis, sugar degradation, and charring.

The Supplementary Information provided by the ANOVA shows that pressure has a low effect on TRS yields. However, the cross term between temperature and pressure has a positive effect; the cross term may capture the effect of liquid-phase density on TRS yields. Since the dielectric constant depends on liquid-phase density, the influence of density on hydrolysis may be to accelerate reactions with polar transition states (Rogalinski et al., 2008).

The results presented in this section seem to indicate that pressure plays a minor role on TRS yields, at most. However, sufficient pressure is required to maintain liquid in its water phase. The liquid solvent phase provides superior heat transfer compared to the vapor, can better solvate transition states, and provides hydroxide and hydronium ions as catalysts. Provided that the pressure is greater than the saturation vapor pressure of water, the reaction temperature can be varied to control reaction rates and sugars conversion without risk of operation under vapor-liquid-equilibrium conditions.

3.3.4. Composition of the hydrolyzate

Hydrolyzate products were analyzed to determine concentrations of sugars and inhibitors compounds, with results summarized in Table 6. The total yields of each component followed similar trends with respect to pressure and temperature. Glucose was the dominant monosaccharide present in the hydrolysate, followed by the hemicellulose sugars (mainly xylose with small amounts of galactose and arabinose). Glucose most likely originates from cellulose hydrolysis, especially its amorphous domains (Rogalinski et al., 2008). Water hydrolyzes glycosidic bonds present in cellulose by electrophilic attack; increasing reaction temperature and hydronium ion concentrations increase the hydrolysis rate. Glucose yield exhibits a broad maximum over the range of ln R_0 from 9 to 11.

Xylose likely arises from hemicellulose, which typically is hydrolyzed in the range 190–220 °C (Allen et al., 1996; Mayanga-Torres et al., 2017; Prado et al., 2014). The hemicellulose content of straw consists primarily of a xylan polymer backbone with glucuronic acid and arabinose side chains. Accordingly, hydrolysis of the hemicellulose contained in sugarcane straw produces xylose, arabinose and galactose (Lavarack et

al., 2002; Zhu et al., 2013). Xylose yield reached a maximum of 2.29 % at ln R_0 equal 9, similar to the behavior observed by Klinchongkon et al. (2015) in their study of passion fruit peel treatment by SCW. This behavior may be consistent with the relationship between hemicellulose hydrolysis rates and temperature. Specifically, Jacobsen and Wyman (2002) studied xylose monomer and oligomer yields for uncatalyzed hydrolysis of sugarcane bagasse and showed a model where xylose reacts further to furfural and other degradation products.

Galactose and arabinose yields followed similar trends compared to xylose, albeit at reduced quantities. Hongdan et al. (2013) observed similar trends in hemicellulose sugar yields in their study of sugarcane bagasse under batch conditions, with the maximum yields occurring at 180 °C and 40 min of reaction time. Hongdan et al. (2013) attributed their finding to degradation of arabinose to produce furfural and galactose into hydroxymethyl furfural (HMF) with increasing reaction severity.

The decreased sugar yields observed at temperatures above 200 °C may be attributable in part to sugar decomposition to secondary products, such as furfural and HMF. HMF is produced by the dehydration of 6-carbon sugars obtained from the hydrolysis of cellulose, while furfural is a result of the dehydration of 5-carbon sugars resulting from the hydrolysis of the hemicellulose (Asghari & Yoshida, 2010). Table 3 shows that yields of HMF and furfural both increase with increasing temperature. The furfural and HMF yields are of similar orders of magnitude, with the furfural yield greater than the HMF yield at all temperatures less than 250 °C. Both furfural and HMF yields exhibit maximum with respect to severity, at severity factors of 12 and 13, respectively. The observed maximum is likely attributable to polymerization of the two compounds to produce chars and/or further degradation to produce short chain organic acids.

The total monosaccharides yield (Table 6) was less than the TRS yield, which suggests that about 60–70% of the sugars present in the hydrolyzate were in oligomeric form. The degree of polymerization of the solubilized oligosaccharides decreases with increasing temperature (Prado et al., 2014; Rogalinski et al., 2008; Zhu et al., 2013). This suggests that the glycosidic bond may be easier to hydrolyze in oligosaccharides than in cellulose itself, so that oligosaccharides may exist only briefly before hydrolyzing to form monomers (Lü & Saka, 2010; Prado et al., 2014).

Hemicelluloses contain acetyl and uronic acid side chains, which can be released during SCW treatment. The hydrolyzate pH decreased from an initial value of

5 to approximately 3 (data not shown). The acidic conditions catalyze cellulose and especially hemicellulose hydrolysis. Consistently, hemicellulose hydrolysis was maximized at acidic conditions. Nonetheless, increasing acidity did not improve hemicellulose sugar yield, which may be attributed to degradation of sugars under severe conditions. This is in agreement with findings reported by Phaiboonsilpa and Saka (2011) and Ciftci and Saldaña (2015).

Table 6 - Sugars and inhibitors obtained by subcritical water hydrolysis of sugarcane straw (g/100 g bagasse).

Temperature (°C)	Ln(R_0)	Glucose	Xylose	Galactose	Arabinose	Monosaccharides	HMF	Furfural	Total inhibitors
190	8	1.5 ± 0.2	1.5 ± 0.4	0.6 ± 0.3	0.78 ± 0.05	4.38 ± 0.95	0.80 ± 0.2	1.1 ± 0.3	1.8 ± 0.5
200	9	2.1 ± 0.4	2.3 ± 0.7	0.7 ± 0.1	1.0 ± 0.2	6.1 ± 1.4	0.93 ± 0.2	1.9 ± 0.3	2.83 ± 0.5
225	11	1.7 ± 0.5	1.4 ± 0.9	0.42 ± 0.001	0.8 ± 0.5	4.32 ± 1.901	1.79 ± 0.003	2.0 ± 0.1	3.79 ± 0.103
250	12	1.1 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.4 ± 0.2	2.4 ± 0.5	2.12 ± 0.01	1.60 ± 0.02	3.72 ± 0.03
260	13	0.89 ± 0.06	0.5 ± 0.1	0.3 ± 0.2	0.3 ± 0.2	1.99 ± 0.56	0.97 ± 0.02	1.22 ± 0.001	2.19±0.021

3.3.5. TG Analysis

The sugarcane straw feed and treated solid samples were analyzed using TGA to determine the scope for improving the hydrolysis yields. The Supplementary Information provides raw and intermediate data In brief, raw TGA mass loss data were converted into differential thermograms (DTG). The DTG data were then fit using the methods recommend in the literature (Cai et al., 2013) to determine mass composition in 5 categories: semi-volatile, hemicellulose, cellulose, lignin, and char. The semi-volatile components are likely similar in composition to the acetone extractable components quantified in Table 5, but may also include thermally labile proteins and other hydrophilic small molecules. Table 7 lists the average temperatures and standard deviations attributed to each of these components in the DTG curves; in all cases, the standard deviation was less than about 15 °C, indicating adequate consistency of DTG band locations. The contributions of the individual components were determined by integration, then normalized to unity; Figure 5 contains the results, where all data available at a given temperature were averaged together, irrespective of the treatment pressure as this variable was found to have a negligible effect. As with the bulk analysis (see Table 5), TGA indicates that the holocellulose content of the feed sugarcane straw is about 70 wt%. With increasing hydrolysis temperature, the contribution of the semi-volatile component rapidly decreases, consistent with removal of simple sugars, hydrolysis and removal of proteins, etc. Likewise, the hemicellulose content decreases with increasing temperature; however, even after treatment at 260 °C, the TGA indicates that the straw contains approximately 5-10 wt% hemicellulose. The cellulose content increases after treatment at 190, 200, and 225 °C, which is consistent with its recalcitrance relative to hemicellulose. At hydrolysis temperature greater than or equal to 250 °C, the cellulose content decreases with treatment. As with hemicellulose, the cellulose content of the straw is never removed completely, retaining approximately 30 wt% cellulose after treatment at 260 °C. Lastly, a new band appears after treatment and its intensity increases with increasing hydrolysis temperature. The new band is associated with char formation, produced by degradation and re-polymerization reactions. The sample treated at 260 °C contains more than 20 wt% char.

Table 7. Average temperatures used for fitting DTG curves.

Component	Average Peak Temperature (°C)	Peak temperature Standard Deviation (°C)
Semi-volatile	230	16
Hemicellulose	290	15
Cellulose	335	13
Lignin	351	11
Char	427	8

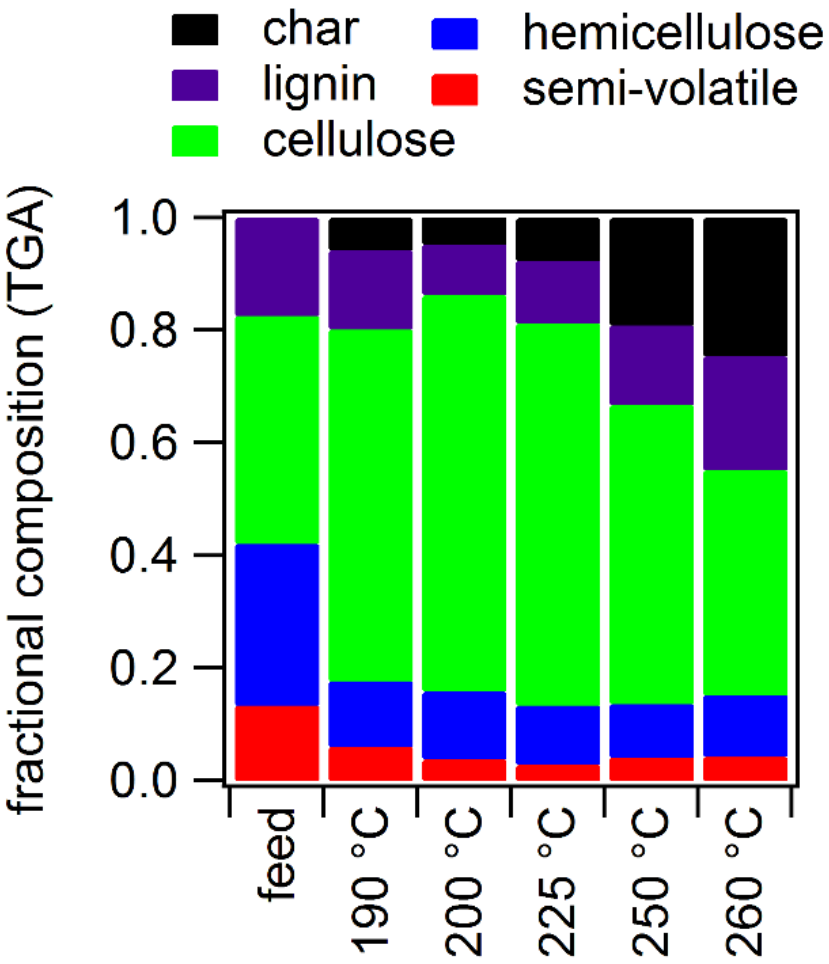


Figure 5. Mass content data obtained for sugarcane straw and hydrolyzed solids, determined using TG analysis.

3.3.6. FI-IR Spectroscopy

FT-IR spectroscopy was used to provide further information on the composition of the hydrolyzed sugarcane straw. In particular, an important objective of the FT-IR analysis was to reconcile differences between the sugars yields, which indicated hydrolysis of holocellulose, and TGA data. The Supplementary Information provides complete details, including representative FT-IR spectra. In all cases, FT-IR spectra contained bands attributable to different biomass components, including lignin (C=C), hemicellulose (C=O), and cellulose (HCC and HCO) bands. In addition, spectra of the treated samples contained bands attributable to the C=C bonds of char (Fuertes et al., 2010). The Supplementary Information provides a detailed account of all band assignments. Table 8 provides locations, assignments and variability of key bands attributable to the 4 main components present in biomass, chiefly lignin, cellulose, hemicellulose, and char.

The composition of treated samples was estimated by integration of the key bands, following a similar procedure as suggested by Acquah et al. (2016). The locations of these 4 bands in the various samples varied by less than 3 cm^{-1}, as would be expected for chemically informed assignments. Because lignin is thought to be recalcitrant to hydrolysis (Pu et al., 2013), the area of the lignin band was used as a normalizing factor for the other 3 components. The resulting areas (relative to lignin) were then plotted, as shown in Figure 6. Consistent with TGA (Figure 5) and bulk analysis (Table 5), the ratio of cellulose to hemicellulose in the sugarcane straw is approximately 3:2. After treatment, the hemicellulose content decreases relative to the feed, and continues to decrease with increasing hydrolysis temperature. Char is present in samples treated at 200 °C (approximately 1% of the total mass) and is an important component (>5%) for samples treated at >225 °C. Similar to TG analysis, FT-IR indicates that char accounts for approximately 20% of the mass of straw hydrolyzed at 260 °C.

The FT-IR results are entirely consistent with the TG analysis, suggesting that sugarcane straw chars at temperatures >200 °C. On the other hand, hydrolyzate analysis indicates that sugar yields peak at approximately 190-200 °C, and then decrease with increasing hydrolysis temperatures. Therefore, the maximum in sugar yield and the appearance of char in the treated solids is coincident at approximately 200 °C. For hydrolysis at temperatures >200 °C, holocellulose is hydrolyzed; however,

holocellulose hydrolysis competes with sugar degradation and especially char formation reactions at temperatures >200 °C. At 200 °C, the balance between hydrolysis and char formation favors hydrolysis, resulting in the observed optimal TRS yield.

In addition to estimation of the organic biomass components, narrow weak bands in the region 3600-3700 cm^{-1} are assigned to O-H stretching vibrations of clay minerals. Complete details including original spectra are provided in the Supporting Information. Specifically, the 3621 cm^{-1} band is assigned to kaolinite and gibbsite, 3695 cm^{-1} band is also assigned to kaolinite (Merlin et al., 2014). The clay likely originates from soil contamination of the straw material, as corroborated by the high ash content measured for the sugarcane straw (6.8 wt%, Table 5). The presence of ash and clay materials in the straw may play a role in the degradation/charring indicated by TGA and FT-IR analysis, as cations are known to catalyze sugar degradation and ring-opening reactions (Wang et al., 2015).

Considering that holocellulose constitutes 72 wt% of the original biomass, the optimized TRS yield accounts for nearly 50% of the original carbohydrate content of the sugarcane straw. This is comparable to yields obtained for cellulose hydrolysis (Sasaki et al., 2000), indicating that SCW hydrolysis of sugarcane straw may be economically viable. At the same time, significant scope remains to increase sugar yields by hydrolyzing the holocellulose that remains after hydrolysis. Improving the TRS yield will require identifying reactor operating conditions, catalysts, and/or auxiliary chemicals that accelerate the rates of hydrolysis reactions relative to char formation reactions.

Table 8. Average band locations and assignments used for FT-IR analysis (Agarwal, 1999; Sevilla & Fuertes, 2009)

Component	Average Location (cm^{-1})	Standard Deviation (cm^{-1})
Cellulose, HCC and HCO bending	912	2
Lignin, C=C Aryl ring stretch	1512	1
Char, C=C stretch	1599	2
Hemicellulose, C=O	1732	3

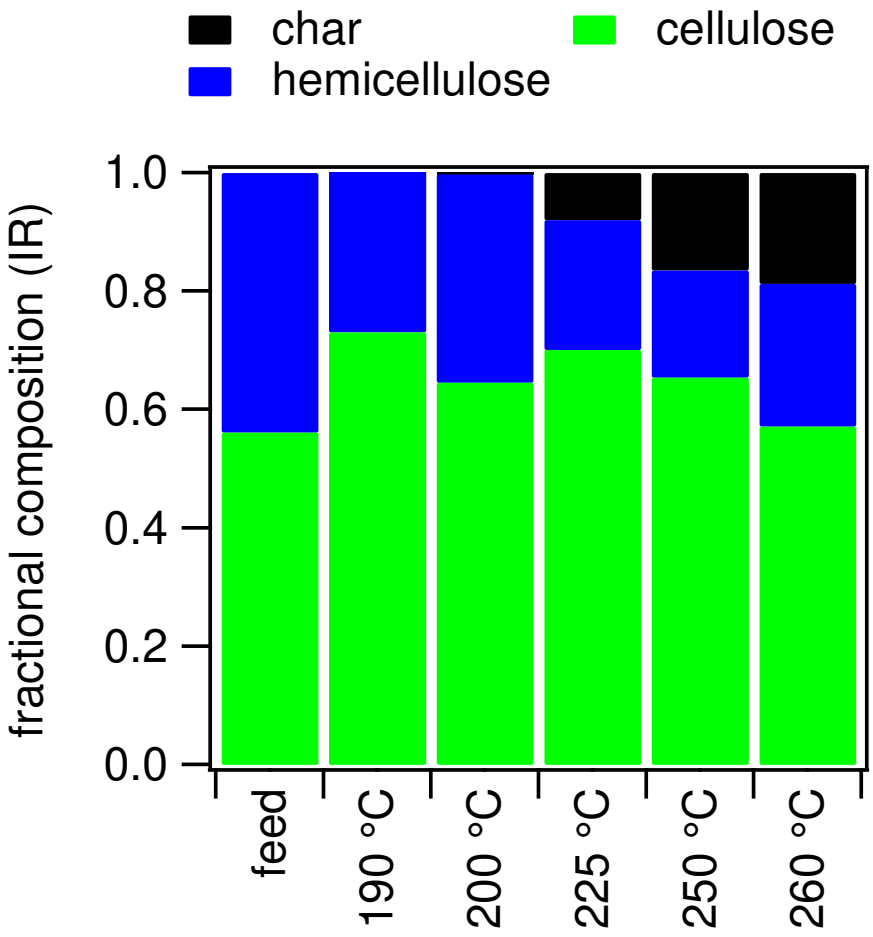


Figure 6. Mass content data obtained for sugarcane straw and hydrolyzed solids, determined using IR analysis.

3.4. Conclusions

Sugarcane straw was hydrolyzed in a semi-continuous reactor using SCW. The main products were glucose and hemicellulose sugars inhibitors as minor byproducts. Optimal TRS yields were observed at 200 °C, reaching values (32 %) that indicate economic potential for hydrolysis of this feed. TG and FT-IR analysis indicated that the optimal sugar yields were coincident with onset temperatures observed for char formation. Temperatures greater than 200 °C resulted in increasing char formation. Interestingly, at the maximum temperatures (260 °C) contained substantial holocellulose content, suggesting scope for further improvements if the inaccessible holocellulose can be hydrolyzed and recovered as sugars.

3.5. Acknowledgements

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4. CAPÍTULO 4 – Casca de laranja

Subcritical water extraction of flavanones from defatted orange peel

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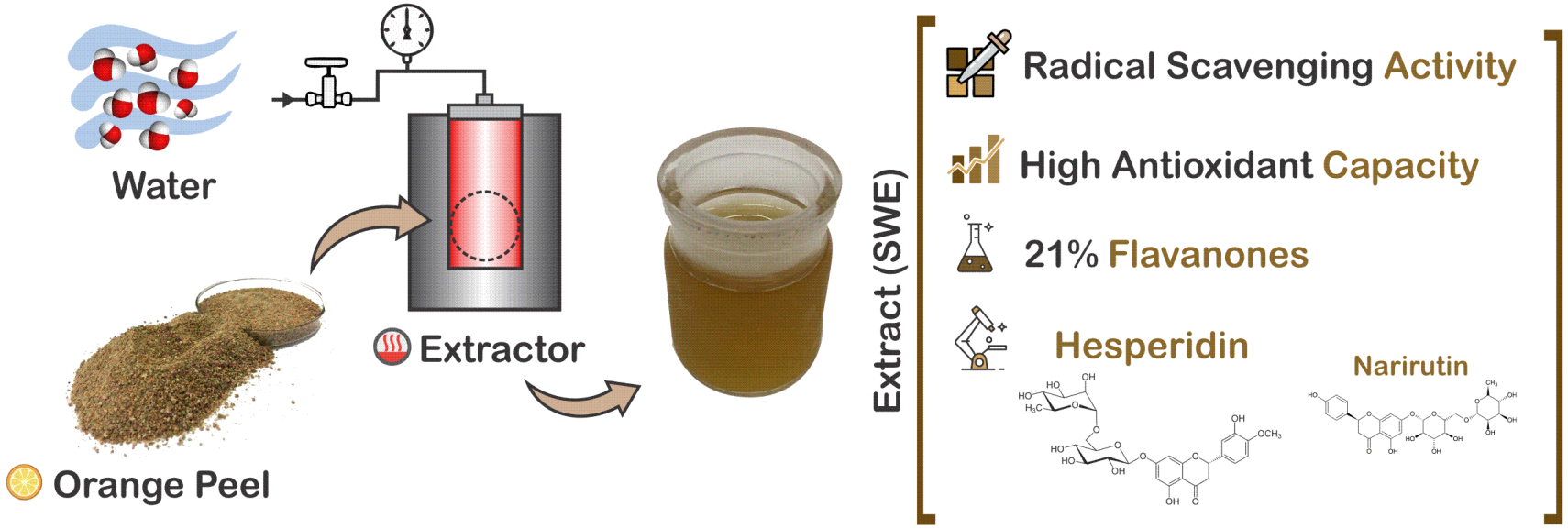
Graphical Abstract



Abstract

Subcritical water extraction (SWE) is a green process that uses water as a solvent for extracting non-polar flavonoids by varying the temperature-dependent dielectric constant. Flavanones, including hesperidin and narirutin, constitute the majority of the flavonoids that occur naturally in citrus fruits. The effects of operating parameters temperature (110 - 150 °C) and water flow rate (10 - 30 mL/min) on the SWE of flavonoids from defatted orange peel (DOP) were studied. The maximum yields of hesperidin (188.74 ± 0.51 mg/g extract) and narirutin (21.98 ± 1.39 mg/g extract) were obtained at 150 °C and 10 mL/min. These yields accounted for approximately 21% of the total amount of these flavanones in the extracts, leading to the purest extracts. SWE was compared with three conventional extraction methods and the results demonstrated that, compared to conventional extractions, SWE is a highly efficient method for the recovery bioactive compounds with high antioxidant activity.

Keywords: *Defatted orange peel, subcritical water extraction, bioactive compounds, flavanones, antioxidant capacity.*

4.1. Introduction

Brazil is the world's largest producer of oranges [1]. In 2016, the orange production in the country was 15.9 Mt, being the main use for the juice production. After juice's extraction, 50% of the fruit is discarded as residue representing approximately 2% of all agricultural residues produced in Brazil [2], which is commonly used as an animal food supplement.

Therefore, orange peel (OP) is the main waste by-product of the juice extraction industry. Nonetheless, OP is an attractive source of bioactive compounds, which include phenolic compounds as the flavonoids. Flavonoids' concentrations in citrus fruits are higher in the peel and seeds [3-6]. Various reports have shown that flavonoids may have positive health effects, including antiproliferative, cardioprotective, anti-inflammatory and antioxidant effects [7-9]. Two flavonoids are found in large amounts in OP: the hesperidin and the narirutin. The hesperidin is a flavanone, which is a type of flavonoid [10]. Hesperidin is being widely used in pharmaceutical industries because it is associated with low risk of spills and certain types of cancer [11], besides its antimicrobial and antioxidant capacity. According to Sigma-Aldrich, up to 102.0 thousand tons of hesperidin could be obtained from the amount of orange bagasse generated per year in Brazil, which could represent a return of USD 2704.5 trillion [12].

Flavanones from orange peel can be obtained by different extraction methods, such as Soxhlet extraction, pressurized liquid extraction, ultrasound assisted extraction and, microwave assisted extraction, where organic solvents are commonly used. However, these solvents can be toxic and environmentally prejudicial, requiring severe solvent removal procedures before the extracts are ready to be consumed or exposed to potential environmental risks. Moreover, the solvents are usually expensive to purify and, generally cannot be easily discarded, taking both time and money. Therefore, the employment of efficient extraction techniques using non-toxic solvents are required, mainly when extracting compounds for people's ingestion, such as bioactive compounds [13].

In this context, a convenient extraction technique using water as solvent is interesting, since water is non-flammable, non-toxic, cheap and environmentally safe. Subcritical water extraction (SWE) takes place at temperatures between the boiling point and critical point of water (100 °C at 1 bar and 374.1 °C at 221 bar), at pressures

high enough to keep water in the liquid state. Under these conditions SWE could be a viable method for the extraction of nonpolar flavonoids, by varying its temperature-dependent dielectric constant (ε). When the temperature of water increases, its physicochemical properties, in particular its relative ε, change. The ε, representing polarity, decreases as temperature increases (e.g., from ε = 53 at 110 °C to ε = 41 at 150 °C), which is close to that of methanol (ε = 33.6 at 25 °C) and ethanol (ε = 24.5 at 25 °C), which are traditionally used extraction solvents. Thus, subcritical water can be used to extract nonpolar flavonoids [5,10,14]. The extraction reactions in subcritical water depend strongly on temperature. However, extract degradation is not only dependent upon temperature, but also the exposure time (resident time), flow rate and solute chemical structure [15]. Degradation of the extracts or the sample matrix, as well as some technical issues involved with SWE, can also affect the extraction's efficiency.

Several works in the literature indicate that it is possible to separate the orange peel essential oil by supercritical CO_2 extraction (SFE) [16-18], generating a defatted residue in the process. Considering the biorefinery context, that is, the total use of raw material, and the process variables, it is possible to extract flavonoids in this matrix using SWE. In this work, we aimed to determine the optimal conditions for SWE of the flavanones hesperidin and narirutin from OP after supercritical CO_2 extraction, varying the extraction temperature (110 – 150 °C) and water flow rate (10 – 30 mL/min), and to compare the results with conventional extraction techniques.

4.2. Material and methods

4.2.1. Chemicals

The extraction solvents used in this work were distilled water and ethanol (Synth, São Paulo, Brazil). For flavanones analysis, water was obtained from a Purelab Flex 3 water purification system (Elga, UK). HPLC grade acetonitrile was obtained from JT Baker, USA and phosphoric acid from Synth. Standards of hesperidin and narirutin were purchased from Sigma-Aldrich (São Paulo, Brazil). Acetone (96%) supplied by Sigma was used for the determination of extractives. Sulfuric acid (96%), acetic acid, HPLC grade sodium chlorite (99%) and sodium hydroxide were purchased from Wako Pure Chem. Ind., Ltd., Osaka, Japan and used for quantification of holocellulose, α-cellulose and lignin content in the defatted orange peel (DOP). For analysis of total pectin, ethanol, sodium decahydrated tetraborate (99.5%), sulfuric acid (96%) and

ethylenediaminetetraacetic acid tetrasodium salt were purchased for Synth (São Paulo, Brazil) and galacturonic acid and carbazol, for Sigma-Aldrich (Sao Paulo, Brazil). For the evaluation of antioxidant capacity *in vitro*, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 6-hydroxy-2,5,7,8-etramethylchromane-2-carboxylic acid (Trolox), 2,2' -azobis(2-methylpropionamidine) dihydrochloride (APPH), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) and fluorescein were purchased from Sigma-Aldrich (São Paulo, Brazil).

4.2.2. Raw material

Orange peel (OP), as a model of juice processing by-product, was supplied by the company CPKelco, Limeira, SP, southeastern Brazil. The residue is named in this work as defatted orange peel (DOP), after SFE of essential oils at 40 °C, 35 MPa and S/F of 32 kg CO_2/kg dry residue. DOP was kept in absence of light at -18 °C in a domestic freezer until the extractions were performed.

4.2.2.1. Sample characterization

Moisture and ash content were measured using the methodology recommended by National Renewable Energy Laboratory, described in the technical report (LAP TP-5100-60956, 510-42618). Protein was determined from total Kjeldhal nitrogen – TKN (4500NORG B,C) using a calibration factor of 6.25 (Gnaiger & Bitterlich, 1984). Extractives were determined quantitatively in a Soxhlet apparatus using the following sequence of extraction solvents: acetone and ethanol for 3 and 6 h, respectively [19].

