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Ederson Rossi Abaide

HIDRÓLISE SUBCRÍTICA DE PALHA E CASCAS DE ARROZ PARA OBTENÇÃO INTEGRADA DE AÇÚCARES FERMENTESCÍVEIS E MATERIAL ADSORVENTE

Santa Maria, RS
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Santa Maria, RS
2019

DEDICATÓRIA

Ao meu pai Silvio João Abaide, a minha mãe Cecília Margareth Rossi Abaide e ao meu irmão Anderson Rossi Abaide, que me oportunizaram o estudo, sempre me apoiando e acreditando na minha capacidade. Dedico a minha companheira Crisleine Perinazzo Draszewski pelo apoio incondicional, amor e paciência na etapa do doutorado.

Dedico também ao meu coorientador, Prof. Dr. Giovani Leone Zabot, que é para mim uma referência como ser humano e profissional.

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“A persistência é o caminho do êxito”

(Charles Chaplin)

RESUMO

HIDRÓLISE SUBCRÍTICA DE PALHA E CASCAS DE ARROZ PARA OBTENÇÃO INTEGRADA DE AÇÚCARES FERMENTESCÍVEIS E MATERIAL ADSORVENTE

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Nesta pesquisa, coprodutos da colheita e da manufatura do arroz, como palha e cascas, foram submetidos à hidrólise com água subcrítica com a finalidade de se obter um líquido hidrolisado contendo açúcares fermentescíveis e um resíduo sólido com capacidade de adsorção maior que a das biomassas *in natura*. Os ensaios foram realizados em uma unidade em escala de laboratório contendo um reator de hidrólise de 50 mL aquecido por resistência térmica, banhos de pré-aquecimento, sensores e controladores de temperatura, manômetros e válvulas de controle de pressão/vazão. Para os ensaios de hidrólise, foram estudadas as variáveis de processo: temperatura (180, 220 e 260°C) e razão mássica água/sólidos (7,5 e 15 g água/g biomassa inicial). A pressão foi fixada em 25 MPa e o tempo de reação total foi de 15 minutos. Várias respostas foram analisadas com o objetivo de verificar a melhor condição de processo, sendo as principais: rendimento cinético em açúcares redutores (AR), composições de açúcares fermentescíveis e inibidores, modificação na morfologia e na área superficial das biomassas hidrolisadas e capacidade de adsorção do sólido residual. Nos experimentos com palha de arroz, os resultados mostraram o maior rendimento de AR de 33,4 ± 4,3 g/100 g de palha de arroz em base seca sob 220°C e razão mássica água/sólidos de 7,5 g água/g biomassa inicial (220°C / R-7,5; corresponde à vazão de 10 mL/min). Para as cascas de arroz, os AR tiveram maior rendimento de 18,3 ± 2,3 g/100 g de cascas de arroz em base seca também na condição de 220°C / R-7,5. As análises do meio hidrolisado por cromatografia líquida de alta eficiência indicaram a presença de arabinose, celobiose, glicose e xilose, além de inibidores como furfural e hidroximetilfufural. Avaliando-se a área superficial para a palha de arroz hidrolisada, observou-se que a melhor condição foi a de 260°C / R-7,5, com área superficial de 10,60 m^2/g. Para as cascas de arroz, a maior área superficial foi de 24,24 m^2/g, verificada para a mesma condição: 260°C / R-7,5. A capacidade de adsorção dos sólidos restantes do processo de hidrólise subcrítica foi avaliada frente ao composto 2-nitrofenol. A palha de arroz submetida à hidrólise subcrítica na condição 180°C /R-7,5 apresentou maior capacidade de adsorção em pH 7 (92.97 ± 1.31 mg/g).

Palavras-chave: Arroz, coprodutos, integração de processos, tecnologia subcrítica, adsorção.

ABSTRACT

SUBCRITICAL HYDROLYSIS OF RICE STRAW AND HUSKS FOR OBTAINING FERMENTABLE SUGARS AND AN ADSORBENT MATERIAL

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In this research, coproducts from rice harvesting and manufacturing, such as straw and husks, were submitted to subcritical water hydrolysis in order to obtain a hydrolyzed liquid containing fermentable sugars and a solid residue with an adsorption capacity higher than the fresh biomass. The assays were carried out at a laboratory-scale unit containing 50 mL hydrolysis reactor heated by thermal resistance, preheating baths, temperature sensors and controllers, pressure gauges, and pressure/flow control valves. The following process variables were studied: temperature (180, 220 and 260°C) and water / solids mass ratio (7.5 and 15 g water/g initial biomass). The pressure was set at 25 MPa and the total reaction time was defined as 15 minutes. Some responses were analyzed in order to identify the best process condition: reducing sugar (RS) yield, compositions of fermentable sugars and inhibitors, modification in the morphology and surface area of the hydrolyzed biomass, and residual adsorption capacity. In the experimental assays with rice straw, the highest RS yield of 33.4 ± 4.3 g/100 g rice straw (dry basis) was obtained at 220°C and water / solids mass ratio of 7.5 g water/g initial biomass (220°C / R-7.5; it corresponds to the flow rate of 10 mL/min). For rice husks, the best yield of RS was 18.3 ± 2.3 g/100 g of rice husks (dry basis) in the condition of 220 °C / R-7.5. The analysis of the hydrolyzed medium by high performance liquid chromatography indicated the presence of arabinose, cellobiose, glucose and xylose, and also inhibitors such as furfural and hydroxymethylfufural. When the surface area for the hydrolyzed rice straw was evaluated, the best condition was 260°C / R-7.5, with a surface area of 10.60 m^2/g. For rice husks, the highest surface area was 24.24 m^2/g for the same condition: 260°C / R-7.5. The rice straw submitted to subcritical water hydrolysis at 180°C / R-7.5 (g water / g initial biomass) presented the highest adsorption capacity of 2-nitrophenol at pH 7 (92.97 ± 1.31 mg/g).

Keywords: Rice, coproduct, process integration, subcritical technology, adsorption.

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LISTA DE ABREVIATURAS E SIGLAS

AR	Açúcares Redutores
BET	Brunnauer, Emett e Teller
CLAE	Cromatografia Líquida de Alta Eficiência
CrI	Índice de Cristalinidade
DNS	Ácido Dinitrosalicílico
FTIR	Espectrofotometria no Infravermelho com Transformada de Fourier
HMF	Hidroximetilfurfural
MEV	Microscopia Eletrônica de Varredura
RMN	Ressonância Magnética Nuclear
RPM	Rotação por Minuto
TGA	Análise Termogravimétrica

Sumário

- CAPÍTULO 1 -

ESTRUTURA DA TESE, INTRODUÇÃO, CONSIDERAÇÕES ACERCA DO ESTADO DA ARTE E OBJETIVOS

1.1 ESTRUTURA DA TESE

Nesta tese, as etapas de desenvolvimento do projeto de pesquisa estão apresentadas em 6 capítulos. Neste **capítulo 1** – ESTRUTURA DA TESE, INTRODUÇÃO, CONSIDERAÇÕES ACERCA DO ESTADO DA ARTE E OBJETIVOS – são apresentados, sucintamente, o tema principal do estudo, os objetivos pretendidos e as etapas envolvidas para a sua realização. As atividades propostas e realizadas são apresentadas na Figura 1. A parte experimental da pesquisa foi desenvolvida no LAPE (Laboratório de Engenharia de Processos Agroindustriais) (Cachoeira do Sul, RS) e no Laboratório Biotec Factory (Santa Maria, RS).

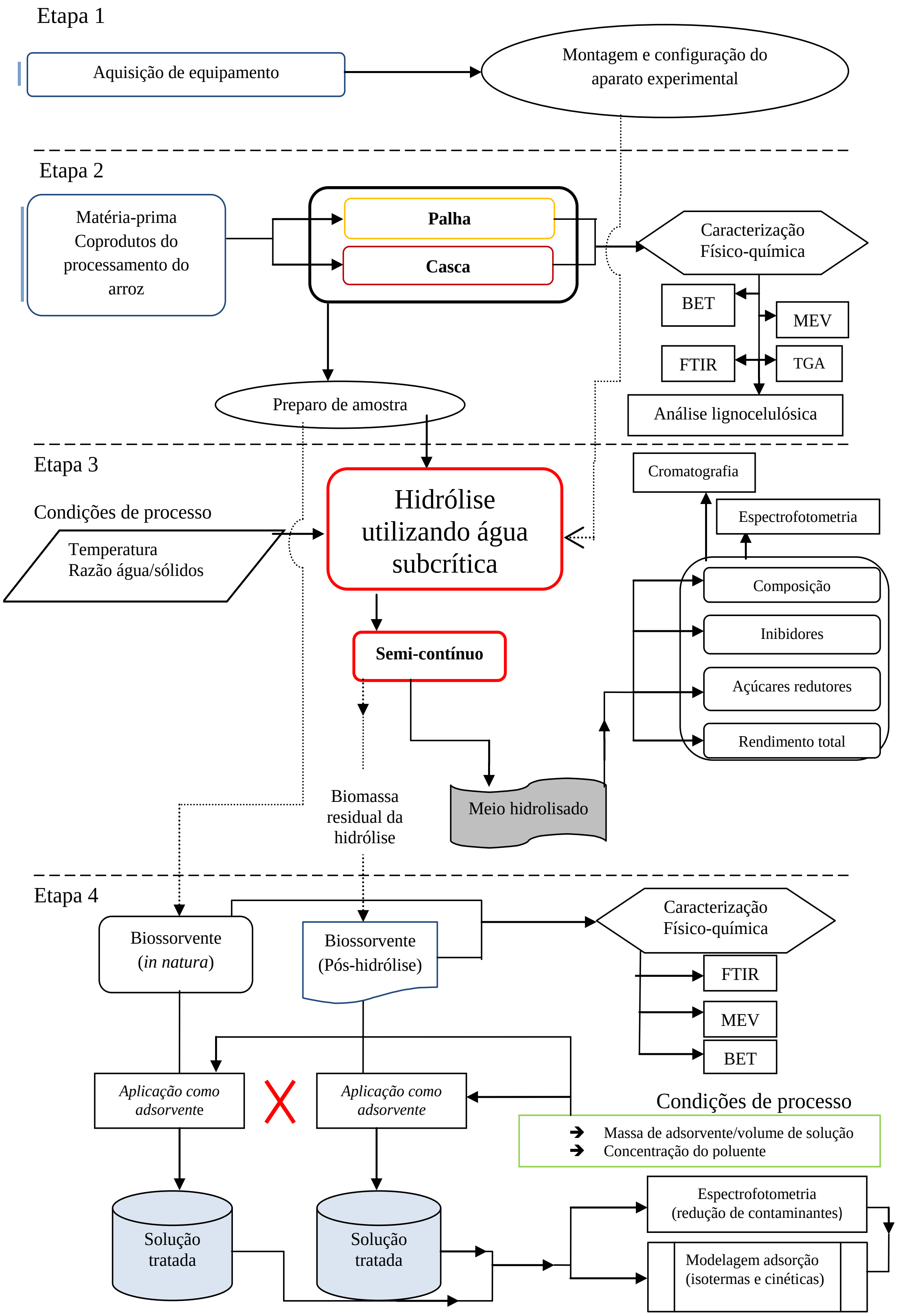
No **capítulo 2** – REASONS FOR PROCESSING OF RICE COPRODUCTS: REALITY AND EXPECTATIONS – encontra-se uma revisão da literatura de tecnologias utilizadas para o processamento dos coprodutos do arroz. No presente artigo são apresentadas as características principais dessas biomassas, como formas de processamento para que sejam obtidos produtos de maior valor agregado, como bioprodutos, combustíveis e materiais para diversas aplicações.

No **capítulo 3** – SUBCRITICAL WATER HYDROLYSIS OF RICE STRAW IN A SEMI-CONTINUOUS MODE – são apresentados os resultados experimentais da pesquisa envolvendo hidrólise com água no estado subcrítico da palha de arroz visando à obtenção de açúcares fermentescíveis. Foram avaliadas a razão água/sólido e a temperatura do processo, discutindo os resultados com foco na aplicação industrial. Também foi estudado o efeito do comportamento transiente da temperatura (reator em aquecimento) sobre os rendimentos dos açúcares obtidos. As principais respostas foram rendimento mássico (g de açúcares/100 g de palha) e eficiência (g de açúcares/100 g de celulose e hemiceluloses).

No **capítulo 4** – OBTAINING FERMENTABLE SUGARS AND BIOPRODUCTS FROM RICE HUSKS BY SUBCRITICAL WATER HYDROLYSIS IN A SEMI-CONTINUOUS MODE – também são apresentados os resultados experimentais da pesquisa envolvendo hidrólise com água no estado subcrítico. Entretanto, as biomassas utilizadas foram cascas de arroz. O enfoque desta etapa foi avaliar a razão água/sólido e a temperatura do processo, discutindo os resultados com base nos açúcares fermentescíveis e um posterior uso do caldo hidrolisado em fermentação para produção de etanol. Também foi estudado o efeito do comportamento transiente da temperatura (reator em aquecimento) sobre os rendimentos dos açúcares obtidos, explicitando quais açúcares foram obtidos.

As principais respostas foram explicitadas em rendimento mássico (g de açúcares/100 g de cascas) e rendimento em volume de solução (g de açúcar/L), sendo que os açúcares estudados foram glicose, celobiose, xilose e arabinose. Os coprodutos que restaram do processo de hidrólise subcrítica para ambas as biomassas também são estudados. Logo no **capítulo 5** – ADSORPTION OF 2-NITROPHENOL USING RICE STRAW AND RICE HUSKS HYDROLYZED BY SUBCRITICAL WATER – as biomassas de palha e cascas de arroz que restaram do processo de hidrólise subcrítica (coprodutos) são avaliadas em relação capacidade de adsorção de 2-nitrofenol. Os ensaios de adsorção foram divididos em duas etapas. Na primeira etapa avaliou-se a capacidade de adsorção de todas as biomassas de palha e cascas de arroz que foram obtidas em diferentes condições experimentais de hidrólise. Na segunda etapa foram realizados ensaios de adsorção em cascas e palha de arroz *in natura* e as provenientes de uma única condição de hidrólise subcrítica (para cada biomassa), avaliando os modelos cinéticos e isotérmicos e os principais parâmetros termodinâmicos.

No **capítulo 6** – DISCUSSÃO, CONCLUSÃO GERAL E SUGESTÕES PARA TRABALHOS FUTUROS – são resumidos os principais resultados oriundos do desenvolvimento do projeto apresentado nesta tese. Esse capítulo reúne as informações mais relevantes obtidas nos capítulos 2 a 5, bem como apresenta algumas sugestões de pesquisas futuras.



Fonte: Autor

Figura 1 - Fluxograma representativo do estudo com todas as etapas da pesquisa

1.2 INTRODUÇÃO

A produção de arroz (*Oryza sativa* L.) é uma das atividades agrícolas mais importantes em todo o mundo, com produção anual estimada em cerca de 480 milhões de toneladas, sendo a terceira “commodity” agrícola mais produzida no mundo, atrás apenas de cana-de-açúcar e milho (USDA, 2015). Em um contexto global, o Brasil é o maior produtor de arroz fora do continente asiático. Na safra de 2015/2016, a área plantada com arroz no Brasil era de aproximadamente 2 milhões de hectares, e a produção foi de cerca de 12 milhões de toneladas. Embora a produção esteja distribuída por todo o país, a maioria desta está concentrada na região centro-sul e, para esta região, cerca de 10 milhões de toneladas são colhidas em cada safra (CONAB, 2016).

De acordo com FAO (2016), a produção mundial de arroz aumentou consideravelmente de 2007 (660 milhões de toneladas) para 2014 (746 milhões de toneladas). Consequentemente, a quantidade de resíduos gerados na produção e beneficiamento do arroz também vêm aumentando nos últimos anos. Quantidades significativas de palhas e cascas de arroz são produzidas anualmente em fazendas e indústrias de beneficiamento do arroz, mas são economicamente subutilizadas (Zalengera *et al.*, 2014). A palha e as cascas de arroz que sobram no local de cultivo e nas unidades de processamento de arroz, respectivamente, passam por um processo gradual de biodegradação que libera metano (CH_4) (Brodt *et al.*, 2014).

A palha e as cascas de arroz são utilizadas pelas próprias famílias produtoras para cozinhar e aquecer água, e grandes quantidades são queimadas em campos abertos para preparar a terra para a próxima estação de plantio. Nas indústrias de processamento de arroz, as cascas são usadas como fonte de energia em caldeiras e para gerar energia elétrica (Shafie *et al.*, 2013; Iye e Bilsborrow, 2013).

De acordo com FAO (2016) e Koopmans e Koppejan (1997), a produção mundial de arroz gera aproximadamente 283 milhões de toneladas anuais de palha de arroz nos campos. A palha de arroz tem capacidade calorífica um pouco inferior (15,2 MJ/kg) à do carvão vegetal (23,1 MJ/kg) (Yang *et al.*, 2017; Oliveira *et al.*, 2017). Além disso, a palha de arroz possui alto teor de metais alcalinos e metais alcalino-terrosos, que causam problemas de funcionamento em caldeiras, como formação de depósitos, incrustações e corrosão. De acordo com Eom *et al*. (2013), metais como Fe (269 μg/g) e Al (99 μg/g) também são encontrados em concentrações relativamente altas.

A casca de arroz é um coproduto gerado do processamento do arroz, representando aproximadamente 23% em massa do arroz coletado. A produção mundial anual deste coproduto é de aproximadamente 149 milhões de toneladas, dos quais 70% são utilizadas para a produção de energia por meio da queima deste material (Regulatory, 2015). A casca do arroz é nutricionalmente pobre, sendo raramente usada como alimento animal.

A casca de arroz tem capacidade calorífica de 16,6 MJ/kg (Basu, 2006), e percentagem significativa de sílica (15 a 17%, em base mássica) (Marin *et al.*, 2015). Aproximadamente uma tonelada de casca de arroz pode gerar 800 kW.h de energia elétrica (Afzal *et al.*, 2011). De acordo com Chungsangunsit *et al.* (2005), as emissões de SO_2 e NO_X em usinas de casca de arroz são menores do que aquelas emitidas por meio da queima de carvão ou óleo, mas maiores do que as emitidas pelo uso de gás natural (Chungsangunsit *et al.*, 2005; Shah *et al.*, 2016).

A palha e as cascas de arroz são materiais lignocelulósicos compostos principalmente de celulose, hemiceluloses e lignina (Moliner *et al.*, 2016; Castro *et al.*, 2016). Os polímeros de celulose e hemiceluloses estão firmemente ligados à lignina através de ligações covalentes e de hidrogênio, o que torna a estrutura altamente robusta e recalcitrante à despolimerização (Limayem e Ricke, 2012). A composição química da palha e das cascas de arroz depende da variedade do grão e da época de plantio. É importante destacar que cada uma dessas matérias-primas representam um desafio tecnológico que precisa ser estudado individualmente devido à composição, à morfologia da micro estrutura vegetal, aos monossacarídeos presentes que constituem essas estruturas e ao tipo de conexões entre eles (Prado *et al.*, 2014).

Como exposto, a palha e as cascas de arroz tem grande utilização no aquecimento da água em caldeiras e ainda na geração de movimento de turbinas para produção de energia elétrica. Entretanto, devido a composição lignocelulósica dessas biomassas pode se pensar em tecnologias adequadas que realizem o seu processamento, de modo a obter produtos com valor agregado e a partir dos coprodutos sólidos restantes, realizar a queima para geração de energia. Isso implica em um maior reaproveitamento da palha e das cascas de arroz.

Há várias tecnologias de pré-processamento que visam à obtenção de produtos de valor agregado a partir de biomassas residuais. Entretanto, há uma série de características necessárias para que a biomassa proveniente destes pré-processamentos seja considerada industrialmente viável, dentre as quais: a tecnologia de pré-processamento deve ser conduzida com degradação mínima e com recuperação de componentes máximos; e a tecnologia deve ter baixa demanda energética ou ser conduzida de forma que a energia possa ser reutilizada em outras etapas do processo (Singh *et al.*, 2016; Hrnčič *et al.*, 2016). Uma destas tecnologias compreende a hidrólise subcrítica, que é considerada ambientalmente correta, pois utiliza água para conversão de biomassa em açúcares fermentescíveis (posterior produção de etanol), sendo capaz de alcançar consideráveis eficiências de conversão (Xu *et al.*, 2015). As tecnologias hidrotérmicas são consideradas ambientalmente corretas porque utilizam água para conversão de biomassa em insumos de interesse industrial, reduzindo a utilização de solventes orgânicos (Xu *et al.*, 2015). Uma das principais vantagens dessa tecnologia é a alta rapidez de reação quando comparada ao processo de hidrólise enzimática, e ainda a não-geração de resíduos tóxicos quando comparada à hidrólise ácida ou básica (Zhu *et al.*, 2016).

Água com condições próximas do seu ponto crítico (T_c = 374°C e P_c = 22 MPa) é um solvente alternativo para hidrólise da biomassa. Nas condições de alta pressão e alta temperatura, há maior facilidade de penetração da água na estrutura complexa de matrizes lignocelulósicas devido a sua baixa viscosidade e a sua alta difusividade. Ainda, há o aumento da constante de dissociação, tornando a água um ácido ou uma base forte, agindo como reagente, solvente e catalisador (Cocero *et al.*, 2018; Moreschi *et al.*, 2004).

É importante destacar que a escolha do uso da água em estado subcrítico ao invés do estado supercrítico para o processo de hidrólise pode ser atribuída a menor produção de compostos inibidores e produtos de degradação. Ao se utilizar a hidrólise da celulose com água em condição supercrítica, elevados rendimentos de oligossacarídeos são obtidos. Em contrapartida, há um elevado rendimento de produtos de fragmentação de glicose, como furfural, eritrose e outros produtos não fermentescíveis (Zhao *et al.*, 2009).

Outra maneira de agregar valor aos resíduos agroindustriais é por meio do uso desses como material adsorvente. A utilização de resíduos agroindustriais como adsorventes tem sido foco de estudos recentes, pois estes adsorventes apresentam inúmeras vantagens, como baixo custo, (levando-se em conta que são gerados em grandes quantidades) possibilidade de recuperação do adsorvato, regeneração do adsorvente e eficiência na descontaminação. Ainda podem ser submetidos a tratamento com determinados reagentes químicos para aumentar a capacidade de adsorção do material, devido a alterações em sua estrutura (Montanher, 2009).

Assim, é possível notar que alternativas podem ser propostas para aumentar a valorização desses coprodutos e tornar sustentável a sua utilização. Uma alternativa é integrar tecnologias de processamento para possibilitar a obtenção de açúcares fermentescíveis a partir da hidrólise da celulose e das hemiceluloses, e a obtenção de material adsorvente, que pode ser utilizado em processos de descontaminação de efluentes em indústrias de corantes, e para remoção de pesticidas, herbicidas, metais e efluentes que possuem elevada carga de poluentes que são dificilmente removidos em tratamentos primários e/ou secundários.

1.3 CONSIDERAÇÕES ACERCA DO ESTADO DA ARTE

É importante destacar que os trabalhos desenvolvidos até o momento, que tem como objetivo a hidrólise da casca e da palha de arroz, não tiveram como foco a reutilização integrada do material residual restante do processo, e que possui potencial adsorvente de moléculas orgânicas poluentes (Leng *et al.*, 2015). Além disso, a tecnologia que utiliza água no estado subcrítico para hidrolisar biomassas residuais ainda tem pouco estudo quando se propõe avaliar o processo em modos semi-contínuo ou contínuo (Prado *et al.*, 2016).

Alguns estudos realizados serviram como base para a fundamentação desta tese. Água no estado subcrítico foi utilizada em modo batelada para hidrolisar a palha de arroz. Foram obtidos rendimentos elevados em açúcares em curto intervalo de tempo quando se compara esse processo com a hidrólise enzimática (tempo longo) e com a hidrólise ácida (rendimento semelhante) (Lin *et al.*, 2015; Lau *et al.*, 2015).