4.2.2.2. Chemical composition of orange peel

Holocellulose, α-cellulose, hemicellulose, and lignin content were measured in extractive-free basis. The holocellulose content was determined as the mass remaining after $NaClO_2$ delignification [20]. The delignified residue (holocellulose) was weighed after drying for 24 h in an oven at 105 °C [21]. Holocellulose (1 g) was then transferred to a flask with 25 mL of 17.5% NaOH aqueous solution and stirred for 40 min at 20 °C. After 5 min, the residue was filtered, and 40 mL of a 10% acetic acid aqueous solution was added to the residue. The residue was filtered again and washed with 1 L of boiling water. The α-cellulose residue was filtered, dried at 105 °C for 48 h in vacuum, and weighed. The amount of hemicellulose was calculated by subtracting the amount of α-cellulose and pectin from holocellulose.

The lignin content in the sample was determined by Klason's method based on acid hydrolysis [22]. This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. The lignin fractionates into acid insoluble material and acid soluble material. The acid soluble lignin content was measured using a UV-Vis spectrophotometer at 240 nm (Hach, modelo DR/4000U, São Paulo, Brazil).

For total pectin determination, a previous sugar-extraction in DOP was perfomed using percolation with 95% ethanol. For the pectin de-esterification, the residue was mixed with Versene solution and the pH was adjusted until 11.5 with 1.0 N NaOH solution, followed by pH adjustment 5–5.5 with acetic acid glacial and pectinase addiction (Pectinase from Aspergillus niger, 1 U/mg; Sigma-Aldrich; St. Louis, USA). After the enzymatic reaction, the assay was made according the carbazole reaction colorimetric method [23], using galacturonic acid as standard. The absorbance was measured at 530 nm using a microplate reader (Synergy HT, Biotek, Winooski, VT, USA), with Gen5 2.0 data analysis software spectrophotometer. In all cases, the composition of the raw material was measured in three independent experiments, and reported as mean ± standard deviation.

4.2.3. Subcritical water extraction

4.2.3.1. Extraction system

A schematic diagram of the semi-continuous SWE unit is shown in Fig. 1 The unit was assembled to extract and hydrolyze lignocellulosic biomasses using subcritical water. The apparatus consists of one extractor (with an internal volume of 110 mL). The maximum working conditions of extractor are 400 °C and 42 MPa. The extractor is constructed of 316 stainless-steel and capped with gasket filters (average pore size 300 µm) to prevent retain sample particles from flowing out. The extractor is heated by an electric heating system type jacket (1500 W) and insulated by ceramic fiber. A liquid high pressure pump (Dual piston pump, model Prep 36 Pump, Apple Valley, MN, USA) was used to deliver water to the extractor. The pressure in the system was controlled by a micrometer valve (Autoclave Engineers, 10VRMM2812, Erie, USA) and measured by manometer. The extraction temperature was monitored by thermocouple (type K) outlet of the extractor. The hot effluent fluid exiting the extractor was cooled to a temperature below 30 °C in a stainless steel shell-and-tube heat exchanger coupled to a thermostatic bath (Marconi, model MA-184, Piracicaba, SP, Brazil) operating at 5

°C (using ethylene glycol 50% as the coolant). The rapid cooling assures that the bioactive compounds are not degraded after extraction. The liquid product was collected after extraction and analyzed to quantify concentrations of sugars, bioactive compounds, and antioxidant activity.

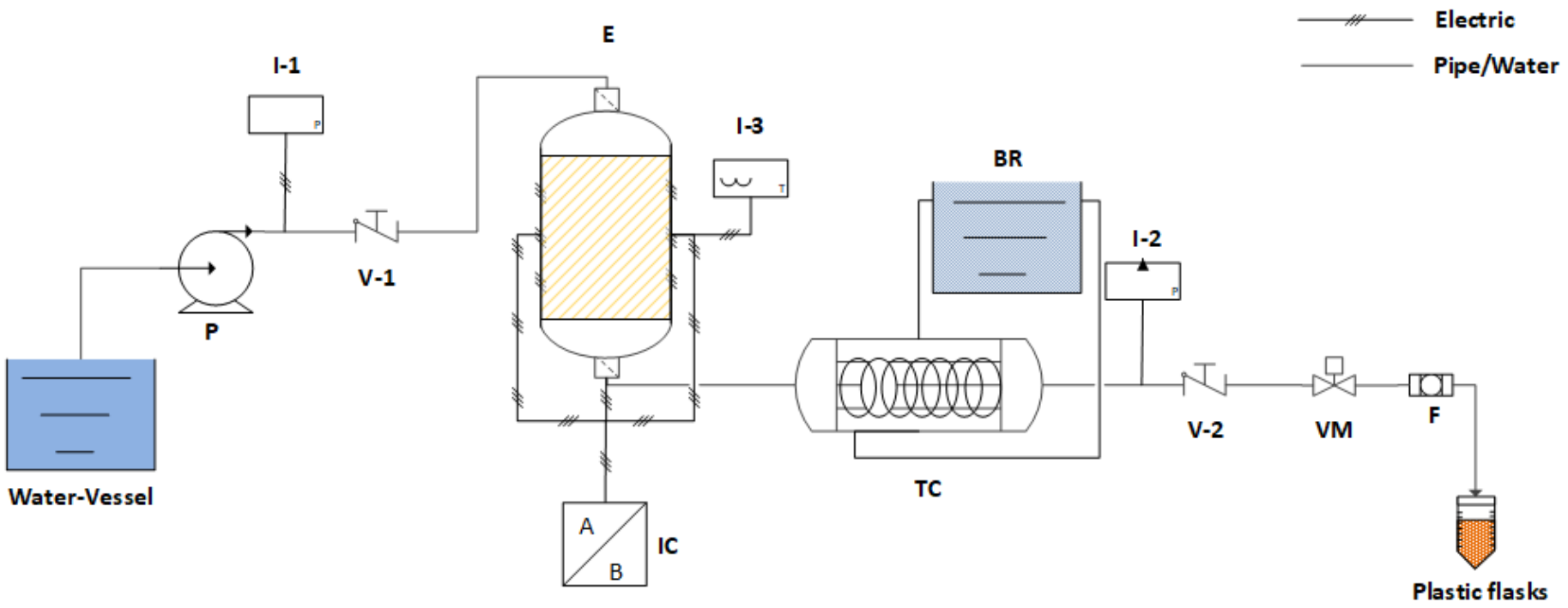


Fig. 1 Schematic diagram of the semi-continuous unit (Lachos-Perez et al., 2016); V-1 to V-2: block valves; VM: micrometer valve; F: filter; BR: refrigeration bath; P: HPLC pump; TC: Heat exchanger; I-1, I-2 : pressure indicators; I-3: temperature indicators; IC: temperature controller;

4.2.3.2. Extraction procedure

Subcritical water extraction (SWE) experiments of defatted orange peel (DOP) were performed in a semi-continuous flow extractor (i.e. batch for the solid and continuous for the liquid). In each experiment, 5.0 grams of DOP were loaded into the extractor. Extraction experiments were performed using two parameters varied at three levels. Temperature was evaluated at 110, 130 and 150 °C and water flow rate at 10, 20 and 30 mL/min. Pressure was kept constant at 10 MPa. Unlike SFE, in which the main operational parameter influencing extraction efficiency is density as a function of pressure and temperature, the most important operational parameters in SWE are temperature and solvent flow rate. Pressure is applied to maintain water in its liquid state [24,25]. Temperature levels were selected to be greater than the normal boiling point and lower than the critical temperature of water (374 °C). The solvent and feed (S/F) mass ratio was 24 kg water/kg DOP. The S/F ratio was selected after preliminary measurements of total phenolic yields at 170 °C and 30 mL/min. when it was verified that all the easily accessible solute had been extracted by convection.

4.2.4. Low pressure extraction methods

In this work, extractions of DOP were conducted using Soxhlet extraction, conventional extraction by solvent, and ultrasonic extraction

4.2.4.1. Soxhlet extraction

The Soxhlet method was performed using ethanol as solvent. In each extraction (performed in triplicates), about 5.0 g of DOP were packed in filter paper and inserted in the extractor. Solvent (100 mL) was added and the system was heated until boiling. Reflux was kept for 6 h, then the recovered extract was weighed and stored under freezing (-18 °C) for further analyses [26].

4.2.4.2. Conventional extraction by solvent

Five grams of DOP powder were extracted with 50 mL of 80% ethanol. The mixture was shaken at 200 rpm in the dark, using a mechanical stirrer for 2 hours at 35 °C [27].

4.2.4.3. Ultrasound-assisted extraction

The ultrasound-assisted extraction consists of transferring 5.0 g of DOP into 50 mL of 80% ethanol. The mixture was then subjected to an ultrasonic probe and

processed ultrasonic power for two hours at 35 °C. The ultrasonic system (Unique Group, model DES500, Campinas, Brazil) is composed of a generator unit of 800 W with variable output power control operating at frequency of 20 kHz and a ultrasonic horn of 13 mm. The mixture resulting from the extraction process was separated by filtration under vacuum and afterwards filtered through a nylon syringe filter (0.22 µm, 25 mm, Analytica, São Paulo, Brazil) and stored at -18 °C until analysis.

4.2.5. Extract evaluation

4.2.5.1. Global yield (X_0)

The extraction global yield (X_0) is defined as the mass ratio between dried extract (m_{ext}) and dry sample (F), as shown in Equation 1. To determine m_{ext}, 5.0 mL of extract was dried at 60 °C in stove (Fanem, 320-SE, São Paulo, Brazil) until constant weight.

$$X_0=\frac{m_{ext}}{F}x100 \qquad \text{Equation 1}$$

4.2.5.2. Reducing sugars

The reducing sugar (RS) content of the extract was determined using the colorimetric method proposed by Somogyi and modified by Nelson [28,29]. After the coloring reaction, sample absorbance at 540 nm was measured using a spectrophotometer (Hach, model DR/4000U, São Paulo, Brazil).. The calibration line was y = 0,5094x - 0,0134 for UV spectrophotometer acquired using standard solution of glucose solution with known concentrations, varied in the range of 0.05–0.45 g/L. A linear equation with R^2 of 0.9923 was established and RS expressed as g of glucose equivalents per g DOP.

4.2.5.3. Total phenolic content

Total phenolic content was determined using the *Folin–Ciocalteau* method as described by Singleton, Orthofer and Lamuela-Raventós [30], with some modifications. Each extract was diluted in distilled water. Triplicates of 0.5 mL diluted sample and 0.5 mL Folin– Ciocalteu reagent were mixed and incubated at dark in room temperature for 3 min. Then, 0.5 mL of saturated sodium carbonate solution and 3.5 mL distilled water were added and the mixture was kept in dark for 2 h at room temperature. The absorbance was read at 725 nm in a spectrophotometer (Hach, model DR/4000U, Colorado, USA) Samples and gallic acid standard curve were read

at 725 nm. The calibration line was y = 0,0148x - 0,0595 for UV spectrophotometer acquired using standard solution of gallic acid solution with known concentrations, varied in the range of 15 – 55 µg/mL. A linear equation with R^2 of 0.9973 was established and total phenolic content expressed as mg of GAE per g DOP.

4.2.5.4. Analysis of flavanones by HPLC

The HPLC analysis of the flavanones present in the sample was performed in the Extract-US system (Patent pending – FAPESP 2013/04304-4). The system is composed of a HPLC pump (PU-2080 – Jasco, Japan), solvent mixer (MX-2080 – Jasco), solvent degasser (DG 980-50 – Jasco), UV detector (UV-2075 - Jasco), 5 x 2 position 10 port valves (Waters, USA), block valves (Autoclave Engineers) and backpressure regulator (Tescom). The software used for data acquisition and processing was ChromNAV (Jasco) while configuration of the system was performed in the Extract-US software (Kalatec, São Paulo, Brazil). The separation of compounds present in the samples was based on a previously developed [31] method and was carried out on a Kinetex C18 (150 mm, 4.6 mm, 2.7 µm, Phenomenex, USA) column using the following gradient of water (0.1% phosphoric acid – Solvent A) and acetonitrile water (0.1% phosphoric acid – Solvent B): 0 min: 7% B; 3 min: 7% B; 7 min: 13% B; 10 min: 18% B; 20 min: 100% B; 22 min: 100% B; 23 min: 7%B with 5 minutes of equilibration time between runs. Flow-rate was 1.1 mL/min, sample volume was 5 µL and absorbance was monitored at 280 nm. Each analysis was performed in duplicate.

4.2.5.5. Antioxidant capacity

The antioxidant capacity of the extracts obtained from DOP was determined using DPPH scavenging assay, ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC), as follow.

The free radical scavenging capacity of the extracts was determined through the DPPH scavenging method (Brand-Williams, Cuvelier, & Berset, 1995) with some modifications. Each extract was properly diluted in ethanol and triplicates of diluted extract (100 µL) were added to 3.9 mL of DPPH ethanol solution (0.024 mg/mL) and kept in dark for 30 min. Next, the absorbance was measured at 515 nm using a microplate reader (Synergy HT, Biotek, Winooski, VT, USA), with Gen5 2.0 data analysis software spectrophotometer. The Trolox standard curve was built (0.01 to

0.25 mg/mL). Results were expressed in mg Trolox equivalent (TE) per g of dried DOP. The equation for the Trolox calibration curve was Y = −0.00038X+ 0.461 and the correlation coefficient was R^2 = 0.992.

The ferric reducing ability of extracts was determined by the FRAP method based on Benzie and Strain (1996) with some modifications. Each extract was properly diluted in distilled water. The FRAP solution was prepared using 0.3 M acetate buffer (pH 3.4), 10 mM TPTZ in 40 mM HCl solution and 20 mM $FeCl_3$. Triplicates of diluted extract (90 µL) were added to 270 µL water and 2.7 mL of FRAP solution and kept in dark for 30 min at 37 °C. Next, the absorbance was measured at 595 nm using a microplate reader (Synergy HT, Biotek, Winooski, VT, USA), with Gen5 2.0 data analysis software spectrophotometer. The Trolox standard curve was built (0.01 to 0.25 mg/mL). Results were expressed in mg Trolox equivalent (TE) per g of dried DOP. The equation for the Trolox calibration curve was Y = 0.00063X+ 0.0151 and the correlation coefficient was R^2 = 1.

The oxygen radical absorbance capacity (ORAC) was performed according to Ou et al. (2013) with some adaptations. All the extracts or standard (Trolox solution; 750 µmol/L) were diluted with potassium phosphate buffer 75 mM (pH 7.4). The range of standard curve used was 5 µmol/L at 120 µmol/L. As blank, only the potassium phosphate buffer 75 mM was used. In each well of black microplate, 25 µL of diluted sample, standard or blank and 150 µL fluorescein working solution. After, the microplate was incubated in the microplate reader at 37 ºC for 15 min, and subsequently, 25 µL of AAPH solution was added to each well. The kinetics read (fluorescence filters: excitation wavelength: 485 nm and emission wavelength: 520 nm) was performed every minute for 80 min at 37 ºC in the microplate reader (SynergyHT, Biotek, Wionooski, USA), with Gen5 2.0 data analysis software spectrophotometer. The equation for the Trolox calibration curve was Y = 0.298X+ 6.49 and the correlation coefficient was R^2 = 0.991.

4.2.6. Statistical analyses

The results were statistically evaluated by one-way analysis of variance (ANOVA), in which significant differences at level of 5% were analyzed by the Tukey's test. The Pearson's correlation test was performed to obtain correlation values (r) between phenolic compounds and antioxidant capacity. The tests were performed

using the software MINITAB® (Release 16.1.0, Minitab Inc., State College, Pennsylvania, USA).

4.3. Results and discussions

4.3.1. Orange peel defatted characterization

Table 1 presents the complete characterization of DOP. The moisture content (6.64%) is in agreement with that found in literature, which ranges from 7.7 to 10% [32-34]. The measured ash content was around 3.71%, which provides information on the quantity of substances mainly from crude sap. The ashes consist of sulphates, oxalates, carbonates and silicates, with calcium, potassium, magnesium and manganese as the most common counterions [35], consistent with the ash content reported in the literature for orange peel [36,37]. As expected, DOP exhibited the highest ethanol extractives amount (17.07%), this being mainly due to the presence of free sugarsand carotenoids in the sample. Ethanol may extract low-molecular-weight carbohydrates, salts, polyphenols and other water-soluble compounds. Protein (6.89%) appears in amounts that fall within ranges observed by other authors [3,33,38].

4.3.2. Chemical composition

Orange peel generally contains between 75-85% carbohydrate [3,33] and its spongy structure has a high presence of polysaccharides in the form of pectin, cellulose and hemicellulose [39]. Orange peel has smaller proportion of lignin content (18.5%) and high pectin content when compared to other lignocellulosic biomass. Low lignin level makes this vegetable an ideal matrix for fermentation-based products, such as ethanol production. However, the presence of pectin requires either harsh pretreatment or application of enzymes for the release of sugars. Pectin combined with proteins and other polysaccharides form strong skeletal plant tissues [40]. This supports the idea that most protopectin units hydrogen bond to cellulose.

In this work, orange peel collected from Sao Paulo showed a pectin yield of 18.53% on dry matter basis. This percentage is similar compared to that found in literature for orange peel [16,37,41]. Many factors can influence the nutrient content of orange peel, including the fruit source and processing method. As Brazil is a tropical country, fruits require less time to grow and get mature and this shorter maturity time may result in a decreased level of pectin in fruits.

Table 1. Composition of the defatted orange peel

Components	**Value (%)**	**Method**
Moisture	6.64±1.45	NREL/TP-510-42621
	% Dry Matter	
Ash	3.71±0.32	NREL/TP-510-42622
Protein	6.89±0.13	NREL/TP-510-42625
Extractives in Ethanol	17.07±0.24	By Soxhlet extractor
Extractive in acetone	2.08±1.07	By Soxhlet extractor
Hollocelulose	39.17±0.64	Sodium chlorite
α-cellulose	27.14±0.81	Kurschner
Hemicellulose	14.88+1.00	By difference
Lignin Soluble	6.64±0.52	NREL/TP-510-42618
Lignin Insoluble	11.86±1.93	NREL/TP-510-42618
Pectin	18.50±2.45	Bitter & Muir, 1962

4.3.3. Influence of process variables on the Global Yield (X_0)

The global yields, reducing sugars and total phenolic DOP extracts obtained by low pressure extraction methods and SWE at different conditions are presented on Table 2. The highest SWE global yields were achieved at 150 °C, although differences were not significant in some cases. The increase of temperature leads to higher X_0 for all flow rates. High temperatures should favor the break of van der Waals, hydrogen and dipole–dipole molecular forces between vegetable matrix and extractable compounds, thus reducing the required activation energy for their desorption. Certainly, surface tension and viscosity decrease when temperature is increased, while the diffusion rate increases, enhancing their penetration into the matrix and speeding up the dissolution of the extract. Therefore, the mass transfer rate is increased, resulting in high global yields [42]. It can be verified that the X_0 obtained by low pressure extraction methods were lower than those obtained by SWE in all operational conditions. The difference between SWE and Soxhlet technics can be explained by the solvent recycle and solvent/solute interactions of Soxhlet, which contribute to enhance the solubility of most compounds of the sample. For Shaker and ultrasound techniques, the difference is possibly due to the higher pressure used in SWE. These results suggest that high pressure helps transporting the solvent into the pores of the vegetable matrix and enhances the solubility of the target compounds [43].

The analyses of variance of the effects of temperature and water flow rate on the global yield showed that both factors and their interaction were significant. The model (F-value = 26.6) corresponding to lowest p-value of < 0.0001 shows the reliability of the model fitting with global yield (X_0). Higher F-value of temperature has the most influential effects on global yield (X_0), confirming what literature reports. Regarding the global yields of SWE, the effect of flow rate was significant and the Tukey's test showed that these values are significantly different ($p < 0.05$). Indeed, the best flow rate must be chosen, considering two main factors including extraction time and extract concentration. In conclusion, shorter extraction time and more concentrated extracts are desirable.

Table 2. Global yields, reducing sugars and total phenolics of extracts from defatted orange peel obtained by low pressure extraction methods and subcritical water extraction (SWE) at different extraction conditions.

Method	Water Flow rate (mL/min)	T (°C)	X_0 (%)	RS (g glucose equivalents/g DOP)	TPC (mg GAE /g DOP)
SWE	10	110	4.44±0.19^{cde}	0.054±0.006^{b}	4,22±1.84^{e}
		130	4.91±0.6^{cd}	0.055±0.001^{b}	12.19±2.00^{bc}
		150	10.63±0.55^{a}	0.096±0.013^{a}	31.70±1.46^{a}
SWE	20	110	5.83±0.6^{bc}	0.060±0.002^{ab}	7.27±1.03^{cde}
		130	6.14 ±0.24^{bc}	0.087±0.020^{ab}	11.88±1.59^{bcd}
		150	9.92±1^{a}	0.093±0.007^{a}	28.53±0.37^{a}
SWE	30	110	5.02±0.43^{cd}	0.048±0.001^{b}	8.76±0.623^{bcde}
		130	5.06±0.05^{bcd}	0.069±0.001^{ab}	13.15±1.78^{bc}
		150	6.98±0.19^{b}	0.071±0.003^{ab}	14.26±3.72^{b}
Soxhlet	-	70	2.91±0.38^{e}	0.076±0.005^{ab}	7.75±0.99^{cde}
Shaker	-	35	2.75±0.09^{e}	0.073±0.001^{ab}	4.42±0.29^{e}
Ultrasound	-	35	3.15±0.05^{de}	0.076±0.005^{ab}	5.83±0.16^{de}

Results are expressed as mean ± standard deviation of the analysis performed in duplicate. Different letters in the same column indicate that the means differ significantly by Tukey test ($p \leq 0.05$). X0(Global yield), RS (Reducing sugars), TPC (Total phenolics compounds).

4.3.4. Reducing sugars yield

During the extraction procedure, some components present in the sample can be released and may interact, even forming new compounds. At high temperatures different chemical reactions take place in organic medium, such as Maillard reactions, which could be promoted under SW, especially under acidic conditions. Many Maillard reaction products are strongly colored, causing browning of the reaction mixture [24,44,45]. The color of the extracts apparently derived both from the extracted compounds and formed Maillard reaction products. Browning reactions increase rapidly with temperature [46] and Cvetanović, Švarc-Gajić, Gašić, Tešić, Zengin, Zeković and Đurović [24] observed that the velocity of these reactions is the highest at temperatures between 140 and 160 °C. Due to the high content of carbohydrates noticed in DOP (Table 2), carbohydrates reacts with hydronium and hydroxide ions, producing sugars. The RS content of the extracts obtained from DOP was determined by colorimetric method, which ranged from 0.048 g RS/g of DOP to 0.096 g RS/g DOP.

The process yield for reducing sugars increased with temperature (Table 2). SWE was used to extract bioactive compounds, however the RS content increased at higher processing temperatures due to the increase in the ionization constant of water (Kw) [47]. This result explains why the Maillard reaction product level of DOP extracts obtained using SWE generally increased at higher extraction temperatures. An, Bagnell, Cablewski, Strauss and Trainor [48] argued that high temperatures are needed to break the glycoside bonds, although monosaccharides and oligosaccharides are more exposed to decomposition at moderate conditions. The temperature increase promotes the reducing sugars production, indeed higher sugar yields could be achieved if the formed sugars were removed from the reaction medium as soon as they were produced, thus reducing their degradation.

It is also important to mention that glycoside flavonoids, such as flavanones, in an organic compound have a sugar portion of monosaccharide. Therefore, the glucoside (including glucose) flavonoids tend to be well extracted at lower temperature than the aglycone flavonoids, by temperature-dependent ε of water [10]. The presence of disaccharides, such as hesperidin and narirutin from oranges peel, tends to make them more soluble in polar substances, so they can be extracted under more optimal extraction conditions than less-polar aglycones.

4.3.5. Total phenolic compounds (TPC)

Table 2 shows data for the extraction of TPC using SWE at 10 MPa and 110 to 150 °C with water flow rates of 10 to 30 mL/min. SWE resulted in higher amounts of phenolics (31.70 ± 1.46 mg AG/g DOP) than the conventional solvent extraction methods. From the data presented on Table 2, it can be observed that the TPC extracted decreased with increasing flow rate. This trend was maintained for all the extracts obtained at different temperatures, although even the lowest SWE yields (30 mL/min) were higher than those of the low pressure extraction methods. These data will be considered in the next section, since this kind of compounds have strong influence on the antioxidant capacity of the extracts. Plaza, Amigo-Benavent, del Castillo, Ibáñez and Herrero [44] detailed that TPC may attune the occurrence and intensity of Maillard and caramelization reactions, thus influencing the final bioactivity of the extracts.

According to literature [15,25,27,49], temperature is one of the most important parameters for the extraction of TPC by SWE. For all flow rates employed, TPC increased with temperature. As well as with global yield, this may happen because at high temperatures the solubility of phenolics increases, and the breaking of chemical bonds, mass transfer rates and molecular diffusion is enhanced. Likewise, surface tension and viscosity of the solvent decrease, promoting the contact between solvent and solutes [50,51] . Analogous behaviors are related in diverse works, showing that from 100 to 200 °C there is a growth on the extraction of phenolic compounds in SWE [24,44,47,52-58].

Solvent flow rate is a parameter that may be adjusted [25,59]. Although, to the best of our knowledge, there are few documented reports that optimize flow rate, the crucial role it may carry out when extracting phenolic compound was emphasized by Srinivas, King, Howard and Monrad [60]. The authors observed that the optimization of flow rate is of major concern in order to effectively dissolve a solute such as flavonoids in SWE.

On the other hand, lignin is a complex high molecular-weight compound made up of three phenylpropane derivatives *p*-coumaryl, coniferyl, and sinapyl alcohols monomers polymerized by a radical coupling process that links them by carbon–carbon (C-C) and ether bonds (C-O-C). The presence of strong C-C and C-O-C bonds in lignin affects its susceptibility to chemical disruption [61]. In lignocellulosic

biomasses, lignin is covalently bonded to hemicelluloses via ether and ester-linked phenolic compounds, such as ferulic acid [62]. SWE induces breaking of such bonds, increasing TPC content in the extracts. As shown on Table 2, increasing temperature resulted in increased TPC content of 5 fold, from 4.22 mg GA/g DOP at 110 °C/10 mL/min to 31.70 mg GA/g DOP at 150 °C/10 mL/min, which implies that higher temperatures enhance breaking of strong interactions between carbohydrates and lignin.

4.3.6. Individual flavanones

Flavanones containing hesperidin and narirutin constitute the bulk of the flavonoids that appear naturally in citrus peel. Indeed, hesperidin and narirutin were the most abundant flavanones present in the extracts. The chromatographic peaks of the extracts were confirmed by comparing their retention times with those of the commercial standard compounds. The calibration curves indicated a highly linear regression of the peak areas versus compound concentrations (R^2 = 0.99 for hesperidin, data not shown, R^2 = 1 for narirutin, data not shown). Chromatogram of standards, and SWE extracts showed specific retention time (RT = 14.63 min for narirutin, and RT = 15.52 min for hesperidin), respectively.

The mean hesperidin and narirutin yields quantified by HPLC for SWE and low pressure methods extracts, as well as the sum of both flavanones, are presented on Table 3. The flavanone yields are reported in terms of mass of dried sample and also of extract. An example of chromatogram obtained by HPLC at 280 nm is shown in Fig 2. The ANOVA analysis for the yields in terms of dried sample show that, for both flavanones, the influence of temperature, flow rate and their interaction are significant ($p < 0.05$) in the studied range. Anurukvorakun [63] studied the extraction of flavanones from citrus fruit and also found that temperature and solvent flow rate affect the extraction process. The statistical analysis for the yields in terms of extract did not lead to conclusive results, because for hesperidin they showed effect in temperature and for narirutin they did not show significant effect, and the behavior was not completely described from the regression analysis. However, this data are shown on Table 3 to support the discussion about the purity of the extracts obtained in each condition.

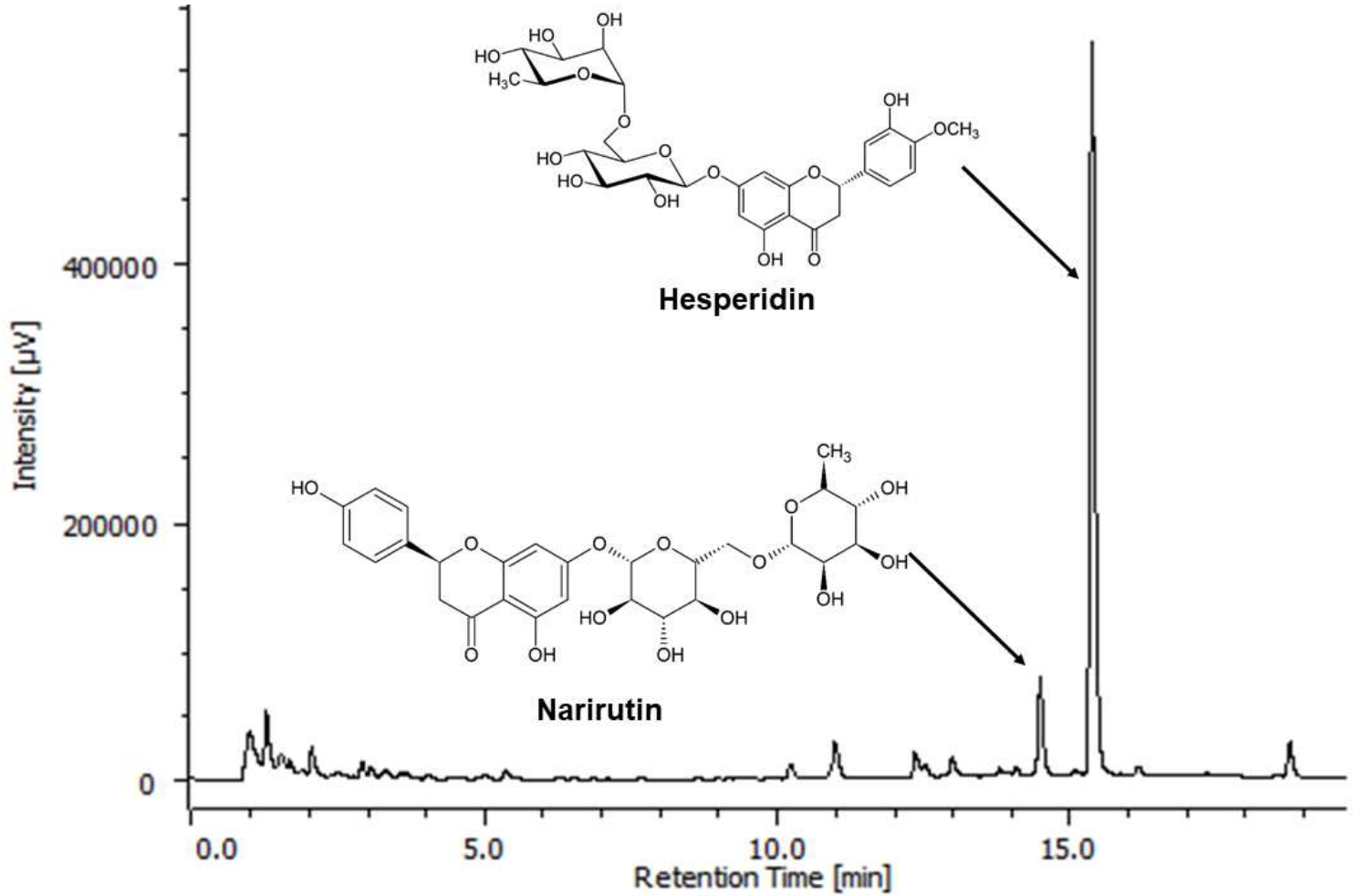


Fig. 2 Typical chromatogram of OPD extracts obtained by SWE (extracts obtained at 150°C and 10 mL/min).

Flavanones such as narirutin, and hesperidin have a nonpolar C_6-C_3-C_6 structure. Nonetheless, SWE may be a viable alternative method to extract nonpolar compounds by changing the temperature-dependence ε of water [5,10]. As shown on Table 2, increasing temperature can not only increase the solubility of flavanones, but also reduce the polarity of water, with both of these changes increasing the extraction efficiency of hesperidin and narirutin, supporting the results of this work. The ε is the main indicator of the polarity of a solvent. The ε of water at 150 °C (45–47) is equal to that of DMSO at 25 °C. As temperature increases the ε of water decreases and less-polar compounds become more soluble [64]. The concentration of hesperidin in the extract was higher than that of narirutin in all evaluated conditions, consistent with the literature data from citrus peel [5,65,66]. Table 3 shows that the hesperidin yield in terms of dried extract by SWE at 150 °C was 9.4-, 10.1-, and 14.3-fold higher than those obtained in terms of mass of dried sample using SWE at 150 °C, 10 mL/min, 20 mL/min, and 30 mL/min, respectively, whereas narirutin showed similar behavior. Also, the sum of hesperidin and narirutin yields at 150 °C and 10 mL/min achieved 210 mg of total flavanones g extract^{-1}, almost 20% of the extract, leading to the purest extracts in flavanones.

On the other hand, increase of flow rate resulted in the increase of superficial velocity and thus quicker mass transfer, and as expected, the flavanone yields decreased (Table 3). The main drawback of using higher flow rates is increasing the extract volume and, therefore, reducing the concentration of the final extract. In practice, the best flow rate must be selected considering two important factors, extraction time and extract concentration [15,63,67]. It is clear that shorter extraction time and more concentrated extracts are desirable. Besides, low flow rates (1-10 mL/min) are usually applied in SWE [62,68-71], in accordance with this work, since our best yield was obtained with the lowest flow rate (10 mL/min). However, high flow rates could mainly enhance the extraction potential, since the total volume of water is increased and decreases the residence time, which prevents the formation of degradation products [42,52,72]. The extraction time and flow rate in SWE require optimization to complete the extraction.

Finally, flavanone (hesperidin and narirutin) yields in SWE were compared with low pressure extraction methods, such as Soxhlet extraction, conventional extraction and ultrasound-assisted extraction using ethanol as solvent. Table 3 shows

that the hesperidin yield by SWE was more than 3.3-, 1.2-fold higher than those obtained by conventional extraction, and ultrasound-assisted extraction, respectively. However for narirutin the best yields were achieved in low pressure extraction methods, which may be explained by the long extraction times of Soxhlet (6 h), conventional extraction (1 h) and ultrasound (1 h), indicating that those methods are more selective for narirutin. Accordingly, further studies are required to evaluate the applicability of SWE, based on the structure and characteristic of various flavonoids. As discussed previously, although the use of ethanol or methanol is frequent in conventional extractions, their use is limited by long extraction time, toxic solvent residue and strict legal statutes.

Table 3. Mean hesperidin and narirutin yields for SWE and low pressure extracts from DOP.

Method	Water Flow rate (mL/min)	T (°C)	Hesperidin		Narirutin		Total Flavonoids	
			mg/g DOP	mg/g extract	mg/g DOP	mg/g extract	mg/g DOP	mg/g extract
SWE	10	110	4.84±1.42^{bc}	109.77±0.21 ^{abcd}	0.87±0.06^{d}	19.68±2.24^{cd}	5.71±1.48	129.45±2.46
		130	7.35±0.56^{b}	152.26±0.27^{abcd}	0.97±0.04^{d}	20.09±3.88^{cd}	8.32±0.60	172.35±4.15
		150	20.00±0.66^{a}	188.74±0.51^{ab}	2.33±0.01^{b}	21.98±1.39^{cd}	22.34±0.67	210.73±1.90
SWE	20	110	6.43±2.10^{bc}	108.91±0.32 ^{abcd}	1.08±0.33^{d}	18.24±3.38^{d}	7.50±2.43	127.15±3.70
		130	7.99±1.44^{b}	130.66±0.30 ^{abcd}	1.16±0.08^{d}	18.91±2.26^{cd}	9.14±1.52	149.57±2.56
		150	18.03±0.62^{a}	182.65±0.54^{abc}	1.81±0.06^{c}	18.31±1.57^{d}	19.84±0.68	200.96±2.11
SWE	30	110	4.31±0.92^{bc}	85.33±0.27^{bcd}	0.90±0.01^{d}	18.11±1.97^{d}	5.21±0.92	103.44±2.24
		130	6.52±0.08^{bc}	128.79±0.25 ^{abcd}	1.07±0.03^{d}	21.15±0.94^{cd}	7.59±0.11	149.95±0.69
		150	8.00±1.07^{b}	114.52±0.34 ^{abcd}	1.13±0.09^{d}	16.14±0.79^{d}	9.13±1.16	130.66±1.13
Soxhlet	-	70	7.28±1.30^{bc}	232.36±30.17^{a}	0.98±0.15^{d}	33.56±0.90^{b}	8.26±1.45	265.92±31.07
shaker	-	35	1.56±0.10^{c}	57.40±1.72^{d}	0.73±0.02^{d}	26.81±0.02^{bc}	2.29±0.12	84.21±1.74
Ultrasound	-	35	3.00±0.04^{bc}	94.98±2.77 ^{abcd}	2.85±0.03^{a}	90.51±2.65^{a}	5.85±0.07	185.50±5.43

Results are expressed as mean ± standard deviation of the analysis performed in duplicate. Different letters in the same column indicate that the means differ significantly by Tukey test ($p \leq 0.05$).

4.3.7. Antioxidant Capacity (AC)

Flavanones present higher AC in a hydrophilic environment [73]. In a lipophilic environment, for example using CO_2 supercritical [3], some flavanones (isosakuranetin, hesperetin, neohesperidin) showed a reduced AC while others (narirutin, naringenin, neoeriocitrin, naringin, eriodictyol) even become pro-oxidant [74]. Several methods have been developed to evaluate the AC of vegetable matrices. Single assays cannot fully evaluate the AC of every component. Different methods assess the AC using different radicals and target molecules [75]. There are different chemical methods reported for measuring AC. These methods are mainly classified into two types. One is the assay based on hydrogen atom transfer, which includes the ORAC assay, and the other is based on electron transfer, which includes DPPH, ABTS, superoxide dismutase and FRAP [76,77]. In this work the antioxidant capacity was evaluated using three different chemical methods, DPPH, FRAP, and ORAC assays, whose results are shown on Table 4.

Extracts obtained by SWE showed AC significantly higher than those extracted at low pressure, and most of them presented statistical difference. This difference may be explained by the long extraction time, for example (6 h) of Soxhlet, Shaker (1 h) and ultrasound (1 h) extraction, in which the extract was kept in contact with the vegetable at the operating conditions. Moreover, the extracts at low pressure may have lower concentration of antioxidant phytochemicals responsible for the free radicals scavenging, since the obtained yields (2.91%; 2.75%; 3.15%) indicate that Soxhlet, Shaker and Ultrasound extraction, respectively, are less selective.

The ORAC, FRAP and DPPH values of extracts obtained by SWE at 150 °C showed the higher yields at all employed flow rates. The values increased remarkably with extraction temperatures (Table 4). The highest values (16.26 ± 0.97, 73.27 ± 11.48 and 319.40 ± 10.85 g TE/g of raw material) of DPPH, FRAP, and ORAC, respectively, were observed at 150 °C/20 mL/min, 150 °C/10 mL/min, and 150 °C/20 mL/min, respectively. The found DPPH, FRAP, ORAC values are consistent with extracts from citrus peel found in literature [3,66].

On the other hand, the effect of different temperatures on the selectivity of SWE for compounds with antioxidant capacity, such as flavonoids, has been studied previously [64,69,78,79]. Higher temperatures mainly contributed to better antioxidant capacity of SWE extracts in all tested experiments. Temperatures higher than 160 °C

were not included because, according to literature, the main antioxidant constituents of DOP, flavanones (hesperidin and narirutin), start degrading [5,10,65]. Structure, position, occurrence and number of sugar fractions in flavonoids (flavonoids glycosides) present a main role in AC. Aglycones are more potent antioxidants than their corresponding glycosides [80].

Table 4. Antioxidant capacities determined by DPPH, FRAP, and ORAC of the extracts from DOP obtained by low-pressure extraction methods and subcritical water extraction (SWE) at different extraction conditions.

Method	Water Flow rate (mL/min)	T (°C)	DPPH (µmol TE/g DOP)	FRAP (µmol TE/g DOP)	ORAC (µmol TE/g DOP)
SWE	10	110	5.50±0.33^{de}	23.83±4.24^{d}	45.57±22.02^{e}
		130	4.45±0.09^{e}	29.34±1.24^{cde}	115.81±25.44^{cd}
		150	10.05±0.09^{b}	73.27±11.48^{a}	227.33±23.24^{b}
SWE	20	110	5.99±0.02^{de}	29.26±0.09^{cde}	147.06±35.10^{cd}
		130	7.20±0.75^{cd}	30.56±1.46^{cde}	119.02±0.89^{cd}
		150	16.26±0.97^{a}	53.93±0.41^{b}	319.40±10.85^{a}
SWE	30	110	4.96±0.25^{de}	24.27±1.31^{d}	92.16±7.58^{de}
		130	5.09±0.09^{de}	25.75±0.30^{d}	111.02±3.67^{cde}
		150	8.70±0.65^{bc}	39.89±2.56^{bce}	161.36±7.22^{bc}
Soxhlet	-	70	10.36±1.12^{b}	29.89±1.67^{cde}	168.72±14.00^{bc}
Shaker	-	35	1.07±0.02^{f}	17.90±0.96^{d}	93.34±8.50^{de}
Ultrasound	-	35	1.07±0.02^{f}	17.90±0.96^{d}	93.34±8.50^{de}

Results are expressed as mean ± standard deviation of the analysis performed in duplicate. Different letters in the same column indicate that the means differ significantly by Tukey test ($p \leq 0.05$).

4.3.8. Pearson correlation

To explore the causes that are responsible for the antioxidant activity of DOP extracts, Pearson correlation between TPC and AC was calculaed. The results

were validated using linear correlation analysis and are shown in Fig. 3. All tests revealed that the four variables showed a high and positive Pearson's coefficients (*r*-value), indicating that the phenolic content is strongly related to the antioxidant capacity. The significant positive correlations (R = 0.730–0.978) were observed between TPC, hesperidin, narirutin and DPPH, FRAP, and ORAC activities of DOP. The highest correlation coefficient, 0.978, was for the correlation between narirutin and FRAP. These results are consistent with Lee, Ko and Chung [47] that reported a correlation coefficient of 0.94 for the correlation between DPPH and the total phenolic content from red ginseng (*Panax ginseng* C.A. Meyer) using subcritical water.

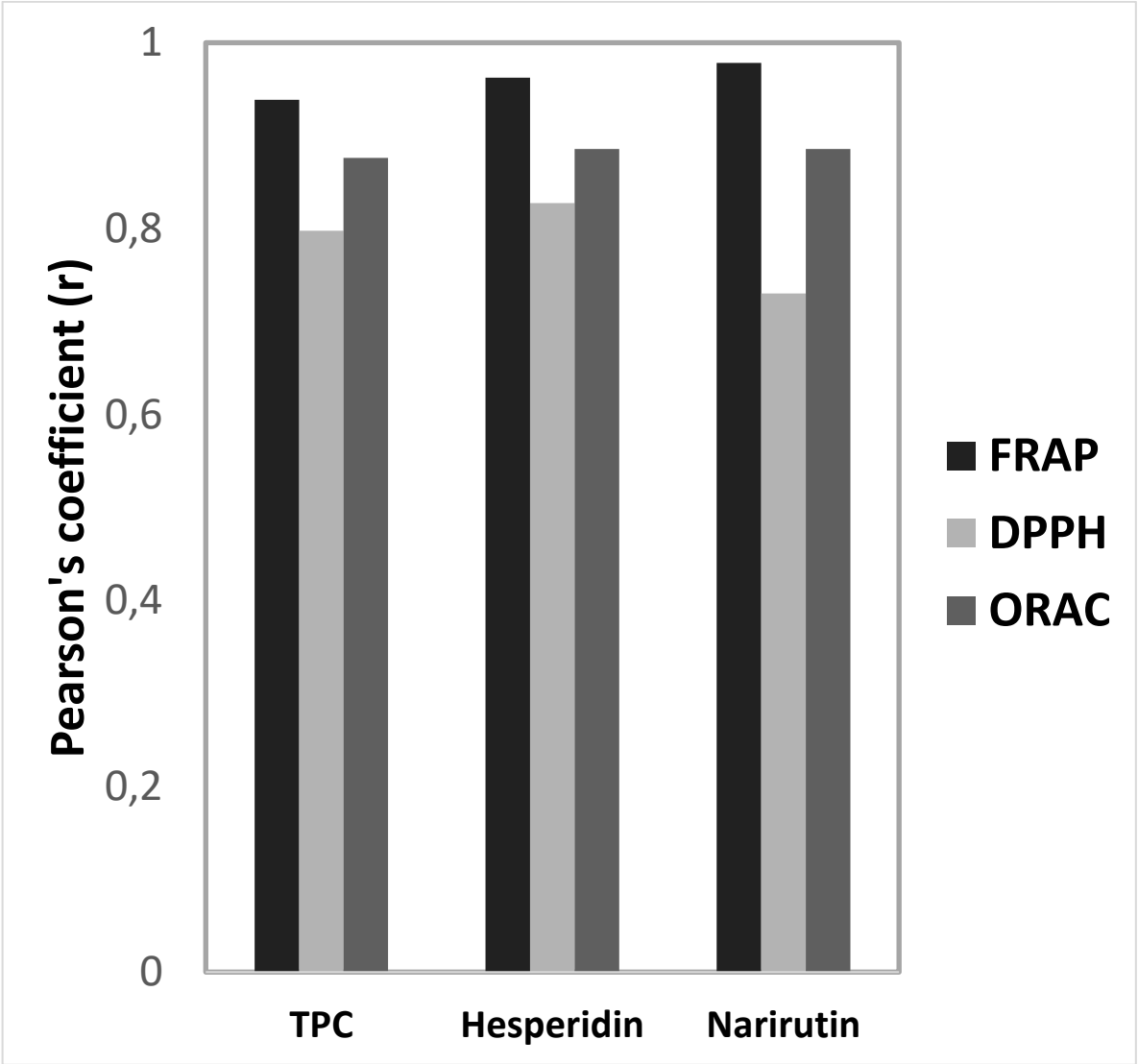


Fig. 3 Pearson coefficient (r) between total phenolic compounds, hesperidin and narirutin of the DOP extracts obtained by SWE at all conditions and their antioxidant capacities determined by DPPH, FRAP and ORAC methods.

4.4. Conclusions

The maximum yields of hesperidin and narirutin were obtained at 150 °C and 10 mL/min. These yields accounted for approximately 21% of the total amount of these flavanones in the extracts, leading to the purest extracts obtained in subcritical water. The findings in this work also demonstrated that, compared to conventional low pressure extraction, SWE is a highly efficient method for the recovery of hesperidin and narirutin from DOP with high antioxidant activity. The extracts obtained by SWE contain phytochemicals that are efficient at donating either protons or electrons to steady free radicals, thus contributing to a relevant high antioxidant capacity *in vitro* of DOP extracts. Thus, the use of SWE in orange peel could be a safe way to recovery phenolic compounds with possible health benefices. However, *in vivo* studies are necessaries to confirm the extracts bioactivities.

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4.6. References

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5. CAPÍTULO 5 – Processo sequencial extração fracionamento

Sequential subcritical water process applied to recover flavanones and sugars from orange peel

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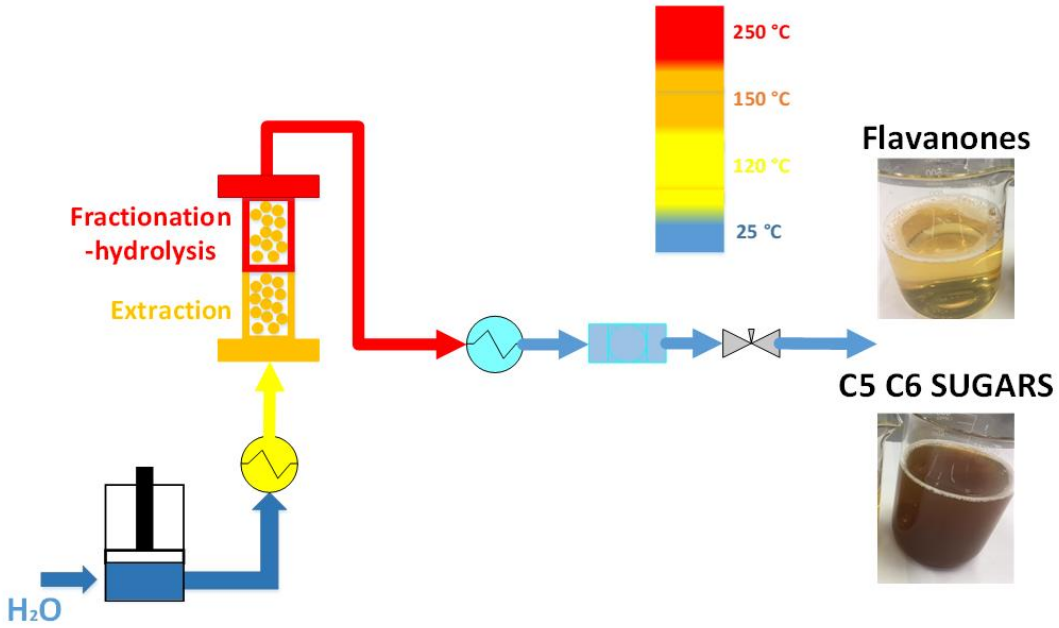
Graphical Abstract



Abstract

The economically viable orange peel (OP) biorefinery can be based on a single process capable of extraction and hydrolysis. The major barrier in OP processing is the lack of an efficient separation technology. To address this issue a unique two-step sequential hydrothermal process technology for the simultaneous fractionation of flavanones and sugars was developed. The first step involves subcritical water extraction of flavanones at 150 °C. In the next step, the residual biomass was subjected to hydrolysis conditions of 200, 225, 250 °C at several different flow rates (10, 20, 30 mL/min). The maximum yields of flavanones (24.4 mg/g OP) were obtained at 150 °C and 10 mL/min. The main products of OP hydrolysis were glucose, xylose, arabinose, and fructose in addition to HMF and furfural as minor byproducts. FT-IR and TGA analysis provided information on the bulk composition of the residual biomass and pectin extracted during hydrolysis temperature above 200 °C.

5.1. Introduction

Rapid population growth will require increased food production, especially in developing countries. In this scenario, a wide variety of biomass types are generated every year, many of which are wastes, which could instead be converted to valuable food, chemical, and energy products. Citrus peels are an especially relevant example of an under-utilized waste resource. In 2017, the world orange production was around 73 million tons. Brazil alone produced 17 million tons, making it one of world's largest orange and orange juice producers (FAOSTAT, 2019).

Fresh fruit goes through several processes to produce fruit juices, with extraction of juice and essential oil as the most important in terms of the product and generation of waste bagasse (FAOSTAT, 2019). The bagasse (about 50% of the fruit) contains peel (60–65%), internal tissues (30–35%) and seeds (0–10%) and has high levels of pectin, proteins, soluble sugars, hemicelluloses and cellulose fibers (Cypriano et al., 2018).

In addition to its primary carbohydrate and protein constituents, bagasse is an attractive source of bioactive compounds, including phenolic flavonoid compounds. Flavonoid concentrations in citrus fruits are greater in the peel and seeds than the pulp, meaning that the bagasse is enriched in flavonoids relative to the juice (Barrales et al., 2015; Cypriano et al., 2018; Lachos-Perez et al., 2018). Flavonoids have received special attention because of their benefits to human health, including antiproliferative, cardioprotective, anti-inflammatory and antioxidant effects (Albuquerque et al., 2019; Chu et al., 2017; Putri et al., 2013). Two flavonoids are especially concentrated in OP: hesperidin and narirutin (Cheigh et al., 2012; Ko et al., 2014). Up to 102.0 thousand tons of hesperidin could be obtained from OP generated each year in Brazil, representing value of USD 2704.5 trillion (Cypriano, 2015). Flavonoids are thermally labile (Ko et al., 2014) and their recovery requires mid-polar solvents, such as ethanol, methanol (Cheigh et al., 2012; Lachos-Perez et al., 2018). Use of these solvents contributes to waste and inefficient processes, since the solvents are recovered only partially and at the cost of increased energy input to the process.

The soluble and insoluble carbohydrate content of OP makes it a potential feedstock that can be used for obtaining high value-added products including bioethanol. OP contains less lignin than other biomass types, which makes it a promising target for enzymatic hydrolysis and fermentation (El Kantar et al., 2018;

Rivas et al., 2008). To maximize the efficiency of the enzymatic step, a pretreatment stage is required to open the lignocellulose matrix and remove hemicellulose. Different pretreatments, such as, steam explosion (Golmohammadi et al., 2018), acid pretreatment (Orange peel waste upstream integrated processing to terpenes, phenolics, pectin and monosaccharides: Optimization approaches), and high voltage electrical discharges pretreatment (El Kantar et al., 2018) have been studied in OP for the production of biofuels. However, these pretreatments can be time and energy intensive and therefore have negative impacts on the environment. “Green technology” and innovative techniques such as subcritical water treatment can be used to reduce the use of hazardous solvents, to contribute to environmental preservation and to decrease the energy consumption.

Water exists in a subcritical state at temperatures between its boiling point and critical point (100 °C at 1 bar and 374.1 °C at 221 bar), at sufficient pressure to keep water in its liquid state. The physicochemical properties of water, in particular its dielectric constant, vary considerably with increasing temperature Specifically, the dielectric constant decreases from its familiar value of 78 at room temperature to approximately 1.0 at the critical point (Lachos-Perez et al., 2017a). As a result, water shifts from being a polar solvent, capable of dissolving salts, to a non-polar one, capable of dissolving various oils. This makes subcritical water a potential multi-purpose extraction solvent (Chakraborty et al., 2012; Miao et al., 2012). When subcritical water extraction is performed at temperatures less than 150 °C, it acts as mid-polar solvent. When subcritical extraction is performed at temperatures greater than 150 °C, it promotes extraction as a nonpolar solvent and hydrolysis of hemicellulose and cellulose to yield simple sugars and sugar oligomers (Wagner & Pruß, 2002).

Based on these considerations, subcritical water has promise for sequential extraction of valuable flavonoids followed by hydrolytic extraction of hemicellulose and cellulose sugars. The challenge is adjusting the treatment temperature to balance the solvent properties of water, biopolymer hydrolysis rates, and flavonoid and sugar degradation rates. Accordingly, this work describes a process for tuning the hydrothermal reaction temperature to satisfy these requirements. Flavanoid extraction was studied at 150 °C, a temperature selected to optimize the solvent properties of water without operating at severe enough conditions to degrade the thermally sensitive

flavonoids. Subsequently, the extracted OP was subjected to flow-through hydrolysis conditions at 200, 225, and 250 °C, temperatures selected for hydrolysis of hemicellulose and exposed cellulose without degradation of the simple sugars. Flow-through conditions were selected to minimize sugar degradation and subsequent char/humin formation. The results of this work provide an engineering baseline for future development of a scaled-up sequential extraction technology.