Ainda, CO_2 supercrítico tem sido usado para modificar a estrutura da casca de arroz a fim de demonstrar mudanças positivas nessa estrutura e aumentar a capacidade de adsorção do material (Franco, 2016). O bagaço de cana-de-açúcar residual do processo de hidrólise com água subcrítica tem a morfologia de suas partículas modificada com aumento na área superficial, o que é um indício de aumento da capacidade de adsorção do bagaço de cana-de-açúcar (Lachos-Perez *et al.*, 2016).

Além disso, biomassas residuais do processo de hidrólise têm sido utilizadas de maneira escassa como material adsorvente. Em um exemplo, o resíduo de palha de arroz submetido à hidrólise enzimática foi reutilizado como material adsorvente de corante, mesmo apresentando baixo valor de área superficial (Kim *et al.*, 2014). Avaliando-se o reuso de biomassa que é gerada do processamento de hidrólise, pode-se observar que a casca de arroz que foi submetida a tratamento hidrotérmico a 260°C, utilizando água, água/etanol e somente etanol, apresentou suficiente modificação na sua área superficial para ser utilizada como adsorvente de corante catiônico (Leng *et al.*, 2015).

De forma geral, até o momento, não foram encontrados trabalhos na literatura, a partir das plataformas de buscas científicas (Scopus e ISI Web of Science, por exemplo), que reutilizam como adsorvente o resíduo da hidrólise com água subcrítica da palha e da casca de arroz. Assim, a proposta deste trabalho surge como alternativa inovadora, que busca integrar rotas de processamento para obtenção integrada de açúcares fermentescíveis e material adsorvente.

1.4 OBJETIVOS

1.4.1 Objetivo geral

O objetivo geral do estudo foi avaliar o processamento de palha e cascas de arroz por meio de hidrólise individual desses coprodutos com água subcrítica visando à obtenção de açúcares fermentescíveis e material adsorvente.

1.4.2 Objetivos específicos

- Caracterização da composição lignocelulósica, físico-química (FTIR), área superficial (BET) e morfológica (MEV) da palha e das cascas de arroz;
- Avaliação de condições de hidrólise de palha e cascas de arroz (individualmente) com água subcrítica por meio dos parâmetros temperatura e razão mássica de água/sólidos para operação em modo semi-contínuo;
- Caracterização do meio hidrolisado em termos de rendimento e composições de açúcares fermentescíveis, inibidores e ácidos orgânicos;
- Caracterização do material sólido obtido após a hidrólise em termos de composição lignocelulósica, morfologia (MEV), área superficial (BET), degradação sob temperatura (TGA) e avaliação dos grupos funcionais (FTIR);
- Análise da capacidade de adsorção do composto 2-nitrofenol por meio de isotermas e cinéticas de adsorção utilizando do material sólido hidrolisado da casca e da palha de arroz e comparação com o material *in natura*.

- CAPÍTULO 2 -

REVISÃO DA LITERATURA

REASONS FOR PROCESSING OF RICE COPRODUCTS: REALITY AND EXPECTATIONS

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Abstract

The increasing interest in reusing coproducts from rice crops, such as straw, husks, and bran, has motivated the writing of this review. The aim is to provide a critical and constructive overview of the main advantages and technological challenges for further processing such coproducts within the biorefinery concept. Current studies and applications are presented and discussed, which mainly include the use of such coproducts on energy and biofuel generation, production of building blocks, adsorption of recalcitrant substances, animal feeding and fertilization crops, extraction of bioactive compounds, and production of carbon-based and silica-based materials. Furthermore, the reality and expectations on processing steps (chemical, biochemical, and thermochemical routes), conventional and novel technologies and value-added products/derivatives with interest in several industrial fields are highlighted. As expectations, some companies and government projects are innovating and trying to use sub/supercritical water hydrolysis as a promising technology with high potential to decompose rice lignocellulosic biomass into small-chain sugars and bioproducts. Overall, as a future outlook for making most of the processing routes of rice coproducts more feasible, more infrastructure and scientific researches are needed to overcome some barriers and drawbacks that still exist in the subject presented in this review.

Keywords: Energy, biorefinery, rice husks, rice straw, biofuel, lignocellulosic biomass.

2.1 INTRODUCTION

Rice (*Oryza sativa* L.) production is one of the most important agricultural activities in the world. Rice is the third most-produced agricultural commodity in the world, behind only the sugarcane and corn commodities (USDA, 2015). China is the largest rice producer (146 million tons) followed by India (103 million tons). These two countries are responsible for approximately 53% of global rice production. In Asia, Indonesia has also a high production (35 million tons), followed by Vietnam (28 million tons) (FAO, 2016). In a global context, Brazil is the largest producer of rice outside the Asian continent. In the harvest of 2015/2016, the rice cultivated area in Brazil was approximately 2 million hectares and the production was approximately 12 million tons. Although the production is distributed throughout the country, the Brazilian Center-South region is responsible for more than 80% of production, with approximately 10 million tons produced each year (CONAB, 2016).

Production of rice in the world has increased in the last few years, going from 660 million tons (2007) to 746 million tons (2014). Consequently, the amount of coproducts generated from rice crop has increased as well (FAO, 2016). Large quantities of rice straw and husks are produced annually in rice farms and processing mills but they are economically underutilized. Although rice cultivation is different from each country, the burning of straw and husks is a common practice. However, the burning of open-pit waste contributes to the emission of hydrocarbons aromatics and dioxins that are harmful to the environment and human health because of their carcinogen potential (Gadde *et al.*, 2009). Another coproduct from rice production is the rice bran that is generated from the process of polishing rice to produce parboiled rice.

Rice straw, husks, and bran contain cellulose, hemicelluloses and lignin with some amounts of proteins, starch, extractives and inorganics (Potumarthi *et al.*, 2013). The most frequent use of rice straw and husks is as a fertilizer additive and in the rice processing plants for the production of thermal and electric energy through steam boilers. Overall, these coproducts are not nutritive and could not be used directly in animals feed. Accompanying the increase of agricultural biomass produced worldwide, the increase of energy and fuel requirements is encouraging the development of researches for using lignocellulosic biomass as a sustainable source of bioproducts and renewable energy.

2.2 SCOPE

The complexity of rice coproducts (physical structure and chemical composition) requires a systematic research and development to better understand the right pre-processing technology for further processing the coproducts aiming at obtaining value-added products and derivatives. Based on this context, the objective of this paper is to provide a comprehensive review of rice coproducts. The methodological approach contains four main parts. The first part (Section 2.3) contains a general characterization of rice straw, husks, and bran. In this part, the main properties and composition of such rice coproducts are presented and discussed. The second part (Section 2.4) is focused on studies for processing rice coproducts and current applications of such coproducts, as in energy production, animal feed and fertilization, use in the formulation of cement and use as a component of several other materials. The third part (Section 2.5) deals with the main products and derivatives obtained from rice coproducts using consolidated and/or novel technologies, such as fermentable sugars, biofuels, biochemical compounds, inorganic materials, energy, and biogas. The fourth part (Section 2.6) includes the reality and expectations about pre-processing steps, treatment technologies, and products with interest in several industrial fields. Therefore, the current applications are critically overviewed and the trends and advances in technology are explored with the purpose to suggest a way forward in a near future.

2.3 RICE COPRODUCTS

Rice processing covers the operations for the production of graded and polished white rice. The main solid coproducts generated during its harvesting and processing are rice straw, husks, and bran (**Fig. 2**). The coproduct remaining in the field after the harvesting step is the straw (0.38 tons for each ton of rice harvested) (Koopmans e Koppejan, 1997). The coproducts generated during the processing are the husks (20%) and bran (8%) (Dechere e Korver, 1996). Therefore, a brief evaluation of these coproducts is interesting when it is desired to know their potentialities in the production of value-added products, bioenergy, and derivatives.

2.3.1 Rice straw

Rice straw is one of the most abundant and less valuable lignocellulosic materials from rice crop, accounting for approximately 283 million tons per year around the world (Shafie *et al.*, 2013). Despite its abundant supply, there are some disadvantages such as a low nutritional value and high inorganic content, which limits its use for animal feed (Eom *et al.*, 2013). The low-quality dietary fibers are unsuitable for being used as animal forage. Although rice cultivation is different from each country, the burning of rice straw occurs in practically all producing countries with the objective of soil remineralization and weed control. However, the burning of open-pit waste contributes to the emission of hydrocarbons aromatics and dioxins that are harmful to the environment (Gadde *et al.*, 2009).

Rice straw has a lower heating value (15.2 MJ/kg) when compared to charcoal (23.1 MJ/kg) (Yang *et al.*, 2017). In addition, rice straw presents problems when subjected to combustion recovery, due to the high content of alkali metals (Fe: 269 µg/g; Al: 99 µg/g) (Eom *et al.*, 2013), alkaline earth metals, and silica. These substances cause problems of boiler operation, such as the formation of deposits, incrustations, and corrosion (Calvo *et al.*, 2012), which limits the use of fresh rice straw as a direct source of energy. In such sense, the knowledge of basic characteristics of biomass is the key to the successful selection of treatment technology aiming at the conversion of coproducts in energy and value-added products. Therefore, the following sub-sections present properties and composition of rice straw.

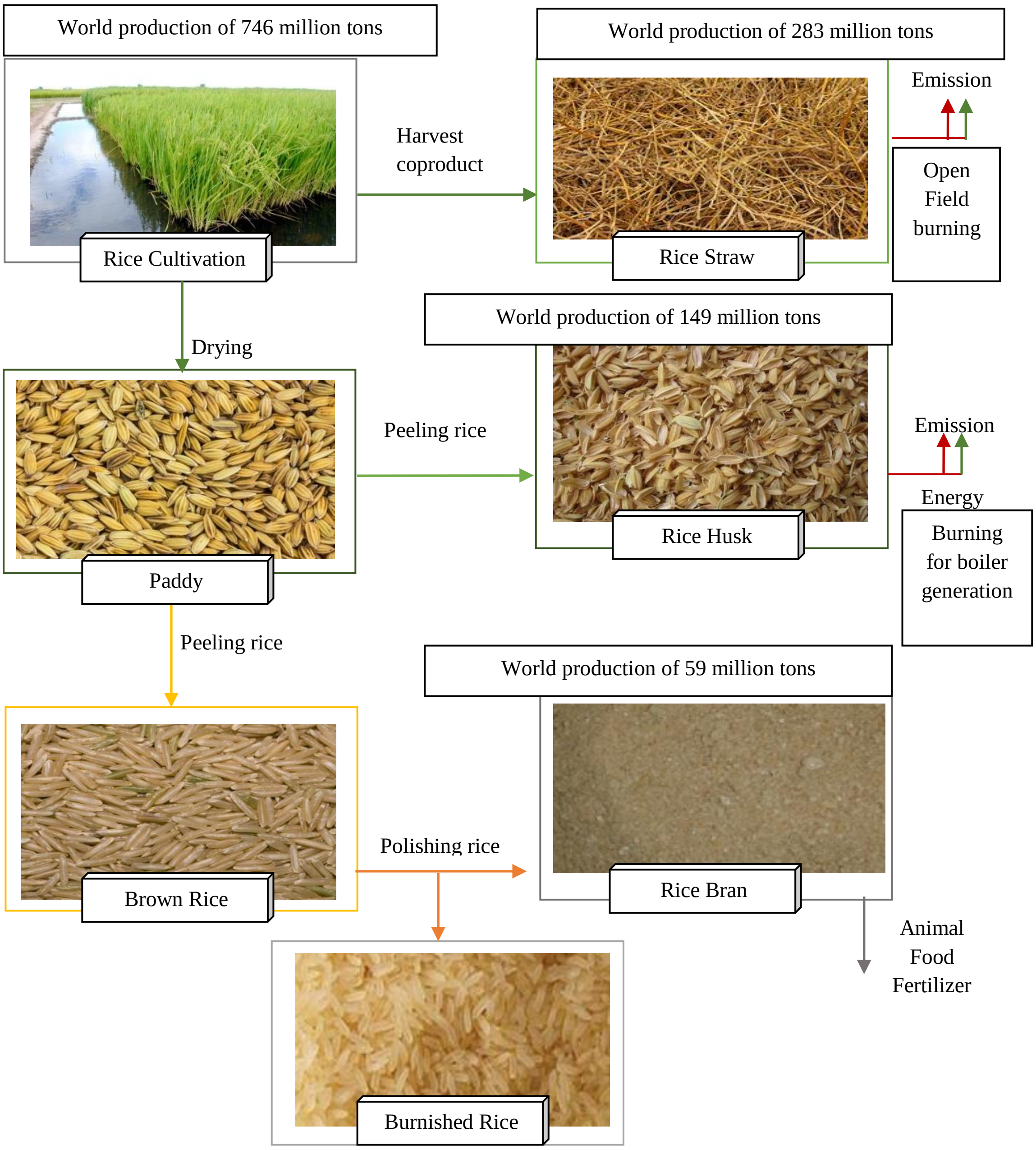


Figure 2 - Steps of rice processing and its coproducts generated from the 2014 annual production; data according to FAO (2016)

2.3.1.1 Proximate and ultimate analyses

The composition and properties of biomass can be described in terms of proximate and ultimate analyses (**Table 1**).