5.2. Material and methods

5.2.1. Chemicals

For flavanones analysis, water was obtained from a Purelab Flex 3 water purification system (Elga, UK). HPLC grade acetonitrile was obtained from JT Baker, USA and phosphoric acid from Synth. Standards of hesperidin and narirutin were purchased from Sigma-Aldrich (São Paulo, Brazil).

Ethanol (99.5%) and cyclohexane (99%) (Sigma) were used for the determination of extractives. Sulfuric acid (96%), acetic acid, HPLC grade sodium chlorite (99%) and sodium hydroxide were purchased from Wako Pure Chem. Ind., Ltd., Osaka, Japan and used for quantification of holocellulose and lignin content in the OP. For analysis of total pectin, ethanol, sodium decahydrated tetraborate (99.5%), sulfuric acid (96%) and ethylenediaminetetraacetic acid tetrasodium salt were purchased for Synth (São Paulo, Brazil) and galacturonic acid and carbazol, for Sigma-Aldrich (Sao Paulo, Brazil). For the evaluation of antioxidant capacity *in vitro*, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 6-hydroxy-2,5,7,8-etramethylchromane-2-carboxylic acid (Trolox), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (APPH), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) and fluorescein were purchased from Sigma-Aldrich (São Paulo, Brazil).

Chemical standards used to calibrate the high performance liquid chromatograph (HPLC) were: glucose (>99%), fructose (>99%), arabinose (>99%), and xylose (>99%). All standards were purchased from Sigma and used without further purification. Type I water was obtained from an Elga Purelab Flex 3 sytem (Veolia Water, Marlow, UK). HPLC grade acetonitrile was obtained from J.P. Baker (Darmstadt, Germany) and phosphoric acid (85% P.A.) was obtained from Ecibra (São Paulo, Brazil).

5.2.2. Raw material

OP was supplied by CPKelco located in Limeira, SP, Southeastern Brazil. OP was ground (batches of 10 g in 20 s) in a knife mill (Marconi, model MA 340, Brazil) coupled to an induction motor operating at 3800 rpm, and separated by sieving using granutest sieves with a mesh of 16, 24, 32, 48, 80 and 100 Tyler series. The final mean diameter was 303 µm.

5.2.2.1. Elemental and proximate analysis of orange peel

Moisture and ash content were measured using the methodology recommended by National Renewable Energy Laboratory, described in the technical report (LAP TP-5100-60956, 510-42618). Extractives were determined quantitatively in a Soxhlet apparatus using the following sequence of extraction solvents: acetone and ethanol for 3 and 6 h, respectively (Szczerbowski et al., 2014). Protein was determined from the mass fraction of atomic nitrogen after applying a calibration factor (6.25) recommended by Gnaiger and Bitterlich (1984). Elemental content was determined by CHN elemental analysis using an Elemental Analyzer Flash model 2000 (Thermo Fisher Scientific Inc, Delft, Holanda).

5.2.2.2. Chemical composition of orange peel

Holocellulose and lignin content were measured on an extractive-free basis according the methodology proposed by Wise et al. (1946). In brief the holocellulose content was determined as the mass remaining after $NaClO_2$ delignification. The delignified residue (holocellulose) was weighed after drying for 24 h in an oven at 105 °C (Teramoto et al., 2009). Holocellulose (1 g) was then transferred to a flask with 25 mL of 17.5% NaOH aqueous solution and stirred for 40 min at 20 °C. After 5 min, the residue was filtered, and 40 mL of a 10% acetic acid aqueous solution was added to the residue. The residue was filtered again and washed with 1 L of boiling water. The lignin content in the sample was determined by Klason's method based on acid hydrolysis (Sluiter et al., 2008). This procedure uses a two-step acid hydrolysis to fractionate the biomass into quantifiable forms. The lignin fractionates into acid insoluble material and acid soluble material. The acid soluble lignin content was measured using a UV-Vis spectrophotometer at 240 nm (Hach, modelo DR/4000U, São Paulo, Brazil).

For total pectin determination, a previous sugar-extraction in DOP was performed using percolation with 95% ethanol. For the pectin de-esterification, the residue was mixed with Versene solution and the pH was adjusted until 11.5 with 1.0 N NaOH solution, followed by pH adjustment 5–5.5 with acetic acid glacial and pectinase addiction (Pectinase from Aspergillus niger, 1 U/mg; Sigma-Aldrich; St. Louis, USA). After the enzymatic reaction, an assay was performed based on the carbazole reaction colorimetric method (Bitter & Muir, 1962), using galacturonic acid as standard. The absorbance was measured at 530 nm using a microplate reader (Synergy HT, Biotek, Winooski, VT, USA), with Gen5 2.0 data analysis software. In all cases, the composition of the raw material was measured in three independent experiments, and reported as mean ± standard deviation.

5.2.3. Sequential subcritical water process

5.2.3.1. Extraction-Fractionation system

Extraction-fractionation hydrothermal experiments of OP were conducted in a semi-continuous flow reactor (i.e. batch for the solid and continuous for the liquid) described previously (Lachos-Perez et al., 2017b; Lachos-Perez et al., 2018). In each experiment, 5.0 grams of OP were loaded into the reactor. The subcritical water extraction conditions were chosen in accordance with results obtained in previous work, in which the best conditions to recover two distinct types of compounds (hesperidin and narirutin) using subcritical water were identified (Lachos-Perez et al., 2018). After recovering flavanone-rich extracts, the reactor was then heated to three different temperatures sequentially: 200, 225, and then 250 °C. Water flow rates were evaluated at 10, 20, and 30 mL/min (Table 2). The liquid product was collected after reaction and analyzed to quantify concentrations of sugars, bioactive compounds, antioxidant activity, and several major degradation products. The liquors were filtered and stored at 4 °C prior to analysis. The solids remaining in the reactor after fractionation were collected in glass flasks, weighed, and stored at −18 °C The collected biomass was dried at 105 °C for 24 h. Solid products were analyzed using Fourier Transform Infrared (FT-IR) spectroscopy and Thermogravimetric Analysis (TGA, details below).

5.2.4. Reducing sugars determination

Reducing sugars (RS) and total reducing sugar (TRS) content of the hydrolyzate was determined using the colorimetric method described by Somogyi and modified by Nelson (Miller, 1959; Nelson, 1944). The samples were subjected to acid hydrolysis conditions to decompose sugar oligomers into monomers prior to detection as TRS. After the coloring reaction, sample absorbance at 540 nm was measured using a spectrophotometer (Hach, model DR/4000U, São Paulo, Brazil). The concentration of TRS was calculated using an external calibration curve based on sucrose standard solutions and expressed as sucrose equivalents. When necessary, hydrolysis product mixtures were diluted with distilled water before the absorbance measurement to ensure that the concentration fitted within the instrumental calibration range.

5.2.5. Total phenolic content

Total phenolic content was determined using the *Folin–Ciocalteau* method as described by Singleton et al. (1999). Each extract was diluted in distilled water. Triplicates of 0.5 mL diluted sample and 0.5 mL Folin– Ciocalteu reagent were mixed and incubated at dark at room temperature for 3 min. Then, 0.5 mL of saturated sodium carbonate solution and 3.5 mL distilled water were added and the mixture was again stored in the dark for 2 h at room temperature. The absorbance was recorded at 725 nm using a spectrophotometer (Hach, model DR/4000U, Colorado, USA) A gallic acid standard curve was determined at 725 nm using samples of known concentration.

5.2.6. Antioxidant capacity

The antioxidant capacity of the extracts obtained from DOP was determined using DPPH scavenging assay, ferric reducing antioxidant power (FRAP) and oxygen radical absorbance capacity (ORAC), the description of those analysis were detailed in a previous paper by Lachos-Perez et al. (2018).

5.2.7. Analysis of flavanones by HPLC

HPLC analysis of the flavanones present in the sample was performed in the Extract-US system (Patent pending – FAPESP 2013/04304-4). The system is composed of an HPLC pump (PU-2080 – Jasco, Japan), solvent mixer (MX-2080 – Jasco), solvent degasser (DG 980-50 – Jasco), UV detector (UV-2075 - Jasco), 5 × 2-position-10-port valves (Waters, USA), block valves (Autoclave Engineers) and

backpressure regulator (Tescom). The software used for data acquisition and processing was ChromNAV (Jasco) and the system was configured in the Extract-US software (Kalatec, São Paulo, Brazil). The separation of compounds present in the samples was based on a previously developed method and was carried out on a Kinetex C18 (150 mm, 4.6 mm, 2.7 µm, Phenomenex, USA) column using the following gradient of water (0.1% phosphoric acid – Solvent A) and acetonitrile water (0.1% phosphoric acid – Solvent B): 0 min: 7% B; 3 min: 7% B; 7 min: 13% B; 10 min: 18% B; 20 min: 100% B; 22 min: 100% B; 23 min: 7%B with 5 minutes of equilibration time between runs. Flow-rate was 1.1 mL/min, sample volume was 5 µL and absorbance was monitored at 280 nm. Each analysis was performed in duplicate.

5.2.8. Quantification of sugars by chromatography

Sugar monomers were analyzed by high performance liquid chromatography with pulsed amperometric detection (HPLC-PAD) to analyze released monosaccharides (glucose and xylose) by anion exchange chromatography. Separation was performed using a Dionex DX-500 (Sunnyvale, CA, EUA) instrument with a CarboPac PA1 column (4 mm × 250 mm), a CarboPac PA1 guard column (4 mm × 50 mm), adopting a linear gradient elution with A (NaOH 50 mM), B (NaOAc 500 mM; NaOH 50 mM), and C (H_2O). The concentration of each monosaccharide was calculated from calibration curves determined from standards purchased from Sigma–Aldrich.

5.2.9. Determination of inhibitors by high-performance liquid chromatography (HPLC)

Inhibitor concentrations present in the hydrolyzate were measured using HPLC in the EXTRACT-US system (FAPESP 2013/04304-4 – Patent pending). The EXTRACT-US system is composed of a HPLC liquid pump (PU-2080, Jasco, Japan), ternary gradient unit (LG 2080-2, Jasco), 3 line degasser (DG 2080-55, Jasco), and UV-Vis detector (UV-7075, Jasco). The sample was filtered through a nylon syringe filter (0.20 µm, Analítica, São Paulo, Brazil) before analysis.

Chromatographic separation was performed using a method adapted from Rostagno et al. (2011). In brief, the compounds were separated on a Fused-core type column (Kinetex C18, 2.6 µm, 100 A, 100 × 4.6 mm, Phenomenex, Torrance, CA, USA). The column was maintained 40 °C and flow rate was 1.1 mL/min. The mobile

phase was composed of water (1% phosphoric acid) (solvent A) and acetonitrile (1% phosphoric acid) (solvent B). The gradient profile was: 0 min, 3% B, 3 min, 5% B; 10 min, 90% B; 12 min, 90% B; 13 min, 3% B. The equilibration time between runs was 5 minutes and the injection volume was 5.0 µL. The absorption detector was operated at 270 nm.

5.2.10. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of OP and treated products was performed using a Netzsch TG 209 F1 Libra. Samples were placed in an alumina crucible and held under a nitrogen flow rate of 20 mL/min. The samples were heated from 35 °C to 800 °C (5 °C/min). Raw thermogravimetric data were converted into derivative thermograms (DTG) using Netzsch software. Magicplot software was used for peak fitting.

5.2.11. Fourier-Transform Infrared (FT-IR) spectroscopy

IR spectra were obtained using a spectrometer (Bruker Vertex 70) equipped with a La-DTGS detector. Dry powder samples were placed on a Specac “Golden gate” diamond attenuated total reflectance cell and spectra collected at 4 cm^{-1} resolution, with 512 scans taken over the 600-4000 cm^{-1} spectral range. Spectra were then averaged and Magicplot software was used for peak fitting and baseline subtraction.

5.3. Results and Discussion

5.3.1. Orange peel characterization

The OP used in this study was analyzed for elemental, extractible, and chemical content. Compositional analysis of the OP feed is required for technical evaluations as differences in soil composition, climate (humidity, temperature), crop season, and planting method result in compositions differences even in the plants of the same species. In the case of OP, the composition and nutrient content further depends on the fruit processing method.

Table 1 provides composition data describing the main constituents of the OP used in this study. Elemental analysis indicates that OP consists mainly of carbon (42 wt%) and oxygen (51 wt%), with less hydrogen (6 wt%), nitrogen (1 wt%), and sulfur. The moisture content was 8.71 wt%, great enough to hinder thermochemical valorization using technologies such as incineration, gasification or pyrolysis (Negro et

al., 2016). Ash content (3.99 wt%) was similar to values published in the literature, which range between 3.5 and 4 wt% (Barrales et al., 2018; Cypriano et al., 2018; Lachos-Perez et al., 2018).

Table 1 show that ethanol extractible content of OP was 17 wt%. The alcohol-soluble fraction of the peel contains various components including the sugars glucose, fructose, and arabinose, which are potentially fermentable to produce second generation ethanol, amino acids, organic acids, flavonoids, vitamins, and volatile component. The lipid content of the OP (3.79 wt%), present as terpenes in the essential oil that were measured after cyclohexane extracted. Previous studies indicate that citrus peel contains about 4 wt% of limonene (Negro et al., 2016; Pourbafrani et al., 2010). Limonene, which is a molecule of great interest in several fields (Barrales et al., 2018; Lohrasbi et al., 2010), must be separated from sugars because it inhibits fermentation to produce biofuels (Pourbafrani et al., 2010).

Table 1. Composition of the orange peel

Components	**Value (% w/w)**
Moisture	8.71 ± 0.03
% Dry Matter	
Ash	3.99 ± 0.04
Protein	6.85 ± <0.01
Extractives in Ethanol	17.15 ± 1.73
Extractive in ciclohexane	3.79 ± 1.04
Holocellulose	39.46 ± 2.13
Lignin Soluble	7.71 ± 3.58
Lignin Insoluble	9.09 ± 1.53
Pectin	19.62 ± 3.24
Sugars	
Glucan	34.22 ± 4.68
Xylan	2.15 ± 0.29
Arabinan	4.72 ± 0.88
Elemental content	
Carbon	42
Hydrogen	6
Nitrogen	1
Oxygen	51
Sulfur	0

Table 1 shows that the main chemical constituents of OP pectin, cellulose, hemicellulose, and lignin; values reported in Table 1 are similar to literature values (Cypriano et al., 2018; Lachos-Perez et al., 2018). No test was made for starch, as this component has not been reported to be present in citrus fruit. Carbohydrates are by far the most abundant of all the constituents, accounting for 60 wt%. The most abundant free sugars were glucose (34.22 wt%), xylose (2.15 wt%), and arabinose (4.72 wt%). The pectin content of the OP used in this study was 19.62 wt%, much greater than lignocellulosic biomass. Pectinase hydrolysis of pectin produces galactose, xylose and arabinose sugars that only can be fermentable by *Saccharomyces cerevisiae* yeast genetically modified that has the ability to assimilate pentoses to produce 2G ethanol.

5.3.2. Extraction evaluation

Composition analysis indicated that OP contains significant amounts of carbohydrates suitable for production of second generation ethanol, in addition to several valuable chemicals such as phenolic compounds (flavanones) and other compounds with antioxidant capacity. In addition, OP contains valuable terpene compounds which must be separated from the sugars prior to fermentation. Accordingly, thermal-gradient, sequential flow-through extraction and hydrolysis of the OP has potential for recovery of terpenes, sugars, and flavanones as part of a biorefinery concept that maximizes OP value. Accordingly, OP extraction was studied at different temperatures and continuous phase flow rates to determine concentrations of free sugars and flavanones that could be obtained. Table 3 summarizes these results, along with measurements of the total oxidation capacity of the extract. The extraction results are summarized in this section.

5.3.2.1. Free sugars and reducing sugars (RS)

Table 3 provides soluble sugar composition data recovered by subjecting OP to flow-through water extraction at three different flow rates and at a constant temperature of 150 °C. This temperature was selected for extraction as an optimum between solubility of midpolar compounds, such as phenols, and potential thermal degradation of the feedstock and extracted components. Different flow rates were studied to investigate the effects of thermodynamics, mass transfer, and thermal degradation on extraction performance. Specifically, under conditions of thermodynamic limitations (i.e., solubility), extraction yields should increase with

increasing flow rate. Likewise, extraction yields of thermally labile components can benefit from increasing flow rates, since exposure times of extracted components to thermally damaging conditions decreases with increasing continuous phase flow rates. Finally, mass transfer limited recovery performance will be independent of continuous phase flow rate, and may even decrease for components which are inaccessible.

Consistent with compositional analysis, the sugars recovered at 150 °C are mainly glucose, fructose and sucrose (Bussolo de Souza et al., 2018; Cypriano et al., 2018), though sucrose concentration were not quantified in this work. Glucose and fructose recovery are nearly independent of flow rates, perhaps by the release of monomeric sugars during the treatments and the quite rapid treatment at 150 °C, which is caused by the high content of soluble sugars in OP (Bicu & Mustata, 2011).

The reducing sugar yield generally decreased with increasing water flow rate, perhaps suggesting that extraction may be limited by mass transfer (Table 3). Subcritical water was used to extract bioactive compounds; however, during the extraction procedure some components present in OP can be released and may interact. At high temperatures (up to 100 °C), chemical reactions carry out in organic medium, such as Maillard reactions. An et al. (1997) indicated that high temperatures are needed to break the glycoside bonds, despite monosaccharides and oligosaccharides are more exposed to decomposition at moderate conditions. Certainly, the best flow-rate must be adopted, regarding two main factors extract concentration and extraction time. In conclusion, shorter extraction time and more concentrated extracts are desirable.

5.3.2.2. Total phenolic compounds (TPC) and Antioxidant capacity

Table 3 shows total phenolic compound (TPC) yields obtained from extraction. As with RS yield, TPC yields decrease with increasing water flow rate, again consistent with mass transfer limited extraction. Accordingly, water flow rate can be adjusted for optimum performance and future work should investigate flow rates less than 10 mL min^{-1}, considering that both TPC and RS yields increased with decreasing flow rate in the range considered (Teo et al., 2010; Wijngaard et al., 2012). In fact, while only a handful of previous studies optimize flow rate, Lachos-Perez et al. (2018) and Srinivas et al. (2010) reported that it can play a crucial role in determining the extraction performance for phenolic compounds.

TPC are valuable for the antioxidant capacity (AC); however, thermal degradation can impair AC and AC depends both on the specific compounds and their environment (Khan et al., 2014). Accordingly, several methods have been developed to evaluate the AC of vegetable matrices. In this work, AC was evaluated using three different chemical methods, DPPH, FRAP, and ORAC assays; Table 3 summarizes the result of AC analysis. Overall, measured DPPH, FRAP, ORAC values are consistent with previous literature data on OP extracts peel (Barrales et al., 2018; Chen et al., 2017; Espinosa-Pardo et al., 2017; Lachos-Perez et al., 2018). Maximum AC values (5 ± 1 for DPPH, 12 ± 2 for FRAP, and 12o ± 10 μmol TE/g of raw material for ORAC) were observed at 20 mL/min (for DPPH and ORAC) and 10 mL/min (for FRAP). Unlike RS and TPC, AC is not maximized at the lowest flow rates, which may imply that the antioxidant compounds can degrade during extraction when their residence time in the thermal zone is great enough.

Table 2. Reducing sugars, total phenolics, antioxidant capacity and hesperidin and narirutin yields of extracts from orange peel obtained by subcritical water extraction at different extraction conditions.

	Extraction (°C)	Water flow rate (mL/min)	Reducing sugars (g/100 g OP)	Soluble Compounds		TPC (mg GAE / g DOP)	Antioxidant Capacity (μmol TE /g OP)			Flavanones (mg/g OP)	
				Glucose	Fructose		DPPH	FRAP	ORAC	Hesperidin	Narirutin
1											
2		10	5.90 ± 0.44	1.24 ± 0.39	1.8 ± 0.63	5.78 ± 0.83	4.18 ± 0.67	12.49 ± 1.90	103 ± 10.64	22.99 ± 0.66	1.38 ± 0.38
3											
4											
5	150	20	3.66 ± 1.35	0.79 ± 0.97	0.77 ± 1.15	3.40 ± 0.73	4.93 ± 0.81	11.00 ± 2.29	122.15 ± 10.48	8.97 ± 0.89	0.36 ± 0.03
6											
7											
8		30	3.34 ± 0.62	0.74 ± 1.84	0;82 ± 1.58	4.31 ± 0.44	2.65 ± 0.66	7.60 ± 0.36	90.44 ± 8.14	9.71 ± 1.21	0.63 ± 0.12
9											

Table 3. Sugars and inhibitors obtained by subcritical water hydrolysis of orange peel

	Water flow rate (mL/min)	Hydrolysis (°C)	Reducing sugar (g/100g)	Monomers (g / 100g OP)				Inhibitors (g/100 g)	
				Arabinose	Glucose	Xylose	Fructose	HMF	Furfural
1	10	200	2.36 ± 0.91	5.03 ± 0.73	5.09 ± <0.01	0.49 ± <0.01	3.42 ± <0.01	1.13 ± <0.01	0.48 ± 0.10
2		225	2.57 ± 0.92	3.80 ± 0.02	7.23 ± <0.01	0.65 ± 0.08	4.98 ± <0.01	2.99 ± <0.01	1.76 ± <0.01
3		250	2.73 ± 0.22	1.18 ± <0.01	2.68 ± 0.05	0.70 ± 0.02	1.27 ± 0.07	1.77 ± 0.20	1.16 ± 0.09
4	20	200	3.65 ± 1.02	4.64 ± 1.29	8.24 ± <0.01	0.62 ± <0.01	5.02 ± 0.19	1.23 ± <0.01	0.55 ± 0.18
5		225	3.07 ± 0.92	4.69 ± 1.22	0.87 ± <0.01	0.36 ± <0.01	2.51 ± <0.01	0.11 ± <0.01	0.58 ± 0.07
6		250	3.18 ± 0.18	2.70 ± 0.07	5.45 ± 0.02	1.28 ± 0.08	2.97 ± 0.33	3.72 ± 0.35	2.17 ± 0.44
7	30	200	5.09 ± 1.65	7.14 ± 0.95	13.44 ± 1.00	ND*	11.94 ± 2.36	1.26 ± 0.24	0.51 ± 0.07
8		225	4.06 ± 0.51	5.31 ± 0.82	10.71 ± 0.94	0.59 ± 0.11	6.71 ± 0.12	2.82 ± 0.31	1.63 ± 0.02
9		250	4.84 ± 0.08	3.95 ± 1.13	7.77 ± 0.82	0.83 ± <0.01	4.09 ± 0.22	3.65 ± 0.22	2.12 ± 0.06

* Not Detected

5.3.2.3. Flavanones

Individual flavanone concentrations were measured in the extracts. Hesperidin and narirutin constitute the bulk of the flavanones that appear naturally in OP; accordingly hesperidin and narirutin were the most abundant flavanones present in the extracts. Furthermore, hesperidin yields were greater than narirutin yields under all conditions, consistent previous reports (Barrales et al., 2018; Cheigh et al., 2012; Chen et al., 2017; Ko et al., 2016; Lachos-Perez et al., 2018). As with TPC, hesperidin and narirutin yields decreased with increasing flow rate, again consistent with mass transfer limited recovery of inaccessible components.

5.3.3. Extraction flow rate

Measured extraction yields of RS, TPC, and individual flavanones generally decreased with increasing flow rates, indicating that extraction of these components was mass transfer limited. Since increasing the flow rate of the extraction phase tends to result in dilute extracts and always increases water use rates, the lowest flow rate that maximizes extraction yields will generally be economically preferred. In this case, 10 mL min^{-1} is clearly the optimal flow rate studied; however, future work should evaluate performance of flow rates less than 10 mL min^{-1} to determine if performance can be further optimized. Likewise, various pretreatment and/or co-treatments might improve extraction performance and/or shift the optimum performance to lower flow rates. For example, mechanical grinding of the OP might expose more of the RS and TPC content, thereby improving extraction performance.

5.3.4. Hydrolysis evaluation

5.3.4.1. Composition of the hydrolysate

Extraction studies at 150 °C indicated that phenols and simple sugars could be recovered under non-reactive conditions, and that performance was generally mass transfer limited. Accordingly, the next step was to investigate performance under reactive hydrolysis performance. Not only will hydrolytic conditions result in degradation of carbohydrates to increase RS yields, but hydrolytic decomposition of complex carbohydrates such as hemicellulose can improve access to the soluble sugars and phenolic compounds which were difficult to recover by extraction at 150 °C. Hydrolysis temperatures of 200, 225, and 250 °C were selected for evaluation, as previous work has found that these temperatures are sufficient for hemicellulose

decomposition while minimizing RS degradation. As in the extraction studies, flow-through hydrolysis was evaluated at three water flow rates, 10, 20, and 30 mL min^{-1}.

Hydrolyzate products were analyzed to determine concentrations of sugars and inhibitors compounds, and Table 4 summarizes the results. Glucose was the primary monosaccharide present in the hydrolysate, originating from the original free sugars as well as hydrolysis of hemicellulose and hydrolytically accessible cellulose (Rogalinski et al., 2008). Given the low concentration of glucose in OP hemicellulose some fraction of the cellulose likely hydrolyzes at these conditions, resulting in the formation of glucose. At a fixed temperature, increasing water flow rate increased the glucose yield, consistent with partial degradation of sugars after their formation. The effects of temperature on glucose yields are complex and depend on the extraction phase flow rate, pointing to complex interactions between temperature and the rates of the various hydrolysis, dehydration, polymerization, and char formation reactions that result in product formation and degradation.

The observation of xylose in the hydrolyzate is interesting. Given its yield relative to other monomers, xylose likely arises from hemicellulose hydrolysis. Hemicellulose typically hydrolyzes in the range 190–220 °C (Allen et al., 1996; Mayanga-Torres et al., 2017; Prado et al., 2014), similar to the range studied here. The hemicellulose content of OP consists primarily of galacturonic acid, arabinose, galactose and smaller amounts of xylose, rhamnose and perhaps glucose. Xylose yield reached a maximum of 1.28 % at an extraction temperature of 250 °C and a flow rate of 20 mL min^{-1}, similar to the behavior observed by Klinchongkon et al. (2015) in their study of passion fruit peel treatment by subcritical water. This behavior may be consistent with the relationship between temperature, hemicellulose hydrolysis rates, and xylose degradation rates (Lachos-Perez et al., 2017b; Prado et al., 2014). Quantities of arabinose found in the hydrolysate indicated the presence of arabans generally associated with pectic compounds, probably intermixed with hemicellulose in the OP cell wall. Pectic substance must be removed prior to fermentation, and some pectin degradation is required to improve access to free sugars for extraction (EAKS & SINCLAIR, 1980) consistent with the results obtained at 150 °C.

Precipitated solid material was observed in the hydrolyzate. The precipitate was probably composed of oligosaccharides that were solubilized at high temperatures but became insoluble during cooling (Gray et. al. 2013). Alternatively, depolymerization

and repolymerisation of lignin structures may occur during the fraction process, giving rise to compounds which precipitate during cooling. The precipitated material was not quantified as water-soluble compounds or as residue; future work should determine its composition and determine its formation will be problematic to commercial operation.

Decreasing yields of sugar monomers with increasing temperature may be a partial consequence of sugar decomposition to form secondary products, such as furfural and HMF. Furfural is a result of the dehydration of C5 sugars resulting from the hydrolysis of the hemicellulose, while HMF is produced by the dehydration of C6 sugars obtained from the hydrolysis of cellulose (Asghari & Yoshida, 2010). Table 4 shows that yields of HMF and furfural generally both increase with increasing temperature. The furfural and HMF yields are of similar orders of magnitude, with the HMF yield greater than the furfural yield at all flow rates and consistent with the relative abundance of C6 and C5 sugars in the hydrolyzate. Increasing hydrolysis temperature to greater than 250 °C was not examined due to increasing HMF and furfural yields and likelihood of char formation.

5.3.5. Solid residue characterization

5.3.5.1. TG analysis

Solids were recovered after extraction and hydrolysis and analyzed using thermogravimetric analysis was used to provide compositional information of the treated OP. Figure 1 shows the differential thermograms (DTG) of hydrolysis residues compared to the OP feed. The original thermogravimetic (TG) data are shown in the Supplemental Material (Figures S1) for reference. The DTG data obtained for the OP feed shows 5 peaks in the range 100-400 °C which are assigned to the volatile oils (~140 °C), pectin (240 °C), hemicelluloses (~280 °C), cellulose (300-400 °C) and lignin (400-500 °C) components of the biomass material using literature values for pure materials (Table S1). DTG data were curve fit using typical peak positions and widths observed in the DTG curves for pure component materials as the initial guess for the nonlinear regression (Table S3). Protein is not fit in the DTG curves as is assumed to be a small component (<10%). For example, Alvarez et al. (2018) used a single peak at 400 °C to fit lignin and protein components of citrus peels.

Figure 2 provides the resulting composition estimates of the OP and treated materials. The estimated composition from DTG is similar to the elemental analysis

and the volatiles is similar to the protein and oils from chemical analysis of the OP feed (Table 1, Figure S2). After treatment at 200 °C, the volatile component and pectin were removed almost entirely. Similarly, hemicellulose content is reduced after treatment, but it remains an important constituent even after treatment at 250 °C. The composition of hollocellulose remains similar with different flow rates at 200 °C and 225 °C, whereas, more hemicellulose is solubilized at 250 °C at the higher flow rates. With increasing reaction temperature (200 °C to 250 °C), the relative amount of lignin increases, suggesting partial holocellulose removal and consistent with the soluble sugar data previously shown in Table 3.

In addition to removal and partial removal of components during hydrolysis, DTG indicates formation of a new components after hydrolysis at 225 and 250 °C. Based on the location of the DTG peak (approximately 410 °C) and its appearance after treatment at ≥250 °C, the new component is ascribed to char. Char content increases with increasing treatment temperature, consistent with behavior previously reported for treatment of waste coffee products and barley bagasse (Mayanga-Torres et al., 2017; Torres-Mayanga et al., 2019). Ma et al. (2017) previously explained that increasing treatment temperature leads to increased sugar degradation rates, and hence greater and charring of the particle surfaces (Ma et al., 2017). Previous work found that increasing the flow rate decreases char formation, likely due to removal of char precursors from the thermal zone before they could undergo char formation (Mayanga-Torres et al., 2017). However, in this study, the char increases with increasing flow rate, suggesting that the relationship between flow rate and char formation may be more complex than first considered, and may involve localized back mixing and eddy formation.

Figure 1. DTG thermograms of orange peel and residues after hydrothermal treatment at for flow rates (a) 10 mL/min, (b) 20 mL/min and (c) 30 mL/min.

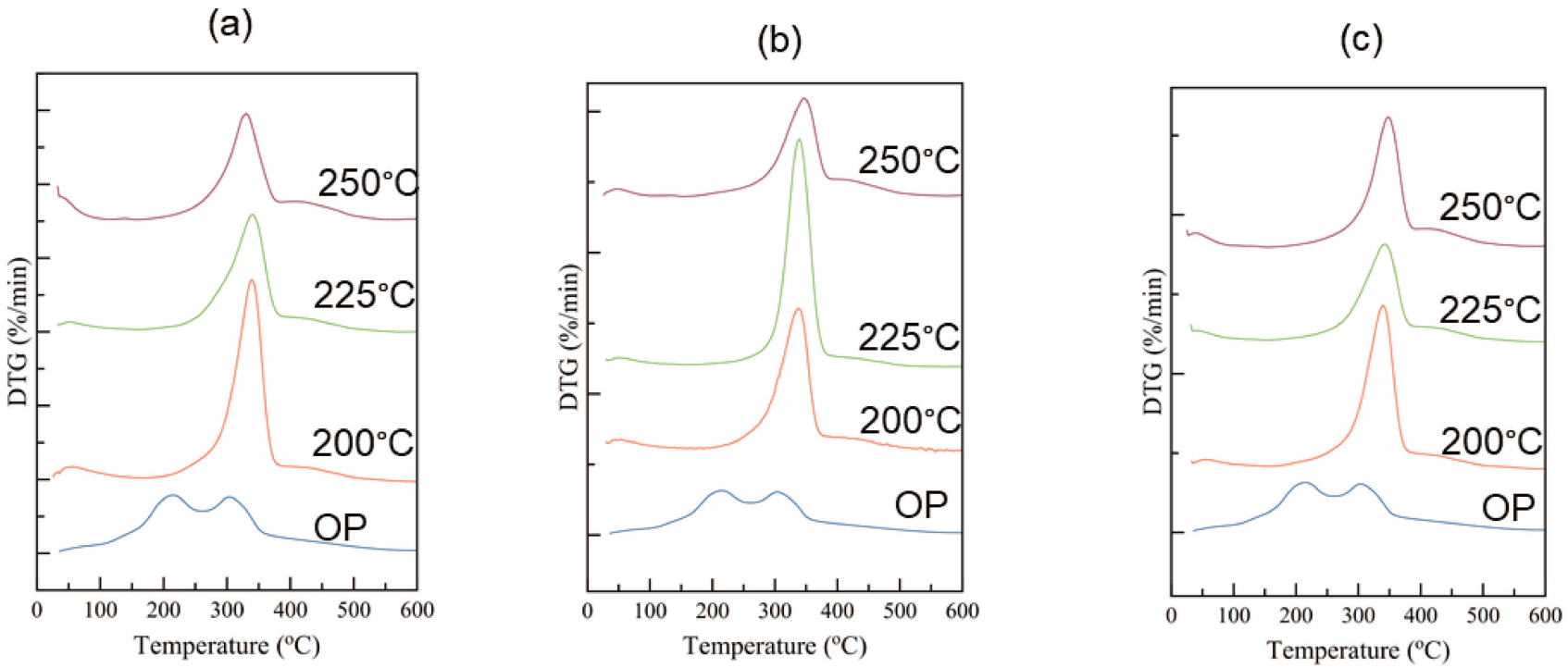
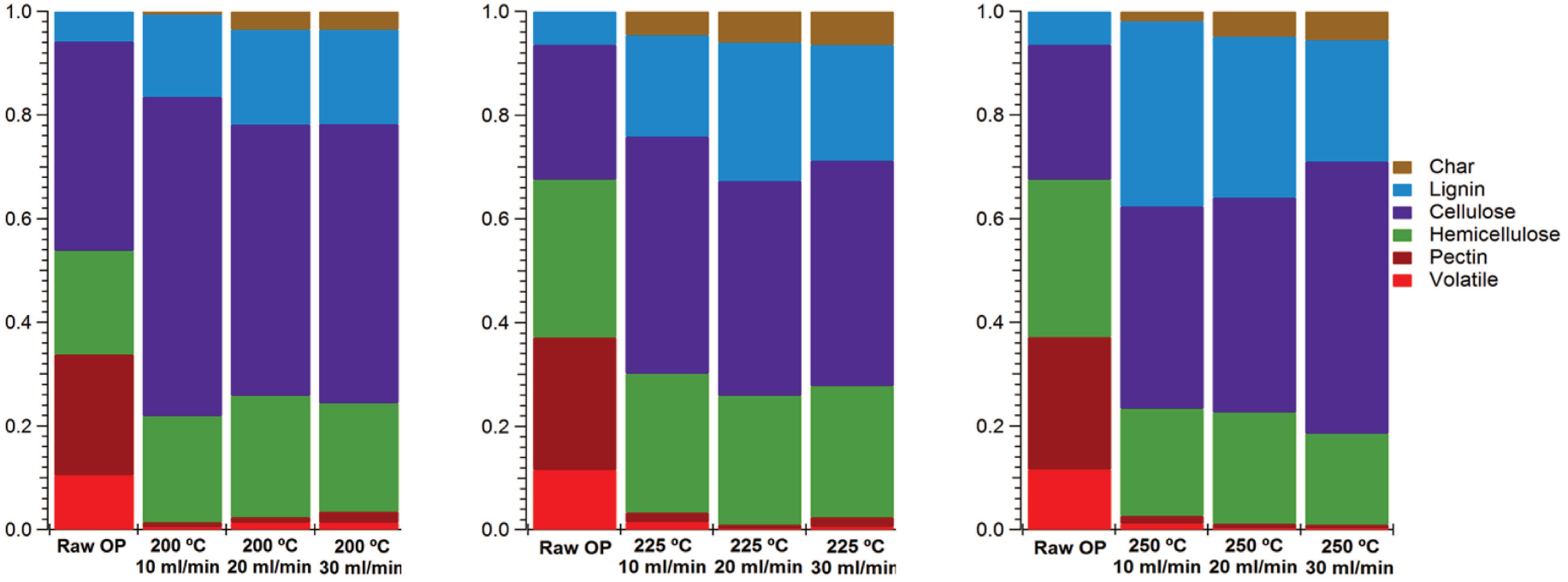


Figure 2. Composition of orange peel and HT residues of differing flow rates at (a) 200°C, (b) 225°C) and (c) 250°C, from DTG analysis.



5.3.5.2. FT-IR Spectroscopy

OP feed and treated materials were analyzed using infrared (IR) spectroscopy to evaluate the effects of the treatment on the chemical composition of the residual solids. Figure S4 shows the IR spectra of raw dried OP compared to that for model pure components including pectin, xylan, cellulose, and lignin. The OP spectrum consists of many overlapping bands, which includes those present in the pure components as well as others not present in the model components. Despite spectral complexity, several distinct bands can be used as indicators of the presence of specific compounds. Beginning with the OP feed, the band at 1735 cm^{-1} is indicative of C=O stretching mode of acetyl groups in hemicelluloses and pectin. Pectin also has characteristic bands at 760 cm^{-1} (ring breathing) and 1226 cm^{-1} (OH bending mode), observed in the spectrum of OP. The carbohydrates, pectin, cellulose and hemicellulose have strong overlapping bands in the region 1000-1200 cm^{-1} due to vibrations of the glycosidic bands between sugar molecules and therefore difficult to distinguish. Lignin, however has a distinctive bands at ca. 1510 and 1590 cm^{-1} due to C=C vibrations of the aromatic rings.

Figure S5 (a-c) shows the infrared spectra of the solid residues from hydrothermal treatments compared to the spectrum of raw OP. For treatments at 200 °C (Figure 4(a)), residual hemicelluloses or pectin is observed after treatment at a flow rate of 10 mL/min, indicated by the presence of the carbonyl band at ~1730 cm^{-1} in the treated material. After treatment at 20 mL/min, the same region contains only a shoulder band at ~1700 cm^{-1}; the shoulder becomes more pronounced after treatment at 30 mL/min. Increasing flow rate from 10 to 30 mL/min extracts more pectin and hemicelluloses, as evidenced by progressive disappearance of the carbonyl band at ~1730 cm^{-1}. Furthermore, the band at 760 cm^{-1} due to the pectin ring breathing mode (Synytsya et al., 2003) is absent in the residue, again consistent with pectin removal. In addition, the glycosidic bands at ca. 1000-1200 cm^{-1} observed from OP, are more defined as several overlapping peaks after HT and increasing flow rate, indicating removal of a proportion of the amorphous hemicelluloses and pectin.

The shoulder band that appears after treatment at 1700 cm^{-1} is attributed to C=O groups from carboxylic acid or ester groups, previously ascribed to char (Torres-Mayanga et al., 2019). DTG analysis indicates that a small amount of char is formed at the conditions where the acid/ester first appears, potentially suggesting that

the acid/ester plays a catalytic role. Bands at ~1510 and 1610 cm^{-1} are more pronounced with increased flow rate and temperature, indicating that lignin and char content increases with increasing treatment and flow rate – again consistent with DTG analysis.

5.4. Conclusions

The sequential hydrothermal removal of flavanones and sugars was studied as an OP biorefinery concept. The maximum yields of flavanones were obtained at 150 °C and 10 mL/min. Optimal reducing sugars yields were observed at 200 °C, reaching values (5.09%) that indicate economic potential for hydrolysis of this feed. TG and IR analysis provided further information about pectin extraction, hemicellulose hydrolysis, and char formation during treatment that can guide future development efforts. This study encourages future work to develop the sequential extraction-hydrolysis technology for OP valorization.

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6. CAPÍTULO 6 – Discussão Geral

A revisão bibliográfica apresentada no **capítulo 2** resume os conhecimentos sobre o processo hidrotérmico e suas principais aplicações na extração, fracionamento, gaseificação e carbonização de compostos obtidos a partir de matérias-primas vegetais usando água subcrítica e supercrítica. O capítulo também resume os trabalhos já relatados na literatura, a influência das principais variáveis de processo e as vantagens do emprego de tecnologias sub e supercríticas com a necessidade de aproveitar a biomassa como um conceito de biorrefinaria.

Nesse contexto, o **capítulo 3** mostrou a hidrólise da palha de cana-de-açúcar baseando-se na hipótese de que seria possível obter açúcares fermentáveis com maior quantidade de açúcares C5, C6 com a menor quantidade de inibidores de fermentação (HMF e Furfural) mediante a aplicação da água subcrítica em diferentes condições de temperatura e pressão. Neste Capítulo, inicialmente foram feitas a caracterização da matéria-prima, a análise química dos hidrolisados por espectrofotometria e por HPLC. Durante a elaboração do trabalho, verificou-se que a hipótese da produção de açúcares era válida, no entanto o rendimento dos açúcares monoméricos C5 e C6 (Glucose: 2,1 g/100g e Xilose: 2,3 g/100g) não eram o suficiente para a fermentação e produção de etanol 2G, além da produção de HMF e furfural que são inibidores da fermentação. Por outro lado, através das análises do resíduo sólido remanescente no reator, caracterizadas por FT-IR e TGA, verificou-se a presença de "*biochar*" que em trabalhos posteriores, realizados pelo grupo de pesquisa mostraram a existência de uma película de *biochar* com conteúdo de hemicelulose e celulose.

Deste modo, decidiu-se usar outra matéria prima (casca de laranja) para continuar dando ênfase no conceito de biorrefinaria. O Laboratório de Alta Pressão em Engenharia de Alimentos (LAPEA), liderado pelo Prof. Dr. Julian Martinez, tem trabalhado com sucesso na extração de compostos bioativos a partir de subprodutos provenientes do processamento de alimentos usando CO_2 supercrítico como solvente de extração para extratos apolares. O resíduo proveniente da extração era comumente descartado, sendo assim surgiu o interesse em seu uso, uma vez que o mesmo é rico em carboidratos e compostos fenólicos polares.

Neste contexto, para o melhor aproveitamento do resíduo após o processo de extração com CO_2 supercrítico, a casca de laranja desengordurada foi a nova matéria prima usada neste trabalho.

O **capítulo 4** mostra a extração de compostos fenólicos (flavanonas) com água subcrítica a condições de temperaturas menos severas e variando a vazão da água. Neste capítulo, uma série de comparações no processo de extração foi realizada. Diferentes temperaturas e vazões do solvente foram utilizadas na extração com água subcrítica. Os resultados obtidos destas condições foram comparados com as extrações a baixa pressão como Soxhlet e extração assistida por ultrassom. Os resultados mostraram que as condições de 150 °C e 10 mL/min foram os que apresentaram melhores resultados em relação aos compostos fenólicos, açúcares redutores e atividade antioxidante. Os rendimentos das flavanonas (hesperidina e narirutina) em SWE foram também comparados com os métodos de extração a baixa pressão usando etanol como solvente. Os resultados mostraram que o rendimento de hesperidina por SWE foram 3,3 e 1,2 vezes maior do que aqueles obtidos por extração convencional e extração assistida por ultrassom, respectivamente. No entanto, para narirutina os melhores rendimentos foram menores do que os obtidos em métodos de extração de baixa pressão, uma explicação pode ser dada pelos longos tempos de extração de Soxhlet (6 h) e ultra-som (1 h), indicando que esses métodos são mais seletivos para narirutina. Outro ponto marcante desta etapa do trabalho foi a elevada quantidade de hesperidina extraída. Para cada grama de extrato seco e desengordurado se obteve aproximadamente 188 mg deste composto, o qual possui elevada capacidade antioxidante e vários benefícios à saúde humana já comprovados.

Assim, a extração com água subcrítica demostrou ser um processo viável para a extração de flavanonas e ambientalmente correto pois usa a água como solvente de extração, desse modo decidiu-se trabalhar em condições de temperatura mais severa (acima de 200 °C) de um modo sequencial com o objetivo de fracionar a biomassa livre de compostos fenólicos e produzir hidrolisados ricos em açúcares C5 e C6.

Desse modo, e tendo como base o processo de fracionamento usado no **capítulo 3**, projetou-se um processo sequencial para poder extrair flavanonas na melhor temperatura obtida no **capítulo 4** e fracionar a biomassa remanescente na extração a temperaturas mais severas (200 °C, 225 °C, 250 °C). Cabe ressaltar que a matéria prima usada no **capítulo 5** foi apenas a casca de laranja, diferente do capítulo 4 onde foi usada como matéria-prima casca de laranja desengordurada

proveniente da extração de casca de laranja com CO_2 supercrítico. De fato, os resultados mostrados neste capítulo evidenciaram rendimentos mais baixos quando comparados aos resultados com a casca de laranja desengordurada, uma vez que a aplicação de $scCO_2$ pode remover a camada lipídica que cobre a superfície da matriz vegetal, assim como também pequenos poros recalcitrantes da biomassa que são facilmente penetrados pelo CO_2 em altas pressões, o que causa uma mudança estrutural e facilita os processos de conversão da biomassa.

Os resultados mostrados no capítulo 5 mostraram que foi possível extrair compostos solúveis (glucose, frutose) na temperatura de extração (150 °C) além da extração de compostos fenólicos com atividade antioxidante. Nas temperaturas de hidrólise açúcares provenientes da hemicelulose e celulose foram hidrolisados, porém houve formação de aldeídos furânicos como HMF e Furfural que são inibidores da fermentação alcoólica para uma possível produção de etanol 2G. De qualquer modo o processo sequencial resulta ser vantajoso pois apenas alterando a temperatura, é possível extrair compostos fenólicos e fracionar a biomassa, visando o conceito de biorrefinaria.

7. CAPÍTULO 7 – Conclusões gerais e sugestões para trabalhos futuros

7.1. Conclusão geral

Neste trabalho, técnicas de extração e hidrólise e processo sequencial extração-hidrólise utilizando água subcrítica a partir da palha de cana-de-açúcar e casca de laranja foram empregadas a diferentes condições de temperatura, pressão, vazão com o intuito de obter extratos com altos teores de compostos fenólicos, e açúcares assim como também a formação de *Biochar*, chegando as seguintes conclusões dadas nos capítulos 3-5.

O processo de hidrólise da palha de cana-de-açúcar mostrado **no capítulo 3** se mostrou tecnicamente eficaz para obter açúcares fermentáveis, sendo possível a produção de açúcares C5 e C6 junto com a formação de "*biochar*" e permitiu as seguintes conclusões pontuais:

- A hidrólise com água subcrítica de palha de cana-de-açúcar permitiu recuperar açúcares redutores totais, açúcares monoméricos como glicose, xilose, galactose, e arabinose, além da formação de compostos fenólicos e furfurais;
- A melhor condição de hidrólise foi obtida a 200 °C e 10 MPa, a qual resultou em rendimento de açúcares redutores totais (ART) igual a 32,1% (m/m) e conteúdo de glicose igual a 2,1% (m/m);
- As informações fornecidas pela análise de variância mostraram que a pressão tem um efeito modesto nos rendimentos de ART. No entanto, a temperatura resultou ser o parâmetro que exerce um maior papel no processo hidrotérmico;
- As análises Termogravimétricas (TGA) e Espectroscopia no infravermelho por transformada de Fourier (FT-IR) trouxeram informações adicionais sobre a formação de "*biochar*".

O processo de extração com água subcrítica mostrado **no capítulo 4** se mostrou tecnicamente eficaz para obter extratos fenólicos (flavanonas) da casca de laranja desengordurada e permitiu as seguintes conclusões pontuais:

- A extração com água subcrítica permitiu recuperar compostos fenólicos como flavanonas: hesperidina e narirutina;

- A melhor condição de extração foi obtida a 150 °C e 10 mL/min, a qual resultou em rendimento global igual a 10,63% (m/m), conteúdo de fenólicos totais igual a 31,7 mg/g de casca e de flavanonas igual a 210 mg/g de extrato;
- Os extratos apresentaram capacidade antioxidante avaliada pelos métodos DPPH, FRAP e ORAC;
- A capacidade antioxidante mostrou correlação elevada e positiva com o conteúdo de fenólicos totais e dos compostos hesperidina e narirutina;
- O processo com água subcrítica foi comparado com técnicas convencionais de extração, como Soxhlet e ultrasom. Nos atributos avaliados rendimento global, rendimento de açúcares redutores, compostos fenólicos, hesperidina e capacidade antioxidante, o processo com água subcrítica na melhor condição mostraram melhor desempenho.

O processo de extração-hidrólise sequencial com água subcrítica mostrado no **capítulo 5**, para a obtenção de flavanonas e açúcares C5 e C6 da casca de laranja mostraram rendimentos baixos comparados ao capítulo 4 pelas possíveis causas já explicadas na discussão geral. No entanto, permitiu as seguintes conclusões pontuais:

- A extração com água subcrítica da casca de laranja permitiu recuperar compostos solúveis como glicose e fructose, assim como flavanonas com capacidade antioxidante avaliada pelos métodos DPPH, FRAP e ORAC;
- A melhor condição de extração foi obtida a 150 °C e 10 mL/min, a qual resultou em rendimento de açúcares redutores igual a 5,9%, conteúdo de fenólicos totais igual a 5,78 mg/g de casca de laranja e de hesperidina igual a 23 mg/g de casca de laranja;
- A hidrólise com água subcrítica da casca de laranja permitiu recuperar açúcares redutores, açúcares monoméricos como glicose, xilose, fructose, e arabinose, além da formação de compostos fenólicos e furfurais;
- TGA e FTIR providenciaram informações sobre a extração de pectina e a hidrólise de hemicelulose a temperaturas acima de 200 °C.

7.2. Sugestões para trabalhos futuros

Levando em conta os avanços desenvolvidos neste trabalho, propõem-se as seguintes sugestões para futuros trabalhos:

- Avaliar economicamente o processo sequencial desenvolvidos neste trabalho na unidade de extração e fracionamento utilizando simuladores comerciais (SuperPro Designer®);
- Estudar processos de separação para purificar os compostos alvos dos extratos das extrações da casca de laranja com água subcrítica;
- Estudar possíveis aplicações quimiopreventivas, bem como a toxicidade, para os extratos através de ensaios *in vitro e in vivo.*

8. CAPÍTULO 8 – Memorial do período de doutorado

Daniel Lachos Perez é Engenheiro Químico, graduado pela Universidad Nacional Pedro Ruiz Gallo (UNPRG) e mestre em Engenharia de Alimentos pela Universidade Estadual de Campinas (UNICAMP). Em 2015, iniciou o curso de Doutorado em Engenharia de Alimentos da Faculdade de Engenharia de Alimentos (FEA/UNICAMP), realizando as atividades de pesquisa no Laboratório de Bioengenharia e Tratamento de Águas e Resíduos (BIOTAR), com bolsa concedida pela CAPES (PROEX – 0487), com vigência de março de 2015 a fevereiro 2019. O trabalho de doutorado foi realizado sob orientação da Profa. Dra. Tânia Forster-Carneiro e a co-orientação do Prof. Dr. Julian Martínez, ambos do departamento de Engenharia de alimentos da faculdade em menção.

Foram cursados 17 créditos que incluem uma participação no Estágio de Capacitação Docente – PED C (CD003) e as disciplinas de: Fontes Renováveis de Energia (PE131), Seminários (TP199) e Processos de Transformação de Biomassa em Biocombustíveis (BI002). A participação no Programa de Estágio Docente (PED C) ocorreu no primeiro semestre de 2016, com atividades de apoio parcial à docência na disciplina de Fundamentos de Cálculos em Processos (TA332). Foram integralizados 4 créditos correspondentes à participação no Programa de Estágio Docente, na disciplina de Operações Unitárias II (TA731) no segundo semestre 2014 e na mesma disciplina de Operações Unitárias II (TA731) no primeiro semestre 2014, ambos no período do mestrado.

Foi realizado um estágio sanduíche de dois meses por meio do programa Santander Mobilidade Internacional estudantes de pós-graduação - edital Santander_031/2018 no Worcester Polytechnic Institute (Worcester, MA-EUA) no período de novembro e dezembro de 2018.

Durante o período de doutorado foram publicados trabalhos em periódicos internacionais e em anais de congressos nacionais e internacionais, como segue:

Artigos completos publicados em periódicos

D. Lachos-Perez, P. Mayanga-Torres, J. Martinez, M.-J. Cocero, G.A. Tompsett, P. Guerra, M.T. Timko, M.A. Rostagno, T. Forster-Carneiro, Sugars and char formation on subcritical water hydrolysis of sugarcane straw, **Bioresource Technology**, 243 (2017) 1069-1077.

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10. Apêndices

APÊNDICE A - MATERIAL SUPLEMENTAR DO ARTIGO "*Sugars and char formation on subcritical water hydrolysis of sugarcane straw*"

The Supporting Information contains detailed information on: 1) Analysis of variance of TRS yields 2) TGA data, 3) IR spectra and band assignments, and 4) Raman spectra.

1. ANOVA. Experimental results of analysis of variance (ANOVA) was fitted by mean square method and the response model coefficients analyzed using F-test are presented in Table SI – 1. The model F-value of 26.6 corresponding to lowest p-value of <0.0001 shows the reliability of the model fit of TRS yield (%). Higher F-value of temperature has the most influence on TRS yield (Y). R^2 value of 0.83 indicated that 83% experimental data gives compatibility with the predicted results of the model. The lower value of a coefficient of variation (C.V) is 11.5, which further confirmed the reliability of the model applied based on experimental design

Table SI – 1. Analysis of variance for influence of parameters (Temperature and pressure) on the TRS yield (X_0)

	Sum of Squares	df	Mean square	F-value	p-Value Prob>F
Source					
Model	488.2	3	162.7	26.6	<0.0001
X_1	379.1	1	379.1	62	<0.0001
X_2	18.9	1	18.9	3.1	0.0973
X_{22}	90.1	1	90.1	14.7	0.0014
Pure Error	97.8	16	6.1		
Corrected Total	586	19			

R-squared= 0.83, Std. dev. = 2.5, Mean = 21.6, C.V%= 11.5

2. TGA. Thermogravimetric analysis provides a valuable tool for the bulk compositions of complex biomass materials and residues. We utilize TGA to estimate the compositional changes of the solid biomass (sugarcane straw) after SCW treatment at the varying conditions. TGA and DTG curves for solid residues from all conditions studied are shown in Figures SI-1 through SI-5. TGA curves for sugarcane straw compared to solid residues from SCW treatment at various conditions. TGA curves generally exhibit features including a small drop (~5% of the total mass) below 100 °C due to moisture loss, a large weight loss ~350 °C due to the decomposition of cellulose and a gradual weight loss at temperatures above 350 °C associated with lignin. Sugarcane straw feed also shows weight loss between 200 and 350 °C due to the hemicelluloses component. Only 19% of the mass remains after heating the sugarcane straw feed to 800 °C under nitrogen compared to 40% mass of the material treated at 260 °C and 12.5 MPa. Hence, a significant amount (~20%) of the treated material residue is already present in a carbonized form prior to analysis. This is consistent with composition estimation from the DTG curves.