Table 1 - Data of proximate and ultimate analyses of rice straw

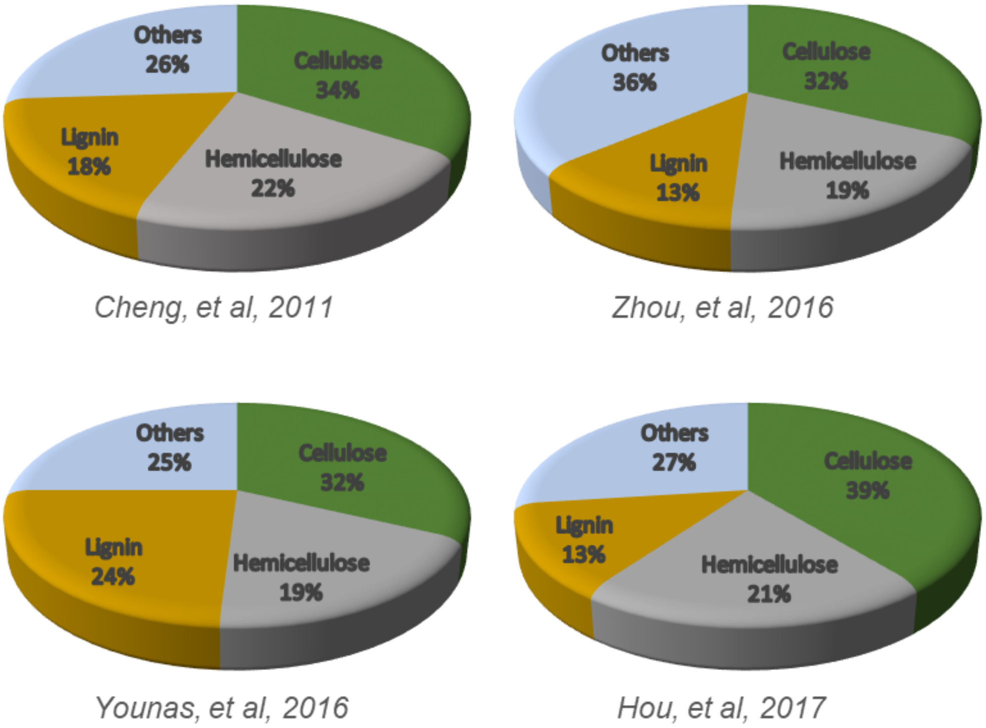
Proximate analysis (wt.%)					
Moisture	Ash	Volatile	Fixed carbon	Reference	
5.99	15.84	71.55	6.62	(Yang *et al.*, 2017)	
-	9.93	71.36	18.71	(Chen *et al.*, 2016)	
-	9.60	75.05	15.35	(Ding *et al.*, 2017)	
13.06	9.22	66.75	10.97	(Chiang *et al.*, 2016)	
Ultimate analysis (wt.%)					
C	H	O	N	S	Reference
46.89	6.21	45.57	1.11	0.23	(Chen *et al.*, 2016)
44.08	6.24	38.57	1.13	0.38	(Ding *et al.*, 2017)
35.61	5.49	35.22	0.9	0.35	(Chiang *et al.*, 2016)
44.23	5.11	39.57	0.89	0.27	(Chen *et al.*, 2017)

The proximate analysis provides the fuel properties on a dry basis, volatile matter and fixed carbon as well as ash content of the material. The volatile substances released from the decomposition reactions contain a series of gaseous molecules of H_2, CO and CO_2 together with other hydrocarbons. The rate of decomposition and the released gas composition is dependent upon temperature and the heating rate of the decomposition reaction. Pyrolysis is used to describe the decomposition reactions. The ultimate analysis provides the elemental composition of biomass. It is performed by the complete combustion of a fuel, with the composition of the final products of combustion analyzed and the main elements of the solid biomass determined (Anukam *et al.*, 2016).

In general, **Table 1** shows a variation in composition for samples harvested in different regions. When comparing the results for the different parameters, rice straw usually contains more volatile matter, which results in a lower char yield when rice straw is combusted or gasified (Qian *et al.*, 2014). Furthermore, it is evident that the main constituents of rice straw are C and O, with a negligible amount of H. The amount of C and O implies high reactivity when used with fuel in a thermochemical conversion system such as gasification (Moliner *et al.*, 2016).

2.3.1.2 Lignocellulosic composition

Rice straw is a lignocellulosic material mainly composed of cellulose, hemicelluloses, lignin, and silica (Castro *et al.*, 2016) (**Fig. 3**). Polymers of cellulose and hemicelluloses are firmly linked to the lignin through covalent and hydrogen bonds, which makes the structure highly robust and recalcitrant to depolymerization (Limayem e Ricke, 2012). The effective utilization of the lignocellulosic material would play a significant role in the economic viability of ethanol processing. In nature, cellulose fibers are embedded in a matrix of other structural biopolymers, primarily hemicelluloses, and lignin. Characteristics such as the crystallinity of cellulose, accessible surface area, protection by lignin, and heterogeneous characteristic of the biomass particles contribute to the recalcitrance of this type of biomass (Zabed *et al.*, 2016). The lignin is the most abundant renewable feedstock consisting of aromatics and its valorization can enable novel uses as value-added chemicals and fuels (Singh *et al.*, 2014).



Cheng, et al, 2011

Zhou, et al, 2016

Younas, et al, 2016

Hou, et al, 2017

Figure 3 - General lignocellulosic composition of rice straw

According to **Figure 3,** some variation in the proportions of structural constituents of rice straw is seen because the chemical composition of rice straw depends on rice varieties, region of cultivation, and growing season. Unfortunately, large variations in composition are considered a disadvantage because they affect the consistency and yield of final products. Therefore, the compositional analysis and structural characterization are the key factors that influence the feasibility of rice straw utilization.

2.3.2 Rice husks

Rice husks are a coproduct generated from rice peeling off, accounting for approximately 23% of rice crop weight. Annual worldwide production of this coproduct is approximately 149 million tons, which approximately 70% is most likely used for energy production by its burning (FAO, 2016). The heating value (16 MJ/kg) is similar to rice straw (Yank *et al.*, 2016). The emissions of SO_2 and NO_X in rice husks power plants are lesser than in coal and oil-fired power plants, but higher than in natural gas plants. In addition, the emission of CO_2 from the combustion of this coproduct is low because rice husks do not contribute to global warming, while the CO_2 produced in the combustion is consumed in the rice crop (Tsai *et al.*, 2007). Rice husks are also used for silica production (Shah *et al.*, 2016). Following the standard presented in the previous section for rice straw, the following sub-sections present properties and composition of rice husks.

2.3.2.1 Proximate and ultimate analyses

Table 2 shows that rice husks have a higher amount of volatile material when compared to the other parameters. This is directly related to the low amount of charcoal generated when the rice husks are submitted to the pyrolysis and gasification processes (Qian *et al.*, 2014). However, the ash content and the fixed carbon content in rice husks are (on average) high. Furthermore, the volatile material increases as the number of fixed carbon decreases (low carbon residue) (Hossain *et al.*, 2017; Lim *et al.*, 2016).

Another way of evaluating the potential of a biomass to be used in thermochemical routes is through ultimate analysis. Thus, **Table 2** presents the values for C, H, O, N and S in rice husks reported by recent scientific studies. These elements constitute pyrolytic gases, which are fuels with high energy value and can supply half of the maximum energy demanded during the pyrolysis (Ningbo *et al.*, 2015).

Table 2 - Data of proximate and ultimate analyses of rice husks

Proximate analysis (wt.%)

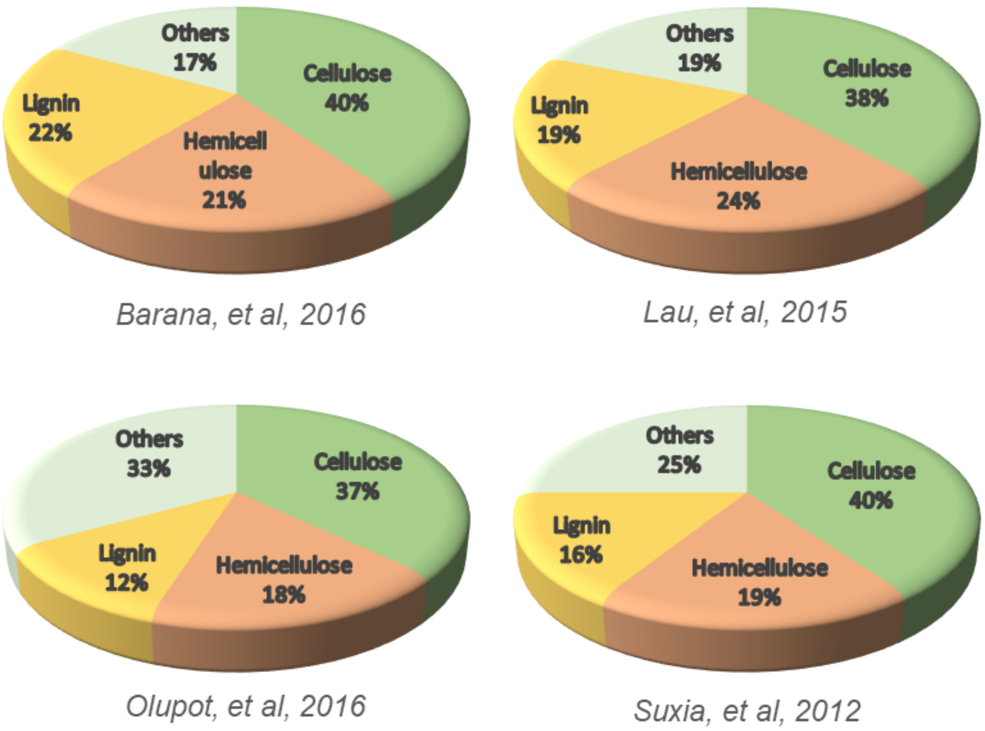
Moisture	Ash	Volatile	Fixed carbon	Reference
8.54	10.41	65.45	15.60	(Hossain *et al.*, 2017)
16.50	5.87	65.13	12.50	(Lim *et al.*, 2016)
-	22.07	62.84	15.09	(Ahiduzzaman e Islam, 2015)
5.30	17.38	62.47	14.85	(Wu *et al.*, 2015)

Ultimate analysis (wt.%)

C	H	O	N	S	Reference
34.48	6.60	44.05	-	-	(Hossain *et al.*, 2017)
43.06	6.08	46.6	4.26	-	(Huang *et al.*, 2013)
46.18	6.08	45.02	2.62	0.10	(Wang *et al.*, 2016)
42.60	5.20	51.30	0.10	-	(Wu *et al.*, 2015)

2.3.2.2 Lignocellulosic composition

An understanding of the physicochemical properties of lignocellulosic biomass is essential for the design and operation of associated biomass conversion processing facilities (Cai *et al.*, 2017). Cellulose and hemicelluloses, a major complex in rice husks, are an abundant renewable carbohydrate source that can be used for producing sustainable energy and chemicals. The cellulose and hemicelluloses are used as an ingredient for biofuel and paper (Pode, 2016). Cellulose is the most abundant substance, with values near to 40%. Rice husks are also a lignocellulosic material composed of lignin and silica (Prado *et al.*, 2014) (**Fig. 4**).