Figure SI-2 shows derivative thermogravimetric (DTG) curves for sugarcane straw biomass resulting from treatment at two different conditions (190 °C, 12.5 MPa and 260 °C, 12.5 MPa). Reaction temperature, particularly above 200 °C, has a significant effect on the residual mass remaining after TGA analysis. In contrast, pressure does not have a significant effect on the amount of char formation and hence remaining char percentage from TGA.

Shaded regions in Figure SI-2 show the range in which peaks are fitted to the curve for the biomass components. Following the peak fitting and composition estimation for

DTG curves described by Cai et al. (2013) we fit the DTG curves for residues produced at different treatment conditions. The peak positions and widths are based on the peak widths and peak temperature of pure components from literature (Table. SI-2).

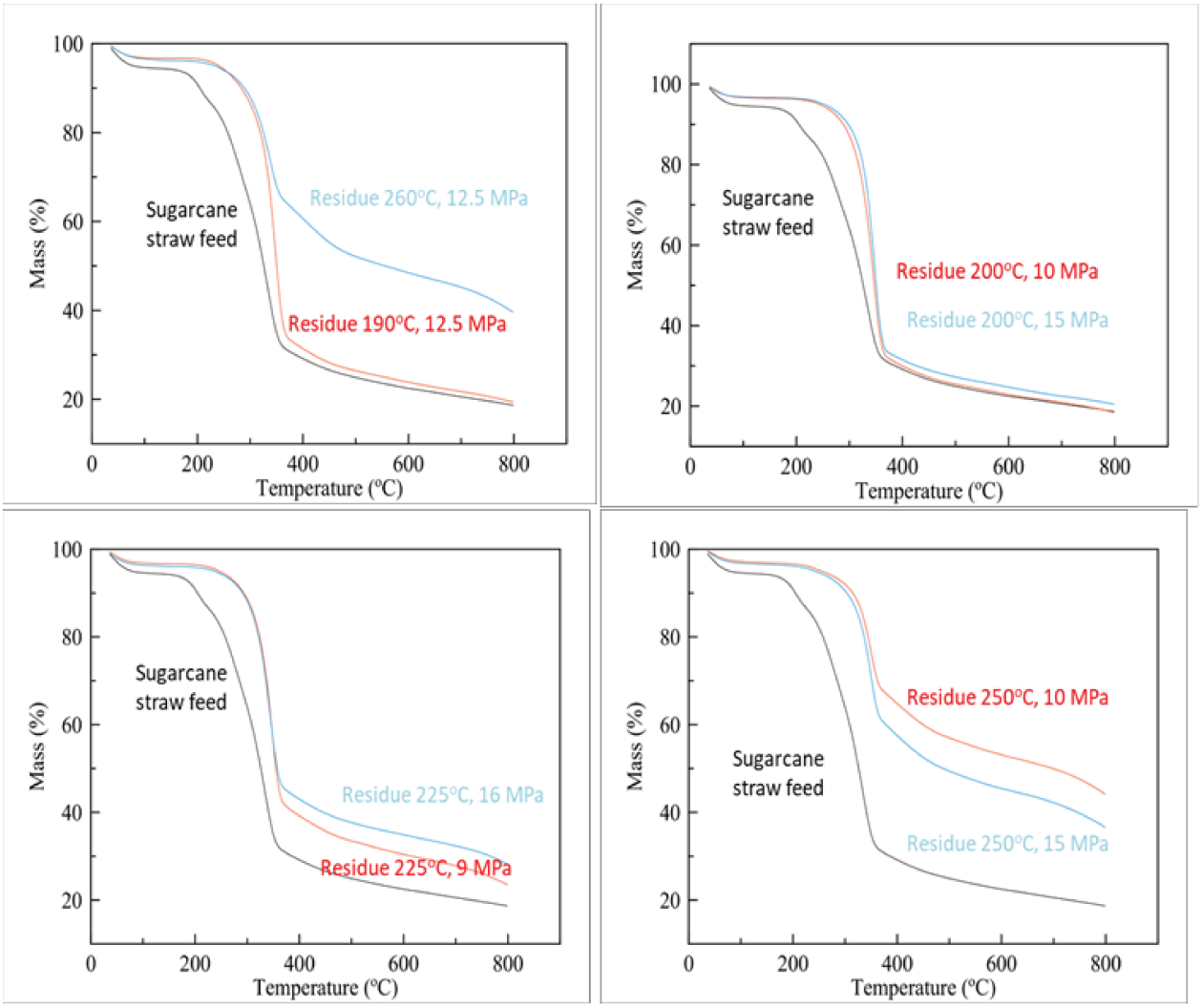

Figure SI-1. TGA curves for sugarcane straw compared to solid residues from SCW treatment at various conditions.

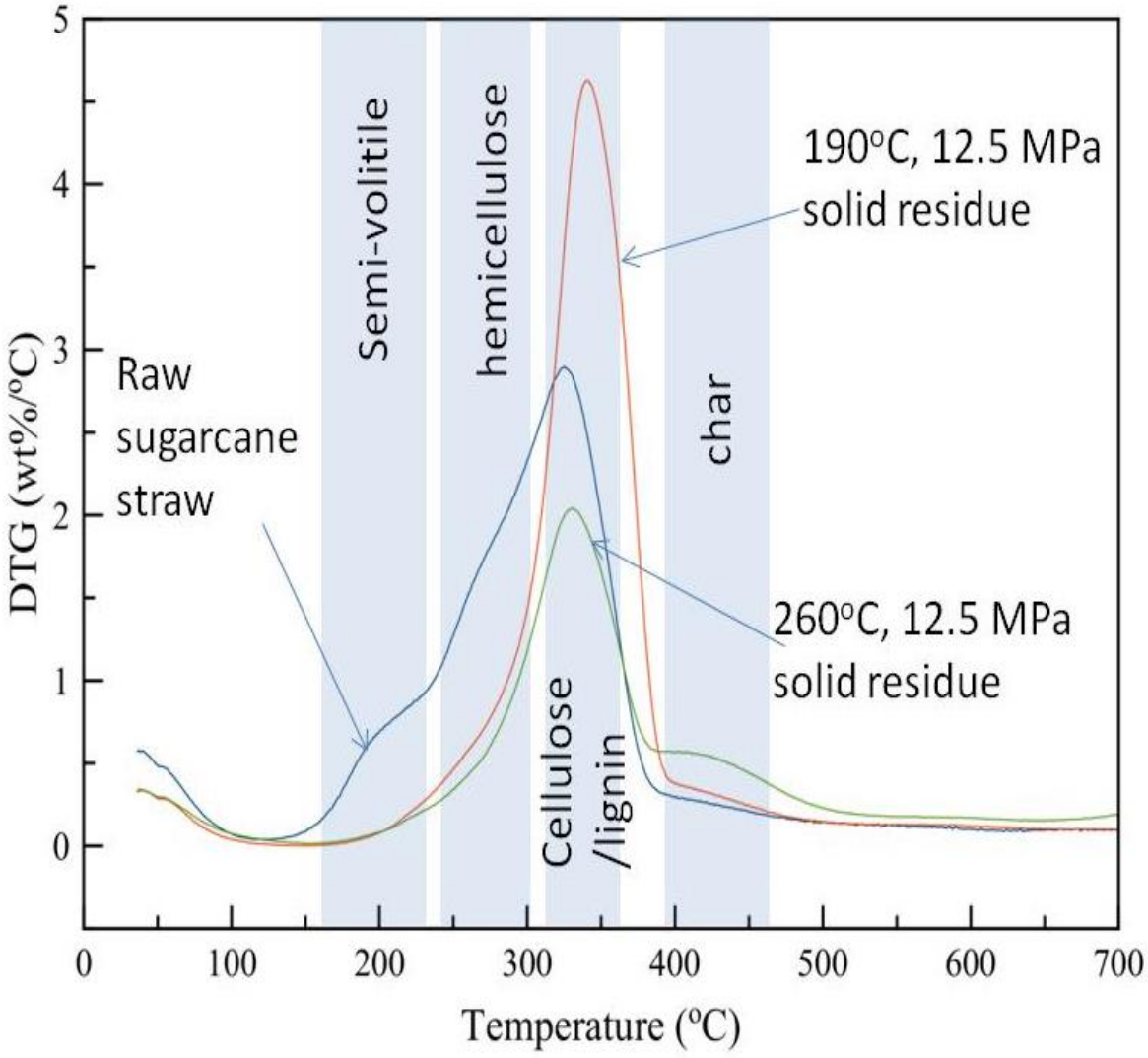

Figure SI-2. DTG curves for sugarcane straw and solid residues after treatment at 190 °C, 12.5 MPa and 260 °C, 12.5 MPa. Shaded regions show the range in which peaks are fitted to the curve for the biomass components.

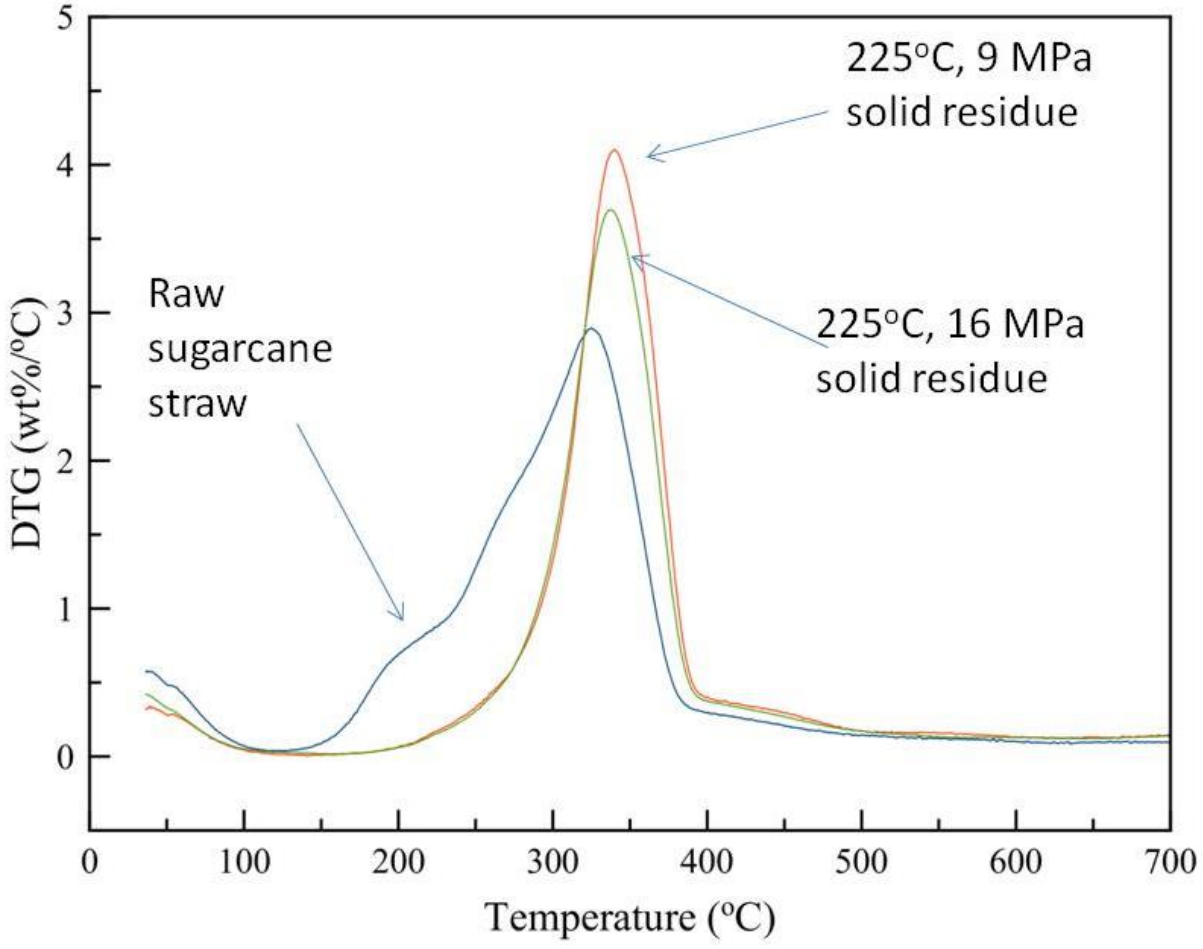

Figure SI-3. DTG curves for sugarcane straw and solid residues from SCW reaction at 190 °C, 12.5 MPa and 260 °C, 12.5 MPa.

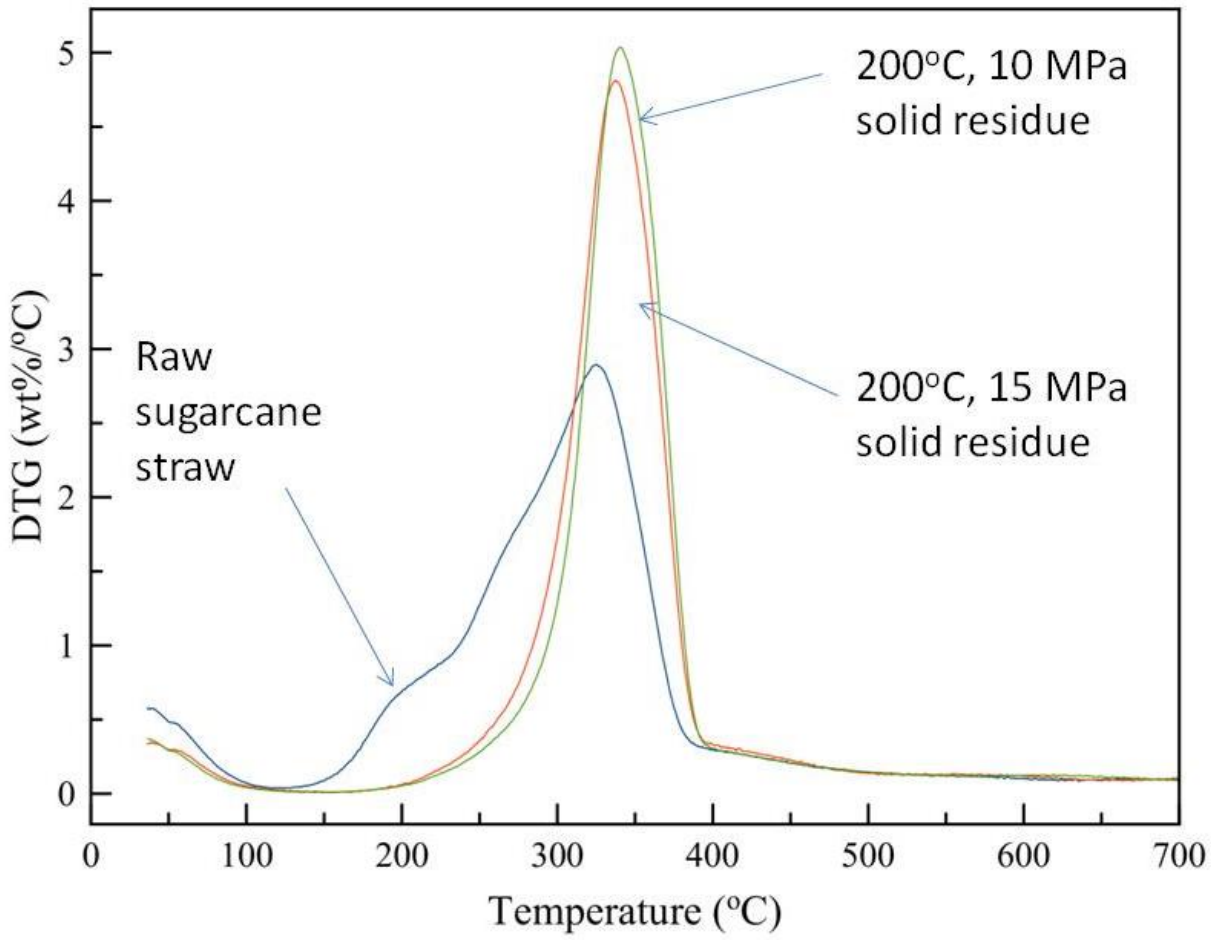

Figure SI-4. DTG curves for sugarcane straw and solid residues from SCW reaction at 200 °C, 10 MPa and 200 °C, 15 MPa.

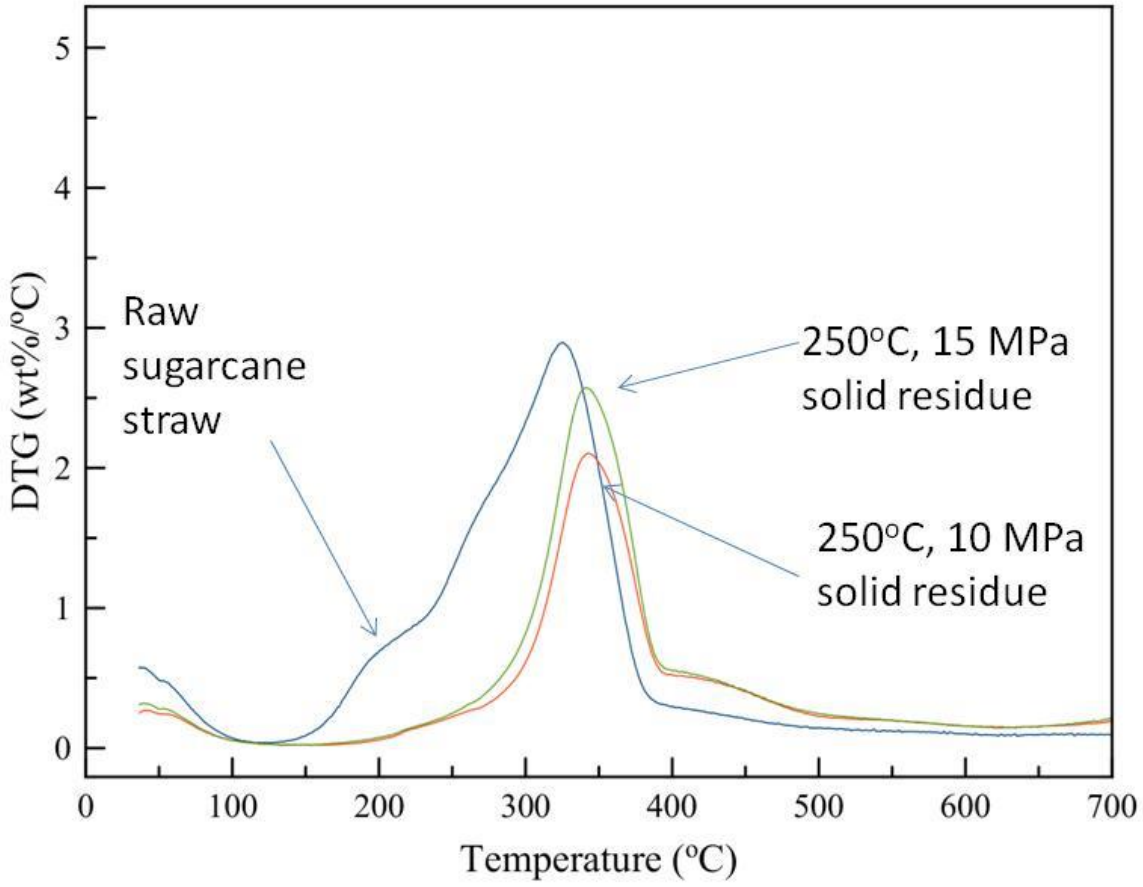

Figure SI-5. DTG curves for sugarcane straw and solid residues from SCW reaction at 250 °C, 10 MPa and 250 °C, 15 MPa.

Table SI-2. DTG peak center, peak range and full width half maximum for biomass components and chars from literature.

Component	Peak center (°C)	Peak base (°C)	Est. Peak FWHM (°C)	Ref.
Lignin	320-350	150-550	160	Watkins et al., 2015
Hemicellulose (straw)	283	175-350	60	Peng & Wu, 2010
Hemicellulose (xylan)	270-309		40	Cai et al., 2013
Cellulose (biomass)	330	280-350	40	Fisher et al., 2002
Cellulose (purified	323-367		40	Cai et al., 2013
Char	400	260-700	100	Fisher et al., 2002
Hydrochar (wood meal)	371-442	350-550	100	Kang et al., 2012

2. IR Spectra and Band Assignments. Infrared ATR spectroscopy was used to characterize the change in the structure and functionality of the solid residues from SCW extraction of the sugarcane waste. Infrared spectra of residues were compared to that of the sugarcane feed material to contrast the differences in composition. Spectra and band positions of all solid residues and feed are shown in the Figures SI-6 through SI-9 and Table SI-3, respectively). Figure SI-6 shows the infrared spectra of sugarcane straw compared to the solid residues after treatment of 190 °C and 260 °C at 12.5 MPa. This covers the entire range of hydrolysis temperatures used and is compared in Figure SI-6 to elucidate the effect of temperature on the process by investigating the solid residue. Bands at ca. 1100 cm^{-1} indicate the solid residues still contains significant amount of carbohydrates, namely cellulose. In addition, the char is greater (C=C band at 1600 cm^{-1}) (Möller et al., 2013) in the 260 °C residue, consistent with TG analysis (Section 3.6). Increasing reaction temperatures cause dehydration and degradation of the carbohydrates, as well as re-condensation to form chars (Sevilla & Fuertes, 2009). Further, the bands in the range 800-1200 cm^{-1} become more narrow and resolved with increasing temperature treatment, indicative of partial hemicellulose removal with hydrothermal treatment (Xu et al., 2013).

The carbonyl band at 1740 cm^{-1} can be assigned to acetyl groups (Xu et al., 2013) for sugarcane straw decreases and new band at 1703 cm^{-1} occurs after treatment at 190 °C and 1701 cm^{-1} for 260 °C reaction. The shift in the carbonyl band position is indicative of removal of esters and formation of formation of surface acid groups (Kang et al., 2012; Mayanga-Torres et al., 2017).

The CH/OH region of the infrared spectra of sugarcane straw and SCW residues (Figure SI-7b, SI-8b, SI-9b, shows several features, including: 1) C-H stretching bands in the range 2850-2960 cm^{-1}; 2) broad O-H stretching band at 3000-3600 cm^{-1}; 3) and sharp O-H stretching bands at 3621, 3651 and 3695 cm^{-1} (sugarcane straw). The narrow weak bands in the region 3600-3700 cm^{-1} are assigned to O-H stretching vibrations of clay minerals. Specifically, the 3621 cm^{-1} band is assigned to kaolinite and gibbsite; the 3695 cm^{-1} band is also assigned to kaolinite (Merlin et al., 2014).The origin of the clay content is likely due to soil contamination within the straw material. After hydrothermal treatment the clay O-H bands are more intense compared to the O-H and C-H bands, indicating the clay ash is concentrated in the residue and is not removed by hydrothermal treatment.

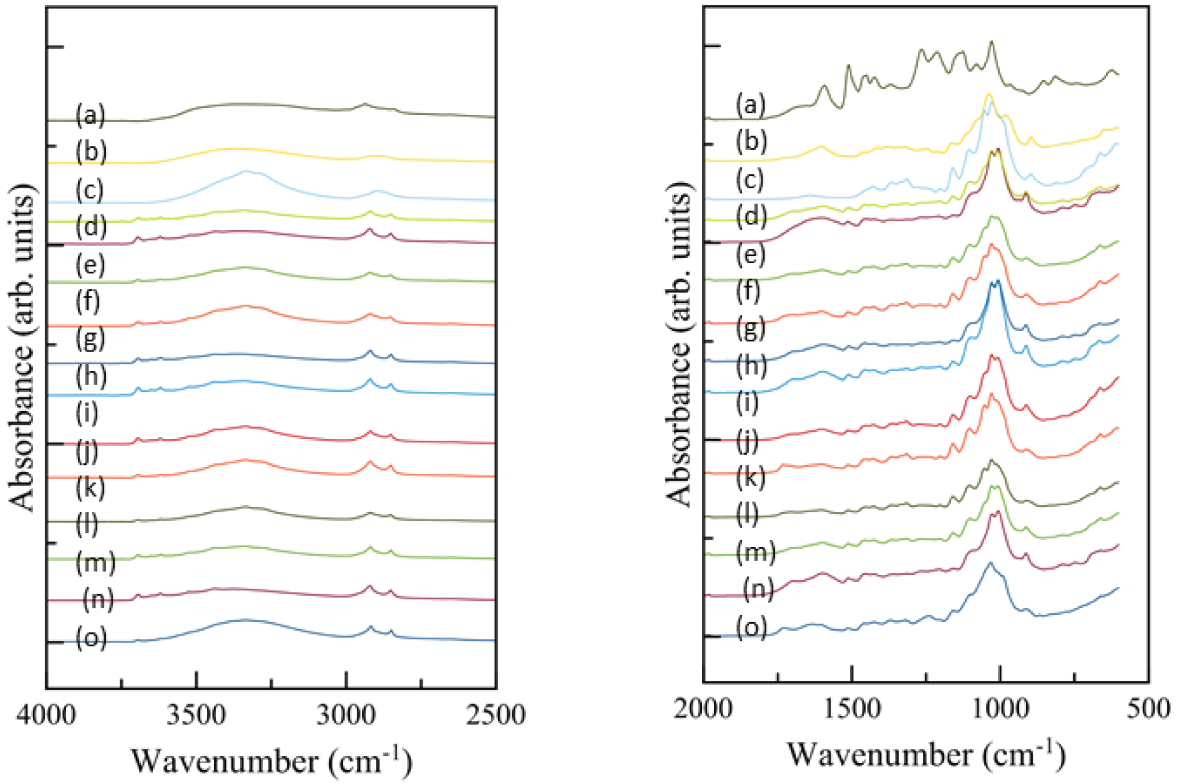

Figure SI-6. Infrared ATR spectra of sugarcane straw and solid residues from all SCW treatment conditions compared to lignin, xylan and cellulose spectra. (a) Kraft lignin, (b) Xylan, (c) Cellulose, (d) Solid residue 225 °C 9 MPa run B1 (e) Solid residue 225 °C 9 MPa run A, (f) Solid residue 225 °C 9 MPa run B, (g) Solid residue 190 °C 12.5 MPa run A, (h) Solid residue 250°C 15 MPa run B, (i) Solid residue 250 °C 10 MPa run A, (j) Solid residue 225°C 9MPa run B, (k) Solid residue 200 °C 10 MPa run A, (l) Solid residue 200 °C 15 MPa run A, (m) Solid residue 225 °C 16 MPa run A, (n) Solid residue 260 °C 12.5 MPa run A, (o) Raw sugarcane straw.