Barana, et al, 2016

Lau, et al, 2015

Olupot, et al, 2016

Suxia, et al, 2012

Figure 4 - General lignocellulosic composition of rice husks

2.3.3 Rice bran

Rice bran, a coproduct of rice processing, is obtained from the outer layer of the brown rice (husked), constituting approximately 10 wt.%. For the 2014 reference year, the rice bran produced was approximately 59 million tons (FAO, 2016; VanHoed *et al.*, 2006). Rice bran is a good source of bioactive phytochemical compounds that have antioxidant properties and are beneficial to health. It consists essentially of cellulose fibers, hemicelluloses and minerals (Bhattacharya, 2011; Sharif *et al.*, 2014). The heating value (20 MJ/kg) (Chou *et al.*, 2009) is larger than rice straw and husks. Differently from rice straw and husks, rice bran can be used for animal feed. In addition, rice bran has been used in the food industry for oil extraction as well (Soares *et al.*, 2016).

2.3.3.1 Proximate and ultimate analyses

Table 3 shows that rice bran has a higher amount of volatile material when compared to the other parameters. There are low data in the scientific literature regarding the amount of volatile material and fixed carbon in rice bran than in rice straw and husks. This is associated with the reduction in research that uses pyrolysis and/or gasification of rice bran. Another relevant aspect is that ash and moisture contents vary to a large extent, which may be related to different varieties of rice grain and crop region.

In the ultimate analysis, the main constituents are C and O with a low amount of H and a negligible amount of S. There are no relatively high changes in the proportion of compounds C, O, H and S when comparing the three rice coproducts (**Tables 1, 2** and **3**). This allows the use of them in some conversion processes aiming at producing biofuels and energy.

Table 3 - Data of proximate and ultimate analyses of rice bran

Proximate analysis (wt.%)

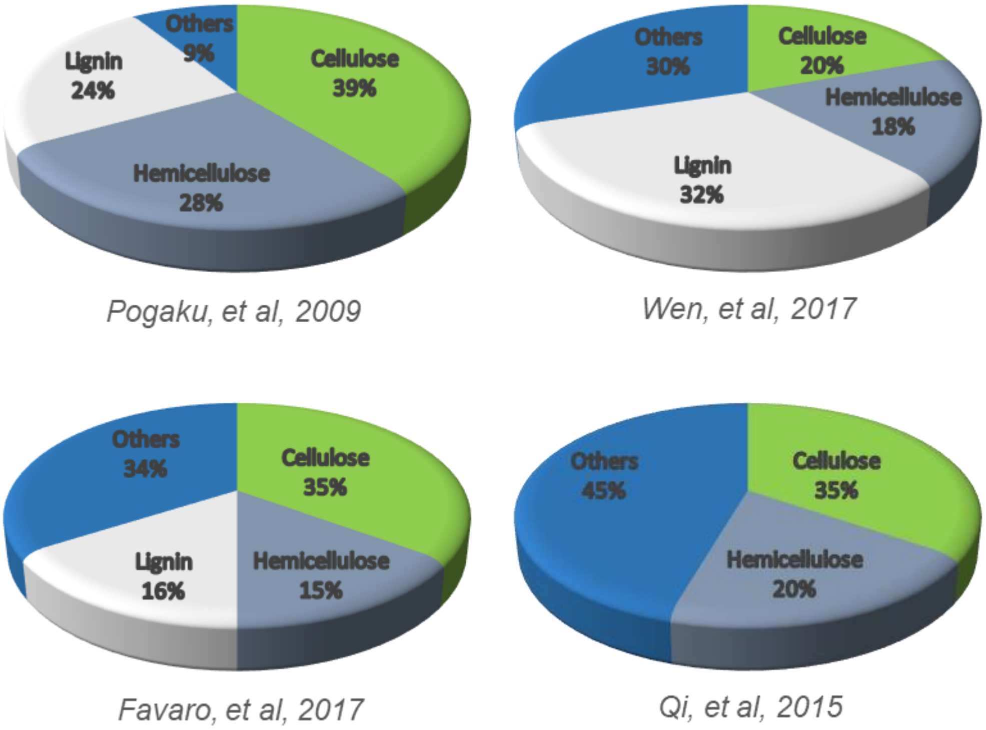
Moisture	Ash	Volatile	Fixed carbon	Reference
16.81	10.94	53.41	35.65	(Tsuchiya e Yoshida, 2017)
6.26	9.40	77.48	6.9	(Rotliwala e Parikh, 2011)
6.70	4.10	85.10	4.1	(Meher, 2015)
9.28	10.07	-	-	(Rafe e Sadeghian, 2017)

Ultimate analysis (wt.%)

C	H	O	N	S	Reference
51.48	5.23	42.62	0.67	-	(Rotliwala e Parikh, 2011)
55.01	8.11	33.77	2.72	0.39	(Chou *et al.*, 2009)
45.67	5.80	46.70	1.78	-	(Mohammed e Olugbade, 2015)
45.12	6.31	42.10	2.27	0.35	(Kanno *et al.*, 2011)

2.3.3.2 Lignocellulosic composition

Rice bran is also a lignocellulosic material mainly composed of cellulose, hemicelluloses, and lignin (**Fig. 5**). There is some variation in the contents of cellulose, hemicelluloses and lignin for rice bran when the different references are compared, which may be due to the method of sample preparation and determination of these structures or due to the crop region/rice variety.



Pogaku, et al, 2009

Wen, et al, 2017

Favaro, et al, 2017

Qi, et al, 2015

Figure 5 - General lignocellulosic composition of rice bran

2.4 CURRENT STUDIES AND WORLDWIDE APPLICATIONS OF RICE COPRODUCTS

This section presents a brief overview about current studies and worldwide applications of rice coproducts such as in energy production, animal feed, and fertilization, use in the formulation of cement, and use as a component of several other materials. The idea is to provide in this section some remarks related to the current use of rice coproducts in different areas. The details about products obtained with such applications are provided in section 2.4 and the technologies used to processing the lignocellulosic biomass are provided in section 2.5.

2.4.1 Construction sector

Since the end of 1960, scientific researches have been carried out on the utilization of rice husks ash in cement concrete as a partial substitute to ordinary Portland cement and/or fine aggregates. Consequently, scientific papers have been published and patents have been registered (Zerbino *et al.*, 2011). The production of concretes and mortars with such coproduct depends on burning the rice husks to obtain ashes of excellent characteristics (Mehta e Pitt, 1976). The use of supplementary materials in non-conventional fiber cement can provide increments in performance, both in the fresh and hardened state, improving its mechanical properties and durability. The use of pozzolan-like rice husks ash as a partial substitute to ordinary Portland cement allows the production of non-conventional fiber cement reinforced with natural fibers because it acts to reduce the alkalinity of the matrix and in the preservation of vegetable fibers if compared to a matrix composed exclusively of cement Portland (Bezerra *et al.*, 2006).

Another current use of rice husks in the construction sector is for designing particle boards as a building material that is lightweight, water-resistant, and of comparable strength to a commercially available medium-density particleboard. A project performed at the University of California focused on using rice husks from rice harvested in the Philippines. The intention is to produce from 2017 to 2019 rice husks plates of 4 in × 8 in to build the prototype houses and storage units for the own employees living in the Philippines who are involved in building them (Kawai *et al.*, 2018). Likewise, panels are being produced with rice husks. Considering the panels are a non-woody material, the main fundamental characteristic is the durability because they are immune to the attack of wood drills. The panels are also indicated to be used in the construction sector because they prevent water absorption and provide excellent resistance (Hancock e Chandramouli, 1974).

2.4.2 Energy generation

Some parts of rice straw and husks are used by families around the world to cook and to heat water. The remaining other larger part is currently burned in open fields to prepare the land for the next planting season or in the rice processing plants for steam production in boilers (Shafie *et al.*, 2013; Iye e Bilsborrow, 2013). An alternative to rice coproducts that are burned in open fields is to use them as compact biomass briquettes for power generation. The residual carbon contained in the rice husks ash can be used and the volume of ash generated in the rice processing can be reduced (Brand *et al.*, 2017). Other advantages of using the biomass in the form of briquettes include the easiness of handling, transport, and storage, increasing energy density, and improving the combustibility and uniform size (Tumuluru *et al.*, 2011). According to Moraes et al. (2017), 73 companies are currently producing biomass briquettes in Brazil, and the location of the briquetting industries is mainly in the South-Eastern and Southern regions of the country. These two regions are the most developed in this sector and they allocate more than 80% of the industries in this activity. Furthermore, the briquetting industries are located near to the major rice farms, which facilitate the transportation of coproducts to the processing locals.

Pellets can be produced with rice straw as well. This kind of pellets was first commercially produced in Nanporo town (Japan). For example, rice straw pellets are currently produced with a diameter of approximately 6 mm and burned in a biomass boiler (with a 400 kW capacity) at a public bathhouse (Ishii *et al.*, 2016). In another example, rice straw and husks collected in Karonga district in Malawi from rice farms and processing generated approximately 16.64 GW.h in the base year 2016. The electricity generated could meet approximately 17% of the energy demand of rural households in the district (Chitawo e Chimphango, 2017).

2.4.3 Animal feed and fertilization crops

Rice bran has a long history as a coproduct in livestock feed. For example, its use in chicken feed dates back to the early 90s (Gul *et al.*, 2015). Rice bran is a cheap coproduct similar in fibers and ash content as broiler litter. Therefore, it is being studied as a replacer of broiler litter in the diets of stocker cattle (Stacey e Rankins, 2004). Furthermore, rice bran has dietary fibers and, recently, its addition in food products is contributing to the development of functional foods that have currently a high demand worldwide (Isaara e Rawdkuen, 2016).

Otherwise, rice husks are poor nutritional material and are rarely used as animal feed. Generally, the husks are used as a fertilizer additive. Residue incorporation into the flooded soil is an alternative to open-field burning in rice-based cropping systems in the Asian continent. Currently, it is an option because rice residues can be plowed into the soil as part of the normal tillage operations for preparing the rice field, and residue incorporation does not require an extra step in land preparation (Bijay-Singh *et al.*, 2013). Composting organic residue is also an alternative to recycling rice coproducts in the form of organic fertilizer. Most composting techniques are off-field residue management options in which the produced compost is not returned to the main production field.

Approximately 37% from 600 million tons of crop residue produced in China in the year 2002 returned to soil as fertilizer (Gao *et al.*, 2002). The major drawbacks of incorporation of rice straw are the immobilization of inorganic nitrogen and its adverse effect due to N-deficiency. Incorporation of rice straw into the soil after rice harvest reduces the decomposition. Furthermore, soil nitrate is immobilized, thus reducing the N uptake and yield of subsequent wheat crops by 40% (Sidhu e Beri, 1989). The incorporation of rice coproducts provides habitat for both harmful and useful organisms (Sharma e Bali, 1998). One of the most important factors determining soil fertility is pH, which may be influenced strongly by crop residue management. When rice residues are returned to the soil, the pH can be increased due to the decarboxylation of organic anions on decomposition by microorganisms (Bacon, 1987).

2.4.4 Adsorption of recalcitrant substances

Adsorption by activated carbon has a potential to improve pollutants removal from water. However, the high production and regeneration costs limit its wide-scale application. Despite the numerous investigations made concerning the production of activated carbon from rice husks, the existing reviews mostly report the application of rice husks activated carbon for removal of heavy metals and dyes (Guo *et al.*, 2005).

Regarding the use of rice straw as an adsorbent, highly porous carbon materials have been produced by an activated pyrolysis process. The adsorbent potential of this material is large, considering its high surface area (1973 m^2/g) and its high adsorptive capacity for the anionic (congo red) dye (531.4 mg/g) and cationic (methylene blue) dye (527.6 mg/g) (Sangon *et al.*, 2017). In another work, experiments were performed to characterize the effect of cation exchange on adsorption behavior of Cu and Zn in single- and binary-metal systems by rice straw biochar made by pyrolysis at 600°C. Cu and Zn in aqueous solution were rapidly adsorbed by rice straw biochar in the first 2 h, reaching equilibrium after 4 h. Adsorption capacity for Cu and Zn were 56.5 mg/g and 38.6 mg/g in the single metal system and 40.2 mg/g and 7.9 mg/g in the binary metal system, respectively (Park *et al.*, 2017). Activated carbon from the residue of desilicated rice husks was also used as an adsorbent of the antibiotic Ciprofloxacin (Zhang et al., 2017). In the study, activated carbon derived from the residue of desilicated rice husks presented an adsorption capacity of Ciprofloxacin of 461.9 mg/g material. The adsorption time for removal Ciprofloxacin was 306.9 min (Zhang *et al.*, 2017).

2.4.5 Production of carbon-based and silica-based materials

In recent years, several studies have been focusing on the use of plant biomass to produce engineering materials. Some attempts have been made to produce advanced materials from rice husks such as SiO_2, SiC, Si_3N_4, elemental Si, Mg_2Si, and active carbon (Soltani *et al.*, 2014).

Silicon-based material with high-purity and crystalline structures is often required for the preparation of battery materials. The conventional process of producing silicon is relatively expensive (Pode, 2016). Therefore, many efforts are being directed to develop a low-cost, high-volume and commercially feasible process for producing high-purity silicon in electrical applications (Acharya *et al.*, 1980). Marchal et al. (2015) synthesized the solar grade silicon (99.9999% purity) from rice husks ash as a biogenic silica source. Rice husks ash was initially purified using acid milling/boiling water wash purification steps and pelletization followed by carbothermal reduction using an experimental 50 kW electric arc furnace operated at 1700-2100°C in batch mode.

Another interesting study is that one carried out by Mishra et al. (1985). In such work, the purification of silicon through calcium reduction of rice husks ash was investigated. Rice husks ash obtained at 500°C was mixed with calcium thoroughly in stoichiometric proportions. The product of this calcination was rice husks silica, which was reduced inside an electrically heated muffle furnace at approximately 720°C. The reduced mass after being cooled to room temperature (25°C) was taken out of the crucible and ground to fine particles.

The reduced product leached with HNO_3 and HF to achieve a high purity of 99.9% silicon. Obtaining silicon of 99.9999% purity by reducing rice husks ash with magnesium at a temperature of 800°C was followed by several successive acids (mixtures of HF, H_2SO_4, and HCl) leaching treatments. Wong et al. (2014) synthesized silicon nanoparticles from rice husks-derived silica via the magnesiothermic reduction process. Subsequently, silicon nanoparticles were used to prepare a binder-free composite of Si-graphene as an anode material for lithium-ion batteries. The Si-graphene composite yielded an initial capacity of 1000 mA.h/g at a high applied current density of 1000 mA/g.

Many attempts have been made to use rice husks ash as a filler for natural and synthetic rubbers. The composites have experienced an enormous growth in the automotive industry due to environmentally friendliness, renewability of these fibers, good sound abatement capability, and improved fuel efficiency resulted from the reduced weight of the components. In one of these attempts, Fuad et al. (1995) reported that incorporation of rice husks ash into polypropylene led to an increased flexural modulus of the composites, whereas tensile strength, elongation and impact strength decreased.

2.4.6 Production of oil, extracts, and biodiesel

The increasing demand for rice bran and rice bran oil as healthy functional food ingredients has led to the emergence of defatted rice bran as a potential byproduct obtained as rice bran meal after the extraction of oil from rice bran (Chan *et al.*, 2013). It is currently possible to apply rice bran oil in the production of bakery foods, improving the baking quality (Kaur *et al.*, 2012). Another application is the use of rice bran extracts in cosmetics, in the treatment of skin-related disorders (e.g. melanin-related disorders), and for minimizing wrinkle. The advantages are the potential antioxidant activity, the absorption of ultraviolet

(UV) radiation and the use of γ-oryzanol as a sunscreen in cosmetic formulations (Indira *et al.*, 2005).

Rice bran oil is commonly used in many Asian countries as a cooking and salad oil, mainly due to the antioxidant and radical scavenging properties of γ-oryzanol (Ghosh, 2007). The current use of rice bran oil for producing biodiesel is typical in countries which produce a large amount of rice, such as United States of America, China, India, Thailand, Brazil, Indonesia, Japan, and Vietnam (Hasan *et al.*, 2014). The blends of crude rice bran biodiesel can be used as fuel in a diesel engine without making any modification to the diesel engine. The brake thermal efficiency of blends with 10% and 20% of rice bran biodiesel blend is almost similar to that of conventional diesel fuel at the compression ratio of 12 (Chhabra *et al.*, 2017).

2.5 INTERMEDIATE PLATFORMS, BUILDING BLOCKS, AND MAIN PRODUCTS FROM RICE COPRODUCTS

Biorefineries are the future of biomass processing because they integrate biomass conversion processes and equipment to produce energy, biofuel, and chemicals. Biorefineries are going to act as analogs to petroleum refineries where a range of chemicals or other products are made from different biomass using different process configuration (Morais e Bogel-Lukasik, 2013). Different platforms can be obtained from renewable raw materials, such as syngas, sugars (C5/C6), lignin, organic solution, plant-based oil, and pyrolysis oil (Jong *et al.*, 2012). Crop-based biorefineries are gaining potential importance in recent years. Consequently, scientific researches in this area are at the forefront of innovation and several pilot-scale plants are being constructed and tested. The second generation biofuels and a variety of chemical compounds of interest are being produced from lignocellulosic biomass (Abraham *et al.*, 2016).

Lignocellulosic biomass is mainly composed of three polymers: cellulose, hemicelluloses, and lignin. Other minor components compose the biomass, such as acetylated substances, minerals, and phenolics. Depending on the type of lignocellulosic biomass, these polymers are organized in complex non-uniform three-dimensional structures to different degrees and with relative composition (Paye *et al.*, 2016) (**Fig. 6**).

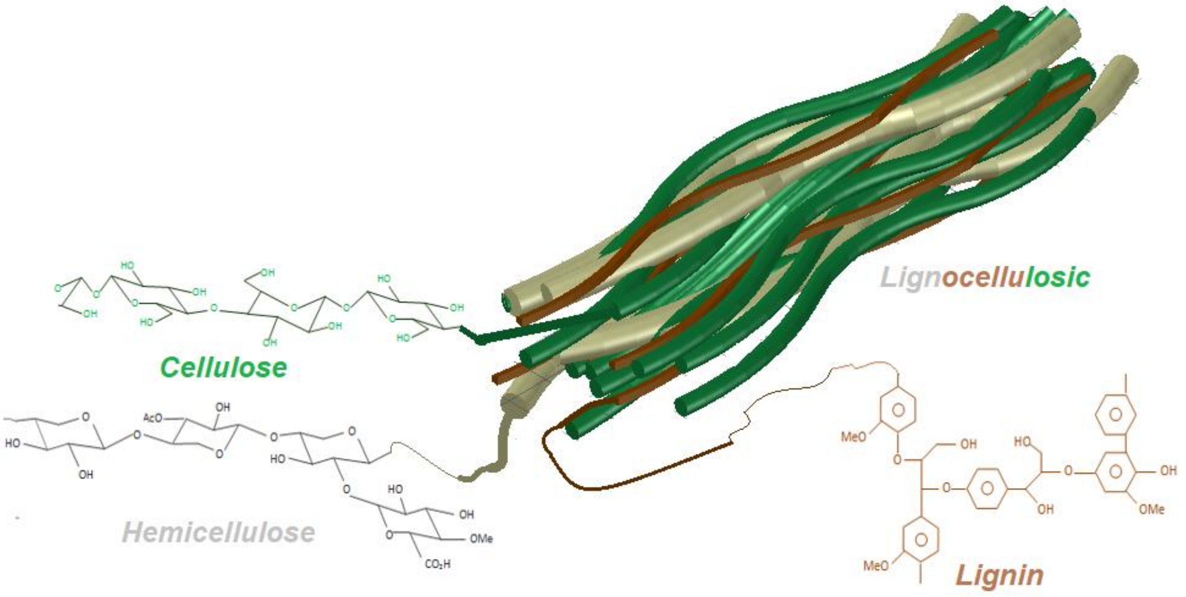


Figure 6 - A typical and schematic structure of a lignocellulosic biomass

Cellulose is the substance that forms the skeletal structure of the plant and it is found almost exclusively in the cell wall. It is also responsible for stiffness and firmness. The major component of lignocellulosic biomass is cellulose. It is a β-glucose polymer where the subunits are linearly bound by β-1,4 (β-β-glucan) glycosidic bonds. A glycosidic bond joins two adjacent moieties, which is formed by the removal of a water molecule, which surrounds the hydroxyl groups of carbons 1 and 4. This disaccharide structure is called cellobiose (Zhou *et al.*, 2011).

Hemicelluloses are the second most abundant natural polymers in the vegetable world after cellulose. Hemicelluloses are a short, highly branched heteropolymer consisting primarily of several heteropolymers including xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan (Sarkar *et al.*, 2012). The degree of crystallinity of hemicelluloses is somewhat lower than that of cellulose, due to the abundance of side chains attached to the main chain, which are basically constituted by acetic acid, pentoses, hexoses and hexuronic acids (4-O-methylglucuronic acid), which are responsible for the solubility of hemicelluloses in water and bases (Kotarska *et al.,* 2015).

Lignin is a three-dimensional polymer of phenylpropanoid units and its cellular glue provides compressive strength to the plant tissue and the individual fibers, stiffness to the cell wall and resistance. The structure of lignin is formed from the oxidative coupling of three different phenylpropane building blocks: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Abdel-Hamid *et al.*, 2013).

Lignocellulosic biomass has a higher amount of oxygen and lower fractions of hydrogen and carbon when compared with petroleum resources. Therefore, in terms of transporting fuels and chemicals, lignocellulosic biomass needs to be depolymerized and deoxygenated. For the production of value-added chemicals, the oxygen often provides valuable physical and chemical properties to the product. Therefore, the production process requires much less deoxygenation (Isikgor e Becer, 2015). The lignocellulosic biomass can be processed to a range of biorefinery streams termed as platforms.

2.5.1 Platforms for producing building blocks and subsequent products

Rice straw, husks and bran have a high amount of cellulose, as evidenced in **Figures 3, 4** and **5**. Certainly, these rice coproducts show potentialities for the production of platforms. Platforms include single carbon molecules, such as biogas, syngas, 5 and 6 carbon carbohydrates from starch, sucrose or cellulose, a mixed 5 and 6 carbon carbohydrates stream derived from hemicelluloses, lignin, oils, organic solutions and pyrolytic oils (Jong *et al.*, 2012).

2.5.1.1 Xylose

Xylose is the main pentose or C5 carbohydrate in hemicelluloses. This platform can be obtained from lignocellulosic biomass but a major challenge is to obtain clean feed streams of these carbohydrates in a low-cost way (Bozell e Petersen, 2010). Xylose leads to the production of many value-added building blocks and products such as xylitol, arabinitol, and xylaric acid chemicals (Kordowska-wiater *et al.*, 2013). Xylitol is used as a sustainable and naturally occurring sweetener with all the sweetness of sugar with fewer calories. Another derivative obtained from xylose is levulinic acid, which is an important biorefinery building block (Jong *et al.,* 2012). In this context, it is important to evaluate the amount of xylose in rice coproducts and their potential to obtain building blocks for sequential reaction on products of interest.

Rice straw hydrolysate is rich in xylose, which can be used for the production of bioethanol from the fermentation process. In such case, the production of bioethanol through the addition of rice straw hydrolysate for the fermentation of xylose using *Pichia stipitis* was evaluated (Lin *et al.*, 2016). The researchers observed an increase in cell mass of *P. stiptis*, when using this hydrolysate. The yield of ethanol was 0.45 g ethanol / g substrate, an increase of 51% when comparing the yield using hydrolysates of other biomasses such as plywood and bamboo. In another work on xylose production and use, Suxia et al. (2012) reported the production of xylose from rice husks for the sequential obtaining of furfural. Under optimal conditions (120 mL extract volume (sulfuric acid), 2.1 g of catalyst, 177°C and a reaction time of 4.8 h) the xylose yield reached 97 wt.%.