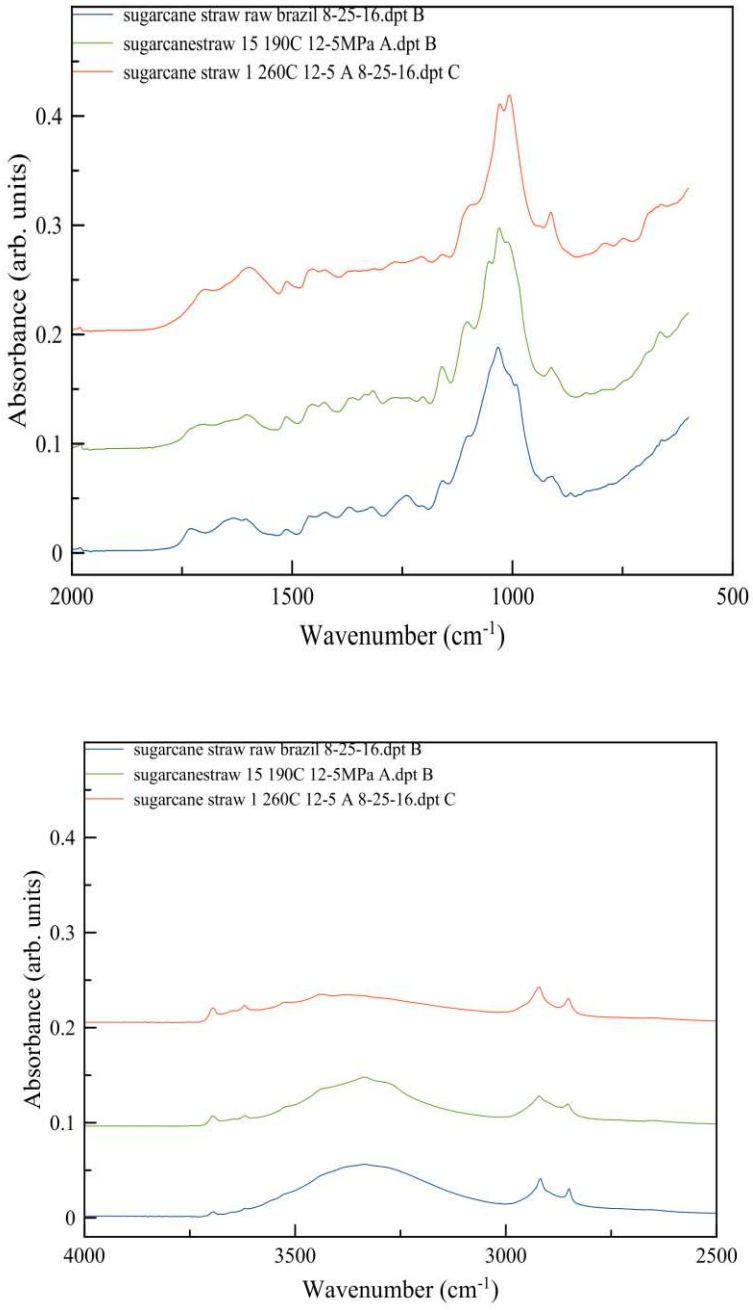

Figure SI-7. Infrared spectra of (a) sugarcane straw compared to solid residue from SCW extraction at 190 °C, 12.5 MPa and 260 °C 12.5 MPa. (a) fingerprint region, (b) O-H/C-H region.

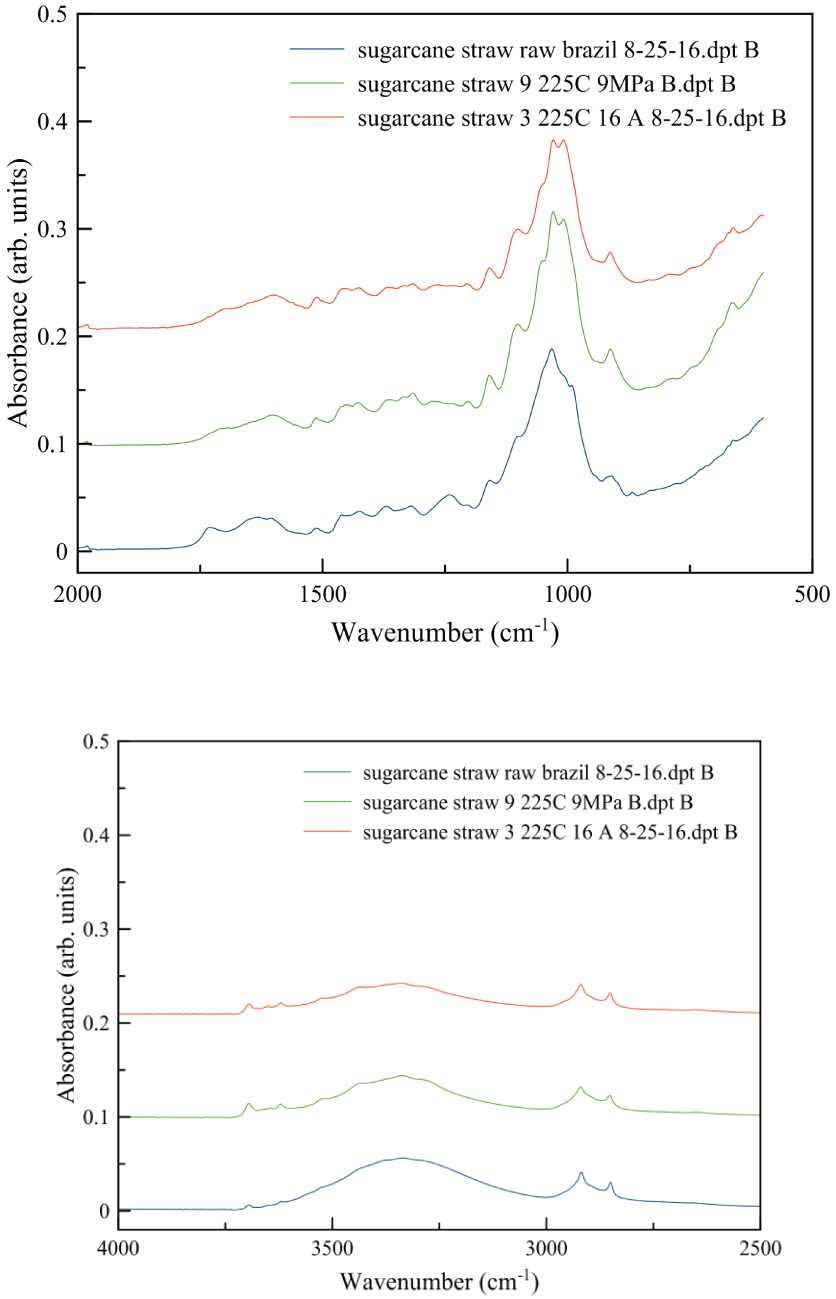

Figure SI-8. Infrared spectra of (a) sugarcane straw compared to solid residue from SCW extraction at 225 °C, 9 MPa and 225 °C 16 MPa. (a) Fingerprint region, (b) O-H/C-H region.

The effect of hot compressed water pressure on the removal of carbohydrates from sugarcane straw was investigated. Figure SI-8 shows the infrared spectra of sugarcane straw feed compared to the solid residues from treatment at 225 °C for pressures 9 and 16 MPa. Only minor differences in the infrared spectra are observed for samples produced at the same temperature but different pressures (9 and 16 MPa). Pressure does not have a significant effect on the hydrothermal extraction of carbohydrates from sugarcane straw and neither does the composition of the solid residue vary much with pressure. In the sample treated at 225 °C, aromatic char is present, as indicated by a strong band at 1600 cm^{-1}, assigned to C=C stretching mode. The carbonyl band at 1730 cm^{-1} for sugarcane straw is absent after treatment and a band at 1710 cm^{-1} is present indicative of removal of esters and formation of formation of surface acid groups (Kang et al., 2012; Mayanga-Torres et al., 2017). Hemicellulose removal with hydrothermal treatment is indicated by the narrowing of carbohydrate bands in 900-1300 cm^{-1} region.

In addition, weak OH bands at 3500-3700 cm^{-1} are assigned to the presence of clays/soil contamination. Solid residues from treatment at 200 °C and 250 °C show similar infrared spectral trends to those shown above for increase in temperature and pressure of SCW treatment (Figure SI-9). In conclusion, from infrared spectroscopy, temperature has the most effect on the solid residue composition. Increasing the treatment temperature, removes carbohydrates but forms char, particularly above 200 °C. This is consistent with the TRS analysis which shows a maximum in sugar yields at 200 °C.

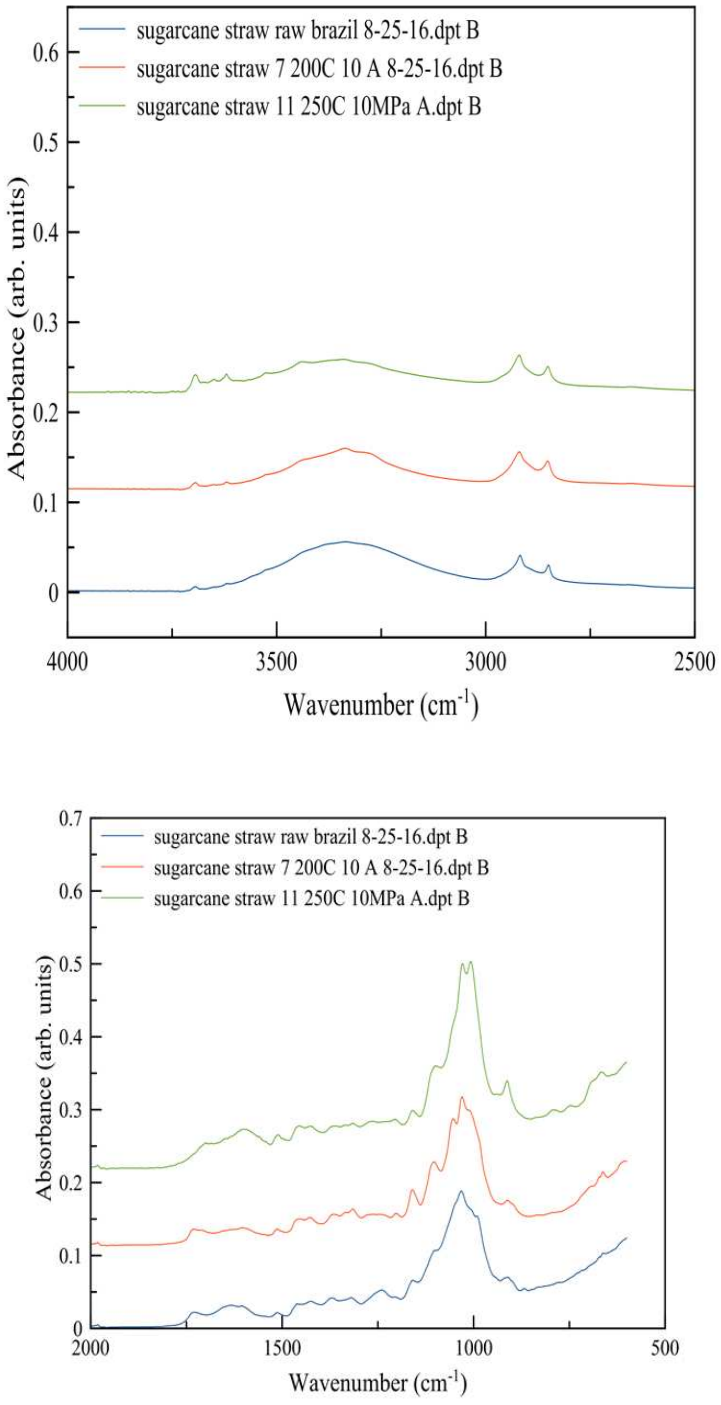

Figure SI-9. Infrared spectra of (a) sugarcane straw compared to solid residue from SCW extraction at (b) 200 °C, 10 MPa and (c) 250 °C 10 MPa. (A) Fingerprint region, (B) O-H/C-H region.

Table SI-3. Band positions (cm^{-1}) and assignments of Fourier transform infrared (FTIR) spectroscopy of sugarcane straw and solid residues from SCW treatment.

Sugarcane Straw feed	200 °C, 15 MPa	250 °C 15 MPa	260 °C, 12.5 MPa	225 °C 16 MPa	Assignment	Ref.
661	669	667	661	662		
	694	693	688	672		
		751	748	692		
781	795	793	790	746	skeletal deformation of aromatic rings, substituent groups, and side chains, lignin, char	Heitner et al., 2010; Kang et al., 2012
868	837			794	C-H aromatic ring, lignin	Guo et al., 2009
911	915	913	914	914	Skeletal CH bending, cellulose	Barsberg, 2010
993					C-O, cellulose	Kang et al., 2012
1006	1015	1007	1007	1008	CO, CC, CCO Cellulose, O-H angular deformation in kaolinite and gibbsite	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Merlin et al., 2014
1033	1031	1030	1030	1029	CO, CC, CCO, HCO, HCC, cellulose, hemicellulose Si-O axial deformation in kaolinite or O-H angular deformation in gibbsite	Xu et al., 2013, Blackwell, 1977; Cael et al., 1975; Merlin et al., 2014
	1054				CO, carbohydrates	Merlin et al., 2014
1100	1106	1095	1096	1095	CO, CC, COH -cellulose	Cael et al., 1975
1159	1161	1159	1162	1161	out of phase C-C-O stretch of phenol or/and CO, CC, CCC, CCO, COH Cellulose, hemicellulose	Xu et al., 2013, Blackwell, 1977, Cael et al., 1975
1205	1203	1205	1207	1205	O-H bending, cellulose, hemicellulose	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975

Sugarcane Straw feed	200 °C, 15 MPa	250 °C 15 MPa	260 °C, 12.5 MPa	225 °C 16 MPa	Assignment	Ref.
1242	1236				C-O stretching, hemicellulose	
	1265	1266	1266	1266	aryl-O of aryl-OH and aryl-O-CH3, lignin	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Heitner et al., 2010
1320	1317	1319	1315	1315	CH2 wagging, cellulose, hemicellulose	Xu et al., 2013, Blackwell, 1977, Cael et al., 1975
	1334	1339			aliphatic O-H bend or/and HCC and HCO bending, cellulose	Heitner et al., 2010
1371	1368	1363	1366	1362	C-H bend, lignin	Heitner et al., 2010
1426	1426	1425	1425	1427	C-H in plane deformation, lignin	Xu et al., 2013
1461	1456	1458	1455	1457	O-CH3 deformation; CH2 scissoring, lignin	Blackwell, 1977
1512	1512	1510	1514	1513	C=C Aromatic ring vibration, lignin	Xu et al., 2013; Heitner et al., 2010
		1559				
1604	1603	1598	1597	1599	C=C, aryl ring stretching, symmetric, char, lignin	Xu et al., 2013; Heitner et al., 2010; Kang et al., 2012
1634						
	1702	1701	1701	1700	C=O carbonyl, lignin, char	Xu et al., 2013; Kang et al., 2012
1730					C=O, hemicellulsoe	Xu et al., 2013
2851	2851	2851	2852	2852	Symethric C-H aliphatic	Heitner et al., 2010
2919	2920	2920	2922	2923	Antisymmetric C-H aliphatic	Heitner et al., 2010

Sugarcane Straw feed	200 °C, 15 MPa	250 °C 15 MPa	260 °C, 12.5 MPa	225 °C 16 MPa	Assignment	Ref.
2955	2960	2954	2955	2954	C-H aliphatic	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Heitner et al., 2010
	3293			3283	O-H	
3336	3337	3342	3372	3339	O-H, lignin	Xu et al., 2013
	3437	3447	3439	3434	O-H	Xu et al., 2013
	3526	3526	3526	3523	O-H	
3621	3620	3621	3620	3620	O-H axial deformation in kaolinite and gibbsite	Merlin et al., 2014
3651	3651	3650	3650	3651	O-H, clays	
	3677	2672			O-H, clays	
3695	3694	3696	3696	3697	O-H axial deformation in kaolinite	Merlin et al., 2014

Table SI-3. (cont') Band positions (cm^{-1}) and assignments of Fourier transform infrared (FTIR) spectroscopy of sugarcane straw and solid residues from SCW treatment.

200 °C 15 MPa	200 °C 10 MPa	225 °C 9 MPa	250 °C 10 MPa	190°C 12.5 MPa	Assignment	Ref.
663	664	664	667	663		
696	670	692	688	696		
	695	747	749	745		
		793	792	794	skeletal deformation of aromatic rings, substituent groups, and side chains, lignin, char	Heitner et al., 2010; Kang et al., 2012
834	879			834	C-H aromatic ring, lignin	Guo et al., 2009
914	912	913	913	913	Skeletal CH bending, cellulose	Barsberg, 2010
988	987				C-O, cellulose	Xu et al., 2013
1010	1010	1008	1009	1012	CO, CC, CCO Cellulose, O-H angular deformation in kaolinite and gibbsite	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Merlin et al., 2014
1031	1030	1031	1030	1030	CO, CC, CCO, HCO, HCC, cellulose, hemicellulose Si-O axial deformation in kaolinite or O-H angular deformation in gibbsite	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Merlin et al., 2014
1054	1053	1051	1055	1053	CO, carbohydrates	Merlin et al., 2014
1104	1104	1102	1101	1102	CO, CC, COH -cellulose	Cael et al., 1975
1161	1160	1161	1160	1162	out of phase C-C-O stretch of phenol or/and CO, CC, CCC, CCO, COH Cellulose, hemicellulose	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975
1205	1204	1203	1204	1204	O-H bending, cellulose, hemicellulose	Xu et al., 2013; Blackwell, 1977;

						Cael et al., 1975
	1238			1237	C-O stretching, hemicellulose	
1269	1271	1272	1265	1265	aryl-O of aryl-OH and aryl-O-CH3, lignin	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975; Heitner et al., 2010
1317	1316	1317	1316	1316	CH2 wagging, cellulose, hemicellulose	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975
1333	1334	1335	1336	1336	aliphatic O-H bend or/and HCC and HCO bending, cellulose	Heitner et al., 2010
1366	1367	1366	1365	1367	C-H bend, lignin	Heitner et al., 2010
1427	1427	1430	1428	1430	C-H in plane deformation, lignin	Xu et al., 2013
1455	1459	1452	1458	1453	O-CH3 deformation; CH2 scissoring, lignin	Blackwell, 1977
1516	1515	1514	1512	1512	C=C Aromatic ring vibration, lignin	Xu et al., 2013; Heitner et al., 2010
1603	1605	1601	1597	1602	C=C, aryl ring stretching, symmetric, char, lignin	Xu et al., 2013; Heitner et al., 2010, 14
1705	1712	1709	1699	1704	C=O carbonyl, lignin, char	Xu et al., 2013;
	1732				C=O, hemicellulsoe	Xu et al., 2013
2852	2852	2852	2851	2851	Symmetric C-H aliphatic	Heitner et al., 2010
2920	2921	2921	2920	2920	Antisymmetric C-H aliphatic	Heitner et al., 2010
2962	2955	2958	2953	2956	C-H aliphatic	Xu et al., 2013; Blackwell, 1977; Cael et al., 1975;

						Heitner et al., 2010
3290	3286	3288	3288	3285	O-H	
3336	3335	3340	3342	3334	O-H, lignin	Xu et al., 2013
3430	3434	3431	3438	3438	O-H	Xu et al., 2013
3524	3524	3523	3526	3523	O-H	
3619	3619	3622	3620	3620	O-H axial deformation in kaolinite and gibbsite	Merlin et al., 2014
3650	3651		3651	3646	O-H, clays	
			3673		O-H, clays	
3696	3695	3696	3696	3697	O-H axial deformation in kaolinite	Merlin et al., 2014

3. Raman Spectroscopy

Raman spectra were obtained using a Horiba Xplora Raman microscope. Spectra were excited using either 532 nm (for chars) and 785 nm (raw sugarcane straw) laser wavelength at 10 mW. For each sample, 25 scans of 2 second duration were averaged. A 100x Olympus optical lens was employed to focus the laser on the sample particles. Several (3-5) particles for each material were characterized.

Figure SI-10 shows the Raman spectrum of raw sugarcane straw. Spectral band regions are indicated in for the components in the straw, namely lignin, carbohydrates and carbonyl groups. Band assignments for sugarcane straw are listed in Table SI-4.

Figure SI-11 shows the Raman spectrum of raw sugarcane straw compared to those for solid residues from SCW treated sugarcane straw. The spectra of the treated spectra exhibit significant fluorescence, as indicated by the elevated baseline and oscillating background signal. The fluorescence is likely due to aromatic compounds in the residues, which is problematic for these laser wavelengths. Despite fluorescence, the presence of residual cellulose in the spectrum of residue treated at low temperature (190 °C) can be observed. The spectra of straw treated at 250 °C contain carbon char bands at ca. 1300 and 1600 cm^{-1}. This indicates char formation on the particles of solid residues during reaction.

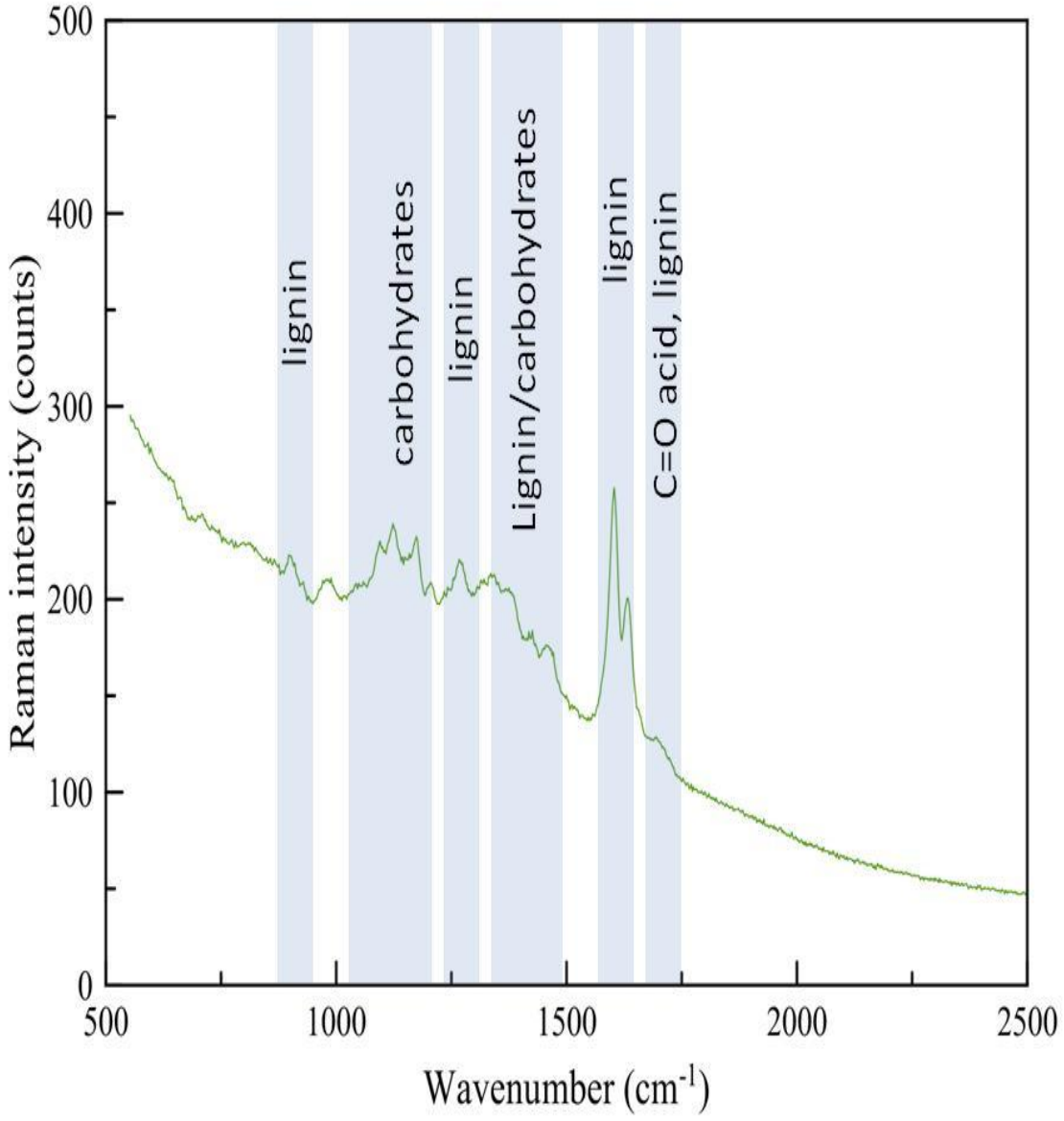

Figure SI-10 Raman spectra of sugarcane straw. Shaded areas show band assignment regions.

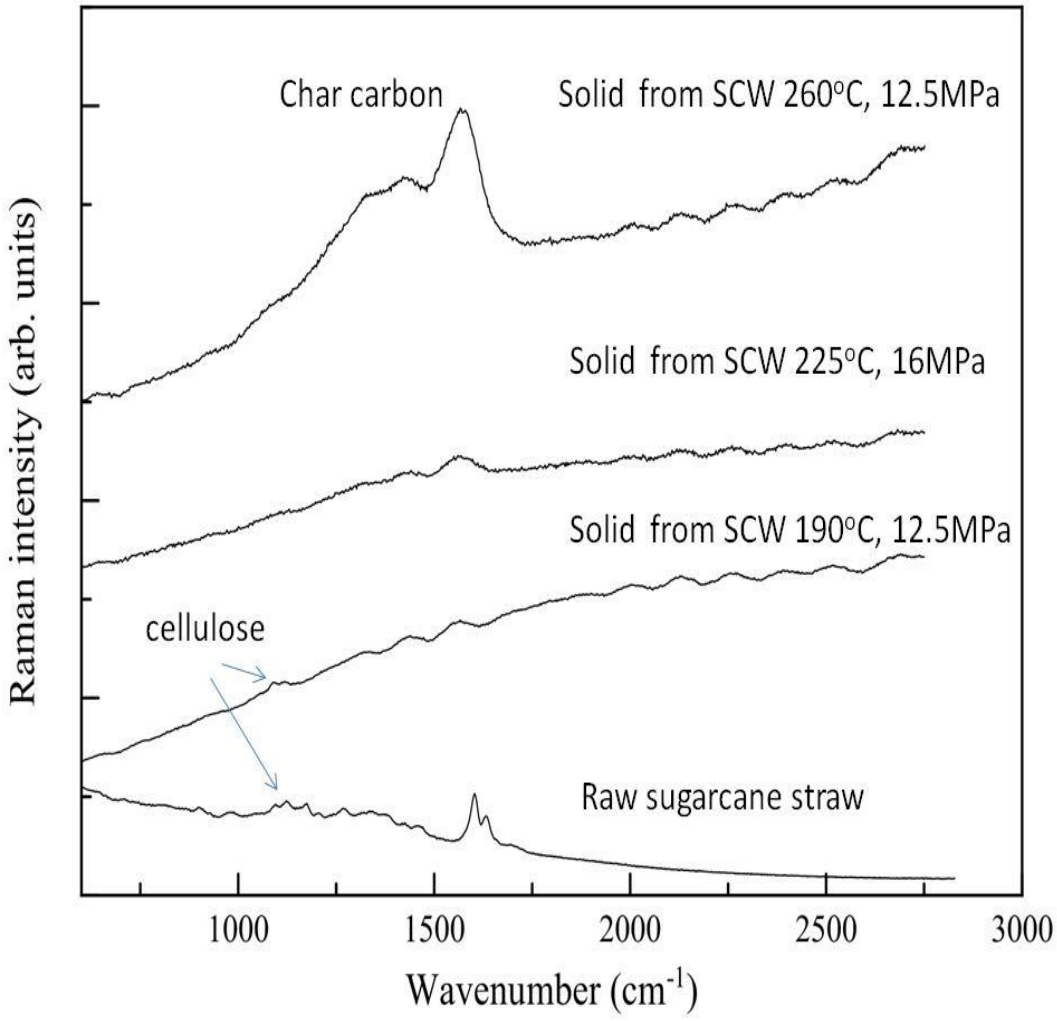

Figure SI-11 Raman spectra of sugarcane straw and solid residues after SCW treatment at three conditions.

Table SI-4. Sugarcane straw Raman spectrum band positions and assignments.