When evaluating the use of xylose from rice bran, it is reported elsewhere the production of nisin from defatted bran by hydrolysis with subsequent fermentation using *Lactococcus lactis* (Liu, J. *et al.*, 2017). Nisin is a natural 34-amino-acid-long antimicrobial peptide, which has been widely licensed in the food industry over 50 countries (Shin *et al.*, 2015). For a 100 g of defatted rice bran, the yield of total sugars was 45.64 g, with 5.66 g of xylose. After performing the fermentation of the hydrolyzate, a nisin content of 3824.53 U/milliliter was obtained (U means "Unit", which is the amount of enzyme that converts 1 μmol of substrate per minute) (Liu, J. *et al.*, 2017).

2.5.1.2 Glucose

Glucose is used as feedstock for the fermentation process to produce a variety of building blocks like sorbitol, levulinic acid, glucaric acid, p-xylene, hydroxymethylfurfural, and other chemicals (Jong *et al.*, 2012). The fermentation process from glucose to lactic acid is also fully established in the market and is commercially available (Cherubini e Stromman, 2011). Sorbitol is produced by catalytic hydrogenation of glucose. It is used in food industry and also as raw material for other products such as surfactants, polyurethanes, and ascorbic acid (Jong *et al.*, 2012). Therefore, it is important to highlight some applications of glucose from rice coproducts.

Cellulose from rice straw is being used for the production of food-grade glucose solution by enzymatic hydrolysis. In the optimum condition (enzymatic solution with 15 Filter Paper Units/g), 103 g/L solution of glucose (414 kcal/L) was obtained (Wang *et al.*, 2017). Another interesting work used rice husks for the production of succinic acid. Using untreated rice husks hydrolysate with a glucose concentration of 19.0 g/L, a succinic acid concentration of 12.5 g/L of solution was obtained, yielding a 59.9% conversion rate

(Bevilaqua *et al.*, 2015). This confirms the potential use of rice husks hydrolysate (glucose content).

Rice bran was used to obtain glucose and lactic acid from simultaneous saccharification and fermentation. Firstly, a fungal mix of amylase and glucoamylase was used to hydrolyze rice bran for obtaining glucose (196 g/L of solution in 45 h of process). Thereafter, the yield of lactic acid 117 g/L of lactic acid, and the productivity and yield reached 2.79 g/L.h (Wang *et al.*, 2015). A productivity of 3.73 g/L.h of lactic acid was obtained using rice bran as a substrate and the microorganism *Lactobacillus rhamnosus* LA-04-1 in a 5 L fermenter (Li *et al.*, 2012).

2.5.1.3 Plant-based oil

A non-sugar-based platform used for the production of building blocks is plant-based oil. The oleochemical industry is the largest producer of bio-based products. According to Taylor et al. (2011), the global oleochemical production in 2009 reached 7.7 million tons of fatty acids. Most fatty acids derivatives are used as surface active agents in soaps, detergents, and personal care products.

Triacylglycerol, the major component of most plant oils, can be used for transesterification reaction to produce biodiesel. Biodiesel production has increased significantly in recent years with a production of approximately 14 million tons. Consequently, approximately 1.4 tons of glycerol are generated (Jong *et al.*, 2012). In this context, it is important to evaluate the amount of plant-based oil from rice coproducts, highlighting the main applications in value-added chemicals.

A scientific work evaluated rice bran oil as a potential and environmentally friendly lubricant in terms of thermal and tribological properties (Rani *et al.*, 2015). This oil presented a higher value for flash point (318°C) and for fire point (323°C) when compared to a commercial lubricant oil (SAE20W40; flash point: 200°C; fire point: 205°C). Furthermore, rice bran oil presented a lower coefficient of friction (0.073) than that found for the commercial lubricant oil (0.117) (Rani *et al.*, 2015). Consequently, rice bran oil presented a higher lubricating capacity and would withstand higher temperatures without ignition.

It is important to mention that no studies could be found in literature where oil extracted from rice straw and rice husks is used for obtaining building blocks and final products. This can be attributed to the fact that the oil content in such coproducts is low (rarely exceeding 1.7 wt.%) (Karagoz *et al.*, 2005).

2.5.1.4 Pyrolytic oil

Pyrolysis is the thermal depolymerization of biomass at high temperatures in the absence of oxygen. The different compounds obtained from biomass pyrolysis depends on the residence time of the vapors released in the pyrolysis process, pressure and temperature (Liu, Y. *et al.*, 2017). The main value-added compounds obtained in the pyrolysis are phenols, organic acids, furfural and levoglucosan (Branca *et al.*, 2011).

A study evaluated the pyrolysis using different lignocellulosic biomass, such as rice straw, rice husks, corncob, and wheat straw. Different pyrolysis temperatures (300–450°C) were tested on the yield and conversion of bio-oil produced. The maximum conversion was obtained for corncob (76.0%) at 450°C, followed by rice straw (66.9%) at 450°C, wheat straw (65.6%) at 400°C and rice husks (65.0%) at 450°C (Biswas, Pandey, *et al.*, 2017). In such evaluation and comparison of pyrolytic oil, rice straw provided a higher conversion than rice husks did, even though the conversion was smaller than corncob.

Another interesting work used rice husks for the production of biofuel by externally heated fixed-bed co-pyrolysis reactor (Hossain *et al.*, 2017). The maximum yield of oil was 41 wt% was obtained from 100% rice husks at 450°C. The pyrolytic oil was evaluated in terms of energy conversion efficiency and its properties were compared with those of diesel. For the rice husks pyrolytic oil obtained in the best condition, density (1050 kg/m^3), flash point (58°C), viscosity (3.8 mPa.s) and energy density (16.3 MJ/kg) were taken into account. For diesel, the parameters were: density of 827 kg/m^3, flash point of 60°C, viscosity of 2.1 mPa.s and energy density of 45.1 MJ/kg (Hossain *et al.*, 2017). With exception of energy density, the properties for both oils were close.

2.5.1.5 Syngas

Synthesis gas (syngas) is a term used to describe a gaseous mixture that consists mainly of CO and H_2 (Brown, 2011). It is produced by subjecting biomass to an extreme heat (over 800-1000°C) in the presence of oxygen (provided in lower quantities necessary to induce combustion) in a process known as gasification (Shen *et al.*, 2015). After the cleaning, the syngas can be used to generate power or can be converted into lower alcohols, fuel and chemical products. Syngas can also be fermented to give methanol, ethanol, ammonia and other chemical building blocks (Jong *et al.*, 2012).

Rice husks syngas is rich in CO, CO_2, H_2, CH_4, and C_2H_4. The produced syngas can be combusted in burners, boilers, gas turbines to produce heat, mechanical power, and electricity. In the work of Zhang et al. (2015), the energy produced from rice husks syngas (product of gasification) was evaluated. For each kilogram of syngas, the highest energy was achieved as approximately 10,062 kJ using a reactor temperature of 1000°C. In the study of Calvo et al. (2012), rice straw syngas produced by gasification presented a maximum energy of 14,700 kJ/kg using a reactor temperature of 850°C.

2.6 TECHNOLOGIES FOR PROCESSING RICE COPRODUCTS

One of the key factors in the production of biofuels and value-added products from rice coproducts, such as straw, husks, and bran, is the selection of the appropriate technology for processing the lignocellulosic biomass. There are various technologies aiming at obtaining value-added products from such biomass. However, there are a number of required characteristics for processing the biomass to be considered industrially viable. Overall, the processing technology must be conducted with minimal degradation and with maximum component recovery. In addition, it should have a low energy demand or should be performed in a way that the energy can be reused in another step of the process (Singh *et al.*, 2016).

Studies published elsewhere dealing with technologies for processing rice coproducts are described in terms of mechanisms involved and advantages/disadvantages or limitations. The technologies are implemented through biological, chemical and thermochemical routes and through possible combinations of them (**Fig.7**).

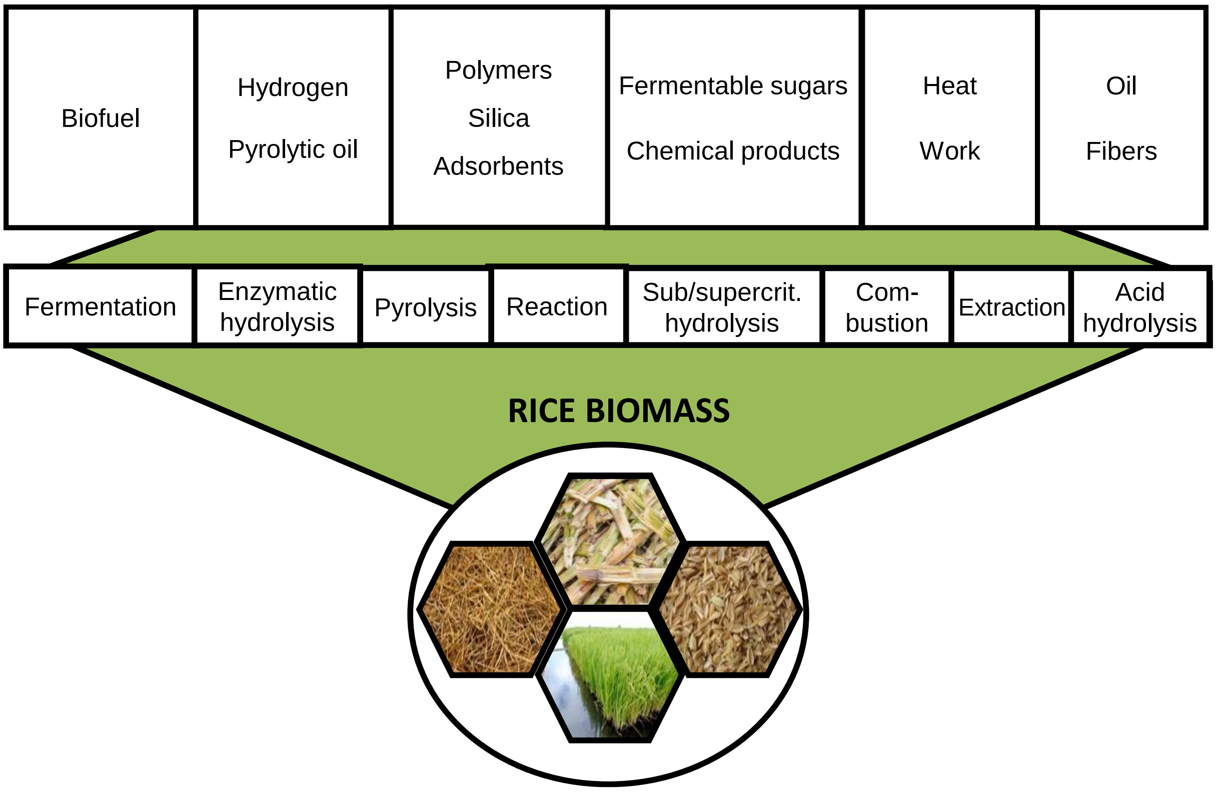


Figure 7 - Technologies, platform, bulding blocks, products, and derivatives in the processing of rice coproducts

Efforts and investments to produce biofuels and value-added products from the coproducts of rice manufacturing are growing rapidly. When analyzing the agroindustrial scenario in this field, the recent outlooks and near future trends, it is possible to gain more knowledge of the main processing technologies. Therefore, an overview of the technologies using different conditions to obtain biofuels, value-added chemicals and other derivatives from rice coproducts is presented in **Figure 7**.

Considering the processing technologies to obtain energy, fuels, value-added products, and other derivatives from rice coproducts, it is possible to highlight the extraction and hydrolysis (chemical pathway), pyrolysis, combustion, gasification and subcritical water process (thermochemical pathway), and enzymatic and microbiology (biochemical pathway). A detailed description of these technologies, including the reality and expectations, and a comparison of their advances and disadvantages/drawbacks are given in the following sub-sections.

2.6.1 Extraction of compounds

This section comprises the extraction of compounds of interest from rice coproducts. These compounds are precursors to a wide range of useful products such as second-generation biofuels, basic chemicals, biochemical chemicals, and bioefficient materials. These compounds can be extracted from rice coproducts of the, being in the form of fibers, silica, and plant-based oil. Supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) have gained attention in the last few years. The main characteristics of these promising technologies are the high-quality of products, the high efficiency and the low impact on the environment. Some works report the use of conventional processes (Majeed *et al.*, 2013) and non-conventional processes (Zigoneanu *et al.*, 2008) for extracting compounds from rice coproducts.