Band position (cm^{-1})	Assignment	Ref.
898	skeletal deformation of aromatic rings, substituent groups, and side chains; δ (C(1) H(β))	Stark et al., 2016
980	CCH and –HC]CH– deformation lignin	Stark et al., 2016
1045	CO, CC, CCO, HCO, HCC, cellulose	Cael et al., 1975
1092	CO, CC, COH -cellulose	Cael et al., 1975
1122	C-O of aryl-O-CH_3 and aryl-OH or/and CO, CC, CCO, COH Cellulose, hemicellulose	Cael et al., 1975
1173	Phenol mode, lignin	Stark et al., 2016
1205	Not assigned	
1268	Aryl-O-CH3 lignin	Stark et al., 2016
1336	aliphatic O-H bend or/and HCC and HCO bending, cellulose	Blackwell, 1977
1373	CH bend, cellulose	Cael et al., 1975
1424	O–CH_3 deformation; CH2 scissoring; lignin, cellulose	Cael et al., 1975
1458	O-CH_3 lignin	Stark et al., 2016
1601	C=C lignin, lignin	Stark et al., 2016
1632	Ring-conjugated C=C stretch of lignin; C=O stretch of lignin	Stark et al., 2016
1694	C=O, acid, lactone, ester?	Stark et al., 2016

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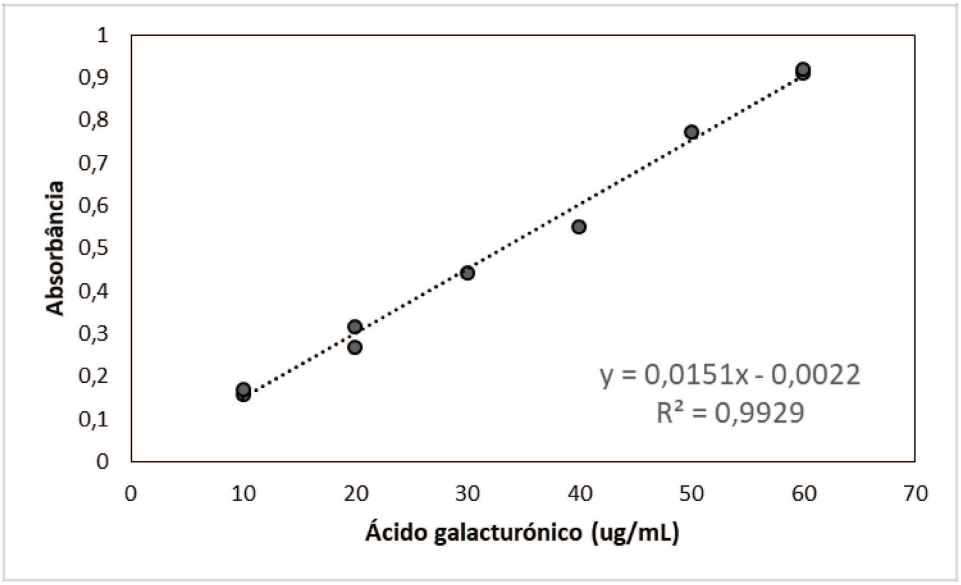
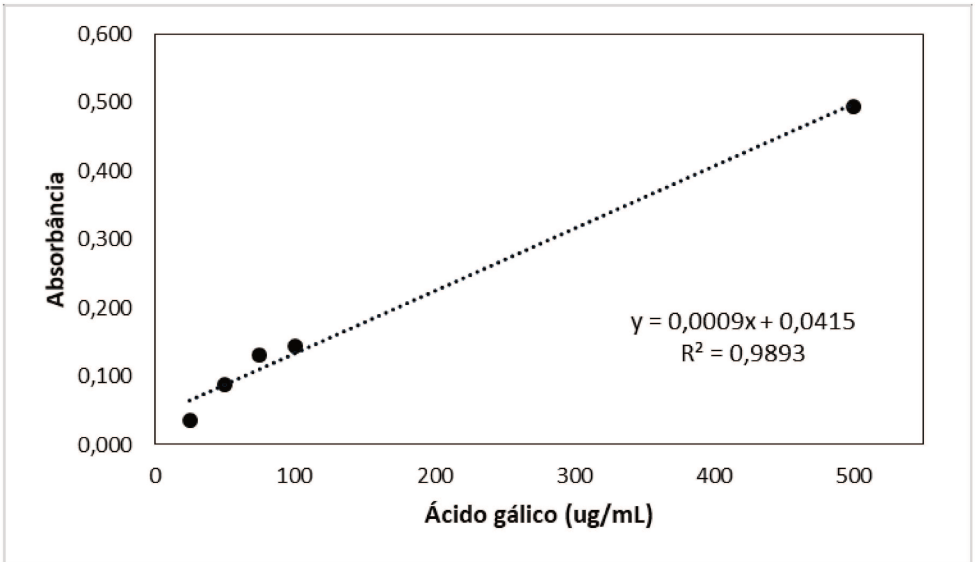
APÊNDICE B - MATERIAL SUPLEMENTAR DO ARTIGO "*Subcritical water extraction of flavanones from defatted orange peel*"

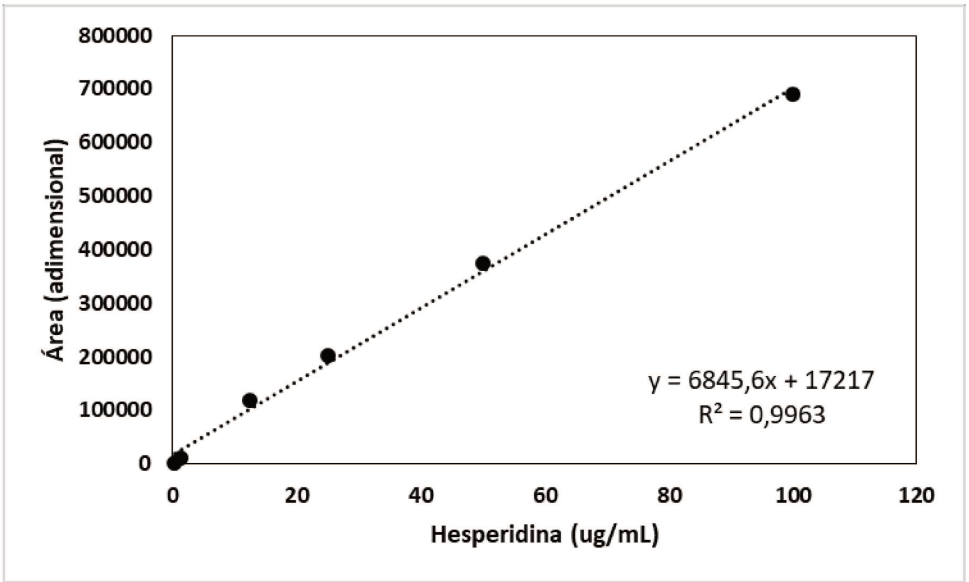
Curva padrão da análise de quantificação de pectina na casca de laranja desengordura



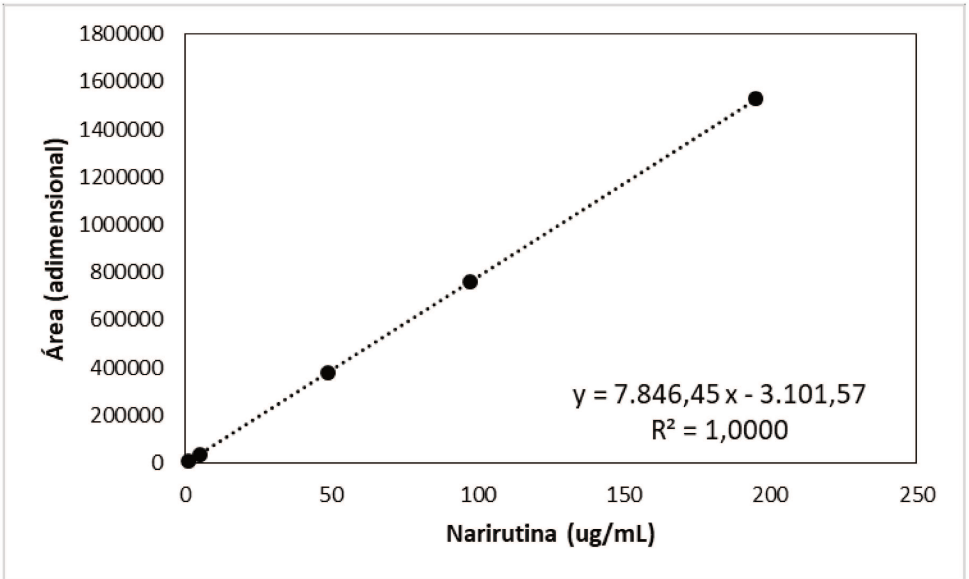
Curva padrão da análise de fenólicos totais



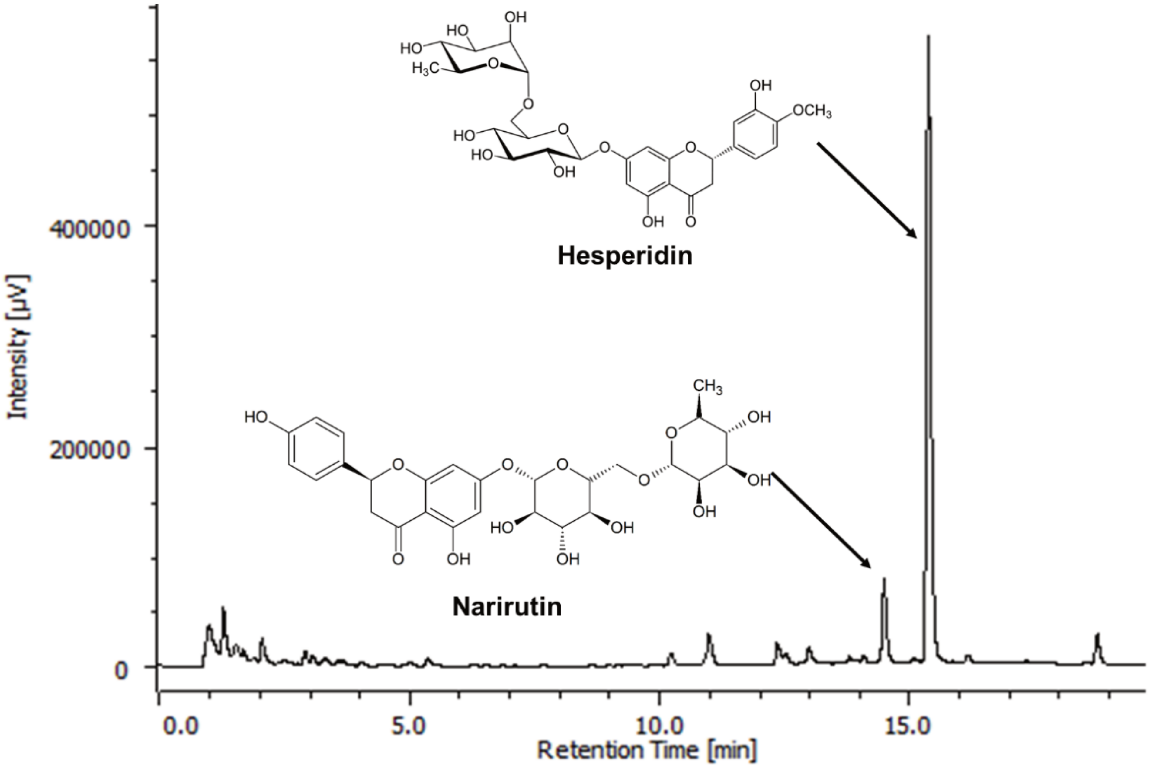
Curva padrão para quantificação da Hesperidina



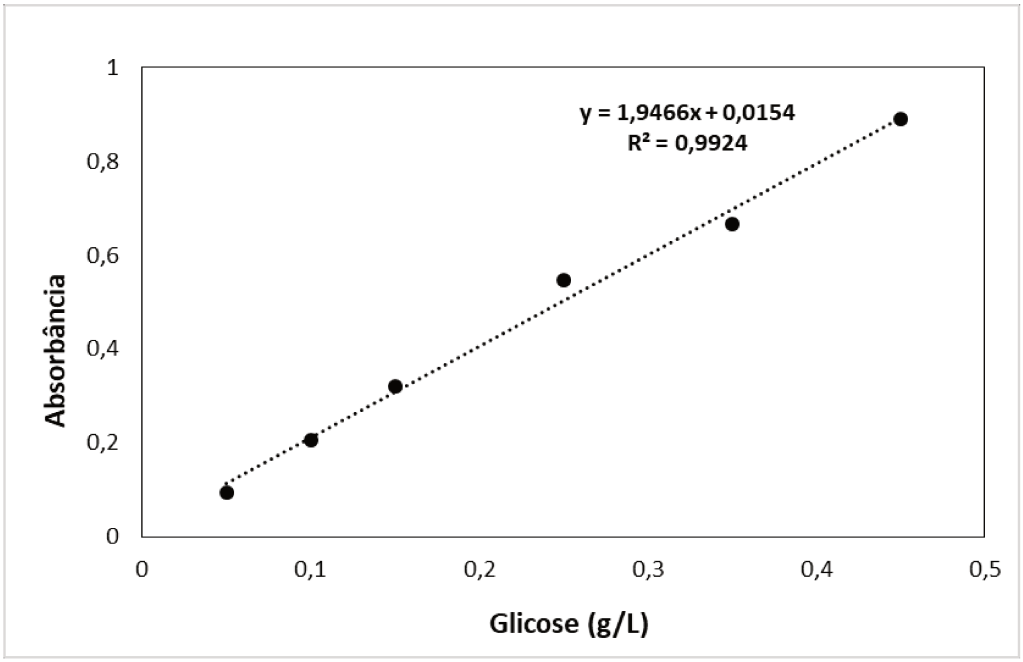
Curva padrão para quantificação da Narirutina



Cromatograma típico dos extratos obtidos a 150 ° C e 10 mL / min



Curva padrão da análise de açúcares redutores



APÊNDICE C - MATERIAL SUPLEMENTAR DO ARTIGO "*Sequential subcritical water process applied to recover flavanones and sugars from orange peel*"

Table S1 Literature DTG peak temperatures for citrus peels.

Compound/Feedstock	DTG Peak temperature (°C) and compound assignment	Ref.
Sweet orange (Citrus sinensis) dry peel 10C/min	47 water soluble products 223 hemicellulsoe 346 cellulose 479 lignin	Miranda et al.
Orange waste (pulp)	50 water 165 hemicellulose 212 hemicellulose 254 hemicellulose 328 cellulose 485 lignin	Lopez-Velazquez et al.
Mandarin orange peel	210 hemicellulose 220 hemicellulose 350 cellulose ~500 lignin?	Sánchez et al.
Mandarin orange peel 40C/min	84 water 242 pectin 280 sh hemicelluloses 371 cellulose	Kim et al
Citrus Unshiu Peel	<100 water 205 pectin 246 hemicellulsoe 322 cellulsoe 385 lignin	Kim et al 2015
Orange peel Citrus peel Lemon peel	150-200 moisture 150-400 hemicellulose and cellulose 200 pectin and hemicellulose 300-400 cellulose	Pathak et al.
R-Limonene	140, 160	Fuenmayor et al
Citrus pectin (10C/min)	249.9	Einhorn-Stoll, H. Kunzek

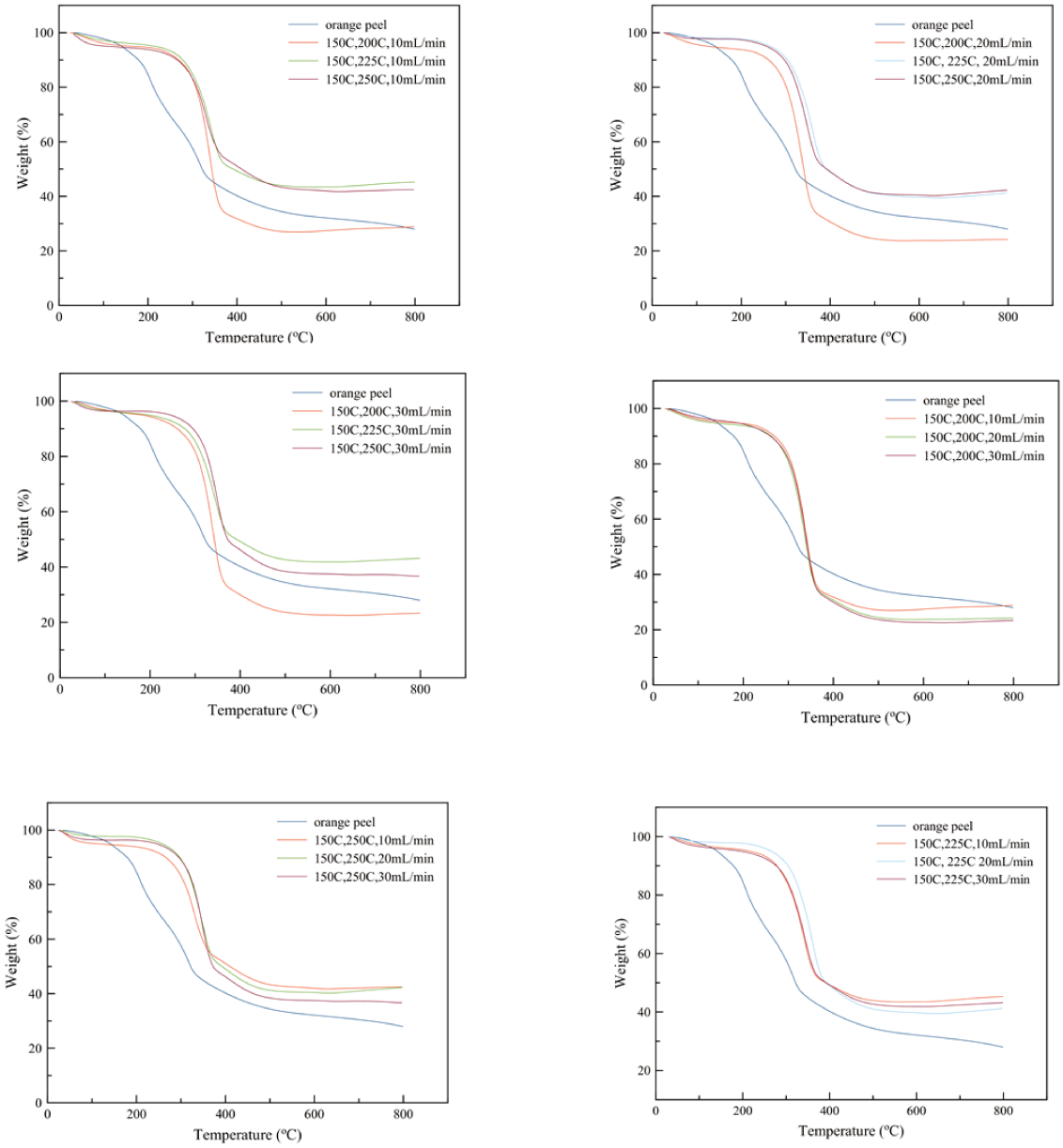


Figure S1 TG thermograms of orange peel and subcritical water treated residues.

Table S2 Percent of hard coke in orange peel residues.

Feed or residue	**Hard coke at 800°C under N_2 from TGA (%)**
Orange peel feed	28.5
Residue after 150°C, 200°C, 10mL/min	28.5
Residue after 150°C, 200°C, 20mL/min	24.4
Residue after 150°C, 200°C, 30mL/min	22.8
Residue after 150°C, 225°C, 10mL/min	45.4
Residue after 150°C, 225°C, 20mL/min	42.8
Residue after 150°C, 225°C, 30mL/min	40.8
Residue after 150°C, 250°C, 10mL/min	42.7
Residue after 150°C, 250°C, 10mL/min	42.7
Residue after 150°C, 250°C, 10mL/min	36.4

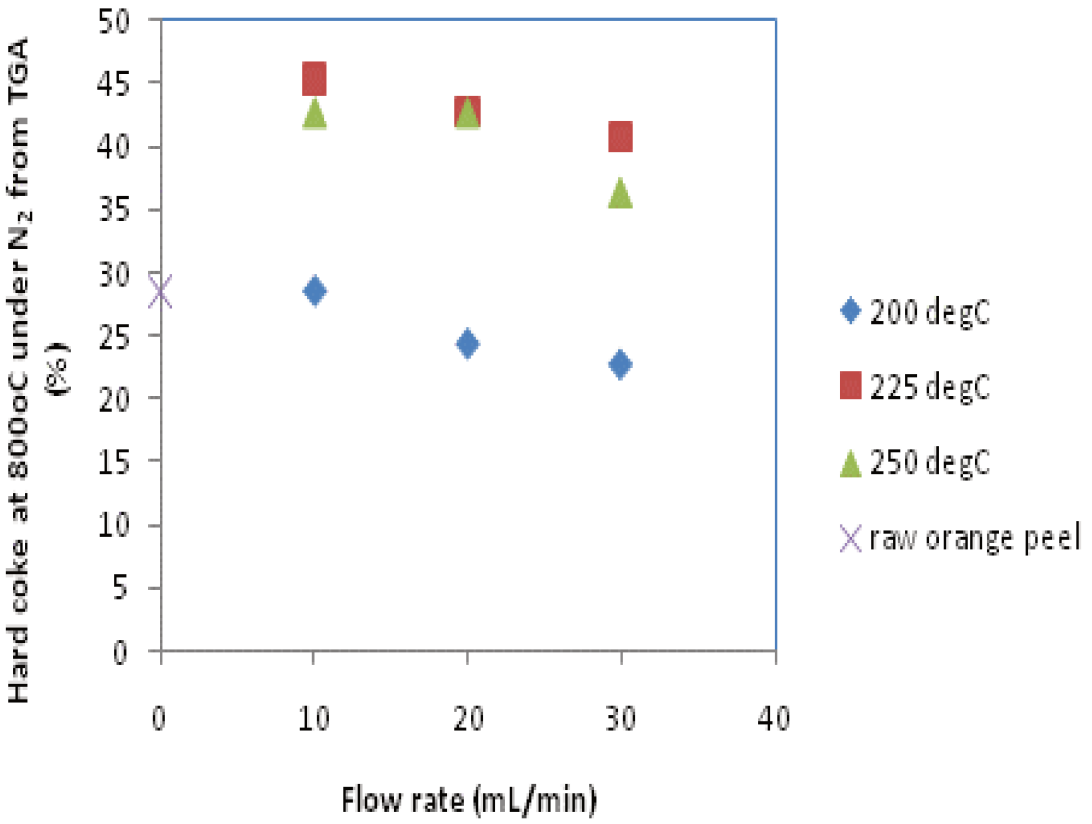


Figure S2 Hard coke in the solid residues fro hydrothermal treatment of orange peel under different water flow rates. Hard coke percentage of weight remaining after thermal decomposition under nitrogen at 600°C, from TGA.

Table S3 DTG peak positions and widths for pure biomass components.

Component	Peak center (°C)	Peak base (°C)	Est. Peak FWHM (°C)	Ref.
Lignin	320-350	150-550	160	Watkins et al.
Hemicellulose (straw) Xylan	283 270-309	175-350	60 40	Peng and Wu Cai et al
Cellulose	330 323-367	280-350	40 40	Fisher et al. Cai et al.
Char	400	260-700	100	Fisher et al.
Pectin	250	210-300	20	Einhorn-Stoll and H. Kunzek
limonene	140, 160	50-175	30	Fuenmayor et al.

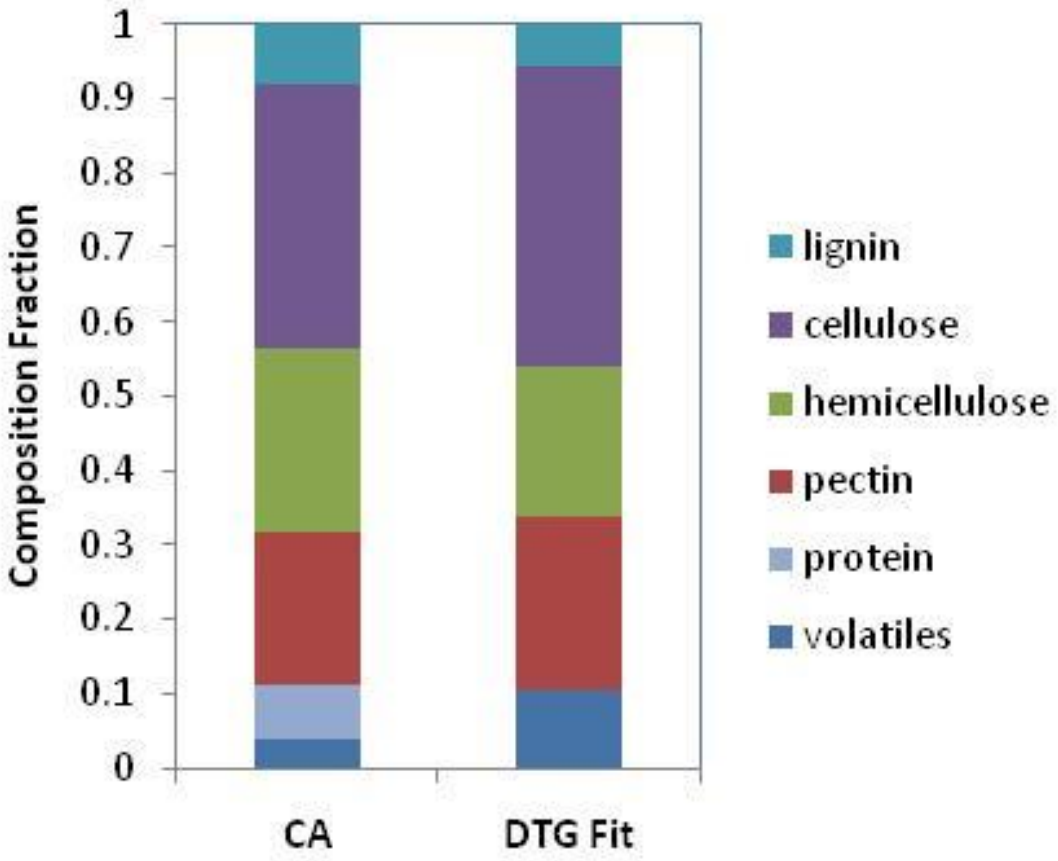


Figure S3. Composition of raw orange peel from chemical analysis and fitting the DTG thermogram. For chemical analysis volatiles is cyclohexane soluble fraction, hemicelluloses includes ethanol soluble sugars and hemicelluloses fraction of sugars, lignin includes Klason and insoluble fractions. Ash content is excluded from the composition fractions. For DTG fit, hemicelluloses fraction is from fit of two peaks at 235 and 273°C.

Table S4 Infrared spectra band positions of Citrus Peel from literature.

Biomass Material	Band positions (cm^{-1})	Assignment	Ref.
H-pectin (orange peel)			Bichara et al.
		C-O-C torsion	
	534		
	637		
	686	Pyranoid ring	
	700sh	COH deformation (ring)	
	738	COH deformation (COOH)	
	760sh	Ring breathing	
	790	COH ring	
		CCOCO	
	888	CCH bending	
	915		
	954	CCH bending	
	990sh	COOH bending	
	1034	C-C, C-O stretching	
		C-C, C-O stretching	
	1085	C-O stretch + OH bend	
	1119	C-C, C-O stretching	
	1156	COC stretch glyc	
	1226	OH bending (COOH)	
	1253	CH bending	
	1335	CH bending	
	1403	COH bending (COOH)	
	1645	H2O bending	
	1740	C=O (COOH)	
	2653	OH stretch (COOH)	
	2942	C-H stretch	
	3493	OH stretching	
Grapefruit peel	614		Iqbal et al.

	762	CH2 (polysaccharides)	
	1065	C-OH stretching (alcohol)	
	1400	COO- (symmetric)	
	1636	COO- (asymmetric)	
	1736	C=O	
	2925	CH stretching	
	3428	OH stretching	
Orange peel (whole)	1066	C-OH	Ng et al.
	3429	OH (pectin, cellulose)	
Orange waste (pulp)	1045	C-O-H, or C-O-R (alcohol ester)	Lopez-Velazquez et al.
	1428	-CH2- and CH3-	
	1620	C=C, aliphatic and/or unsaturated aromatic compounds	
	1736	C=O, esters	
	2925	CH stretching	
	~3500	OH stretching	

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11. Anexo

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