2.6.1.1 Reality

The reality of technologies used for obtaining compounds from rice coproducts indicates the predominance of conventional extraction processes. The conventional processes mainly use solvents (acids or alkalis) for recovering target compounds.

Rice straw and husks are materials with natural fibers composites that consist of cellulose as main fibers, hemicelluloses as an inter-connected branch, and lignin as a binder. A currently conventional treatment for obtaining cellulose fibers from rice straw uses solutions containing a hydroxyl group (NaOH, KOH) to remove lignin from natural fibers (Majeed *et al.*, 2013). An alkaline treatment with a NaOH solution (4% w/v) is indicated to extract the cellulose fibers from rice husks (Johar *et al.*, 2012).

Another interesting compound obtained from rice coproducts is silica. However, before the extraction, it is necessary to reduce metallic impurities by stirring with nitric acid (Adam *et al.*, 2010). Direct extraction of silica can be performed by stirring the acid treated rice husks (after drying) with NaOH solution. During this process, silica is extracted in the form of sodium silicate together with other organic molecules. Afterward, the sodium silicate obtained is converted to silica by adding suitable amounts of mineral acid (Adam e Fua, 2008). Although the content of silica in rice straw is lower than in rice husks, it has been extracted as well. In such case, the rice straw was burned until obtaining an ash. Thereafter, 5 g of ash was dispersed in 500 mL of NaOH aqueous solution (0.5 M) and heated at 100°C for 4 h under vigorous stirring to dissolve silica and to produce sodium silicate. Sodium silicate was neutralized with diluted H_2SO_4 to precipitate silica (Lu e Hsieh, 2012).

Another platform obtained through the conventional extraction process is rice bran plant-based oil. The two most common methods for separating oils from raw materials are extraction and pressing. Mechanical pressing is the most popular method worldwide for separating oil from vegetable oilseeds, using either of two pressing methods, hydraulic or screw (Sayasoonthorn *et al.*, 2012). Extracts of rice bran were obtained using methanol, ethyl acetate and ethanol at 25°C for 3 h in an electrical shaker. The yields were 8.8 wt.% of extract for 100% of dried rice bran using methanol, 5.54 wt.% with ethanol and 7.64 wt.% with ethyl acetate (Arab *et al.*, 2011).

Considering the reality for non-conventional processes, it is interesting to present the application of ultrasound for assisting of polyphenols and antioxidants extraction from rice bran. Three independent variables such as solvent percentage (%), temperature (°C) and time (min) were studied. Effect of ethanol concentration was found to be significant. Extraction yields ranged from 11 to 20.2%. Optimal ultrasonic-assisted extraction (UAE) conditions (54°C, 45 min and the solvent concentration of 67% ethanol in water) yielded an extract with a total phenolic content (TPC) of 6.35 mg gallic acid equivalent/g of dry sample and an antioxidant activity of 55.61% inhibition of radical 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Tabaraki e Nateghi, 2011). In the same trend, rice bran oil was extracted by microwave-assisted extraction with isopropanol and hexane. In the best condition (120°C, using only isopropanol as solvent), 15 g oil/100g fresh rice bran was obtained with an antioxidant activity of 54 % inhibition of radical (DPPH) and without degradation of α-tocopherol during the process (Zigoneanu *et al.*, 2008).

Supercritical carbon dioxide extraction (SFE-CO_2) was also applied for obtaining rice bran oil. Parameters as CO_2 flow rate (1–9 mL/min), temperature (40–80°C) and pressure (20–40 MPa) were tested. At 30 MPa and 80°C, the recovery of rice bran oil was 83.14%, where the recovery is the ratio between the extraction yield of the methodology proposed

($SFE-CO_2$) and the extraction yield of the official extraction methodology, which in this case of Soxhlet using hexane as solvent (Tomita *et al.*, 2014).

2.6.1.2 Expectations

Regarding the expectations of novel routes and technologies or advances in the current technologies to obtain value-added compounds from rice coproducts by extraction, it is possible to highlight some trends in this area. The recent work of Xu et al. (2018) used a combined acid hydrolysis-ultrasonic treatment to obtain cellulose from rice straw. The difference from the current conventional procedures stands for the integration process, which includes a sequential treatment with NaOH or KOH, an acid treatment and, finally, a submission to ultrasonic waves. With respect to the results, the rice straw treated with acid hydrolysis and high ultrasonic power presented uniform rod-like or filamentary structure cellulose fibers with a width of approximately 5 nm and 20 nm and several hundred nanometers in length.

Regarding the extraction of silica, the trends indicate the use of technologies that apply thermochemical routes or ionic liquid treatment for obtaining silica with high purity. The expectations are the extraction of silica and its derivatives with high surface area and pore volume. Regarding the extraction of oil, especially from rice bran, the uses of supercritical CO_2 or compressed liquefied petroleum gas (LPG) seem to be a promising route. In the work performed by Soares et al. (2016) a satisfactory yield of rice bran oil (81.99% recovery) was obtained, with a high advantage of this process as being 15 times faster than the conventional method (Soxhlet extraction).

A microwave-assisted solvent extraction of rice bran oil in two steps termed two-step microwave-assisted extraction (TSMAE) has been adopted. A domestic microwave oven was used for heating rice bran. The effects of microwave power, microwave exposure time and solvent to bran ratio were evaluated. In the best condition in TSMAE, more than 97% oil recovery was reached in total extraction time of 9 min (Pandey e Shrivastava, 2018).

2.6.2 Combustion

Combustion of rice coproducts is one of the most used paths for reusing rice coproducts. Therefore, it is relevant to discuss some aspects and future trends/modifications to be implemented with respect to this process. For example, the bioenergy is already a mature and commercially available technology, based on direct combustion boiler and steam turbine systems at small and large-scale for residential and industrial applications.

2.6.2.1 Reality

The reality of conversion technologies for energy production indicates direct combustion heating and direct combustion power generation. In direct combustion, biomass is utilized as a fuel in a combustion boiler to produce steam (a heat source) in the presence of sufficient air in the combustion chamber. In direct combustion power generation, electricity can be simultaneously generated (cogeneration) using turbines (Natarajan *et al.*, 1998). In the world, the combustion of rice husks is well established for generating heat and electricity. The southeast of Asia alone, for example, has 44 rice husks on-going projects that are based on cogeneration (Carlos e Ba, 2008). Generally, biomass combustion technologies can be categorized into fixed bed and fluidized bed combustion systems (Abdullah *et al.*, 2003).

2.6.2.2 Expectations

Although rice husks are easy to combust, the current technologies available for combustion do not control the temperature in the precise manner which is required to avoid the formation of crystalline silica. In recent years, a new reactor technology has been used to combust rice husks. In Cambodia, a toroidal bed (TORBED) reactor (Dodson, 2011) is operating in the service of controlled combustion of rice husks. In a recent study, a TORBED reactor was used to combust rice husks from Arkansas (USA) at a series of six temperatures, ranging from 700°C to 950°C, without generating crystalline silica (Blissett *et al.*, 2017).

The expectations follow up the trends shown in a work dealing with combustion, especially related to efficiency and reduction of CO, NO_x and SO_2 emissions (Okasha *et al.*, 2014). Integrated and intensified processes, as well as a combination of coproducts and raw materials, are the future outlooks. As shown in the work (Okasha *et al.*, 2014), a co-combustion of rice straw and natural gas was done in a bubbling fluidized bed. The research came about because the used combustor allows a novel jetting-fountain configuration and the conventional operation as well. In the jetting-fountain configuration, natural gas premixed with the air sufficient for combustion proceeds through the jet pipe to create a jet-fountain zone. Only the air required for rice straw combustion passes through the gas distributor. The findings confirm that smooth combustion of natural gas with rice straw can be performed in the novel jetting-fountain fluidized bed. This avoids acoustic effects and explosions of burning bubbles that occur in conventional operations. The performance of the combustor has been found much better when operates in the jetting-fountain configuration.

2.6.3 Gasification and pyrolysis

Gasification can be defined as a thermochemical process which transfers heating value from carbonaceous materials into syngas, tars and biochar at high temperature (up to 500°C) and oxygen-deficient conditions. The gasification process generally involves four consecutive steps, such as drying, pyrolysis, partial oxidation and reduction (Loha *et al.*, 2014). Pyrolysis is a thermal decomposition process performed in the absence of an external supply of air (oxygen). The final pyrolysis products are in the form of gases, oils, and a carbonaceous rich material named char (Bridgwater, 2012). Therefore, it is possible to show the gasification and pyrolysis processes used and the products obtained from straw, husks and rice bran.

2.6.3.1 Reality

The reality of gasification indicates the syngas as the main energy product, being composed of CO, H_2, CH_4 and a mixture of other minor gases. Also, a char residue is produced in gasification, although with lower carbon content than pyrolysis char. Syngas can be used in an internal combustion engine to produce heat, or in a cogeneration system to produce heat and electricity.

On a pilot scale, rice straw and husks gasification and power generation systems are being produced by POWERMAX (China) with a production capacity ranging from 50 kW to 20,000 kW. In this plant, gasification of rice straw and husks includes three steps. The first step is biomass gasification, which converts rice husks into syngas. The second step is syngas purification. The producer gas coming from gasifier usually contains contaminants including dust, coke, and tar. The contaminants are removed by the purification system to ensure normal operation of the gas engine. The third step is a power generating in a gas engine. The high-temperature exhaust gas may be reused by waste heat boiler to generate steam or hot water for civil or industrial use (Wuxi Teneng Power Machinery Co., 2018).

Within the actual scenario (reality), another plant of energy production from the gasification of rice husks is the industrial plant produced by Angkor Bio Cogen Rice Husk Power Project in Cambodia. The plant uses the TORBED system reactor to produce 2 MW of energy (Project, 2016). In India (State of Karnataka), there is a Grid Connected Biomass Power Plant able to generate 500 kW from rice husks. The system comprises two 100 kW gasifier systems, one 200 kW system using 100% producer gas, and another 100 kW system with fuel (Jain e Srinivas, 2012).

With respect to pyrolysis, the main types of pyrolysis are slow, intermediate and fast pyrolysis, which depend on several factors such as heating rate, residence time, reaction temperature, feed rate, among other parameters. In most cases, slow pyrolysis and intermediate pyrolysis are carried out at a temperature below 500°C, whereas fast pyrolysis is carried out at a temperature between 500°C and 700°C (Park *et al.*, 2014). Fast pyrolysis occurs in a few seconds and biomass decomposes in aerosols, vapors, and charcoal obtaining three by-products: bio-oil, syngas and biochar (Heo *et al.*, 2010). The literature indicates that the most suitable technology for rice husks is fast pyrolysis given its higher cellulose and hemicelluloses content as compared to lignin and due to a higher volatile matter content than fixed carbon content (Chen *et al.*, 2011). Some common ways to develop pyrolysis of rice straw and husks are a fluidized bed reaction (Tsai *et al.*, 2007), fixed bed induction heating (Williams e Nugranad, 2000), and entrained flow reaction (Sun *et al.*, 2010).

2.6.3.2 Expectations

The expectations related to gasification and pyrolysis indicates process as rice husks gasification in a two-stage fixed-bed gasifier. This kind of process was recently developed focusing on hydrogen-rich syngas production and kinetics. Tars were generated in a pyrolysis section of the gasifier and subsequently cracked by secondary reactions in the gasification section. Therefore, tar cracking at higher temperatures resulted in the formation of hydrogen-rich syngas (Khonde e Chaurasia, 2016). In order to reduce the formation of tar, the feasibility of enhanced energy yield in gasification of rice straw was investigated using a prepared iron-based catalyst. The main advantage of adding this catalyst was the increasing of energy yield efficiency as approximately 74% (Chiang *et al.*, 2016).

With respect to pyrolysis, bio-oils, in general, are dark brown, free-flowing organic liquids that cannot be used directly as a regular fuel due to their high oxygen content, high viscosity, high corrosiveness, relative instability and complex chemical composition (Bridgwater, 2012). Several methods have already been examined for upgrading the bio-oil quality, namely, catalytic cracking of pyrolysis vapors, hydrodeoxygenation, extracting chemicals, and esterification. Among these methods, catalytic pyrolysis of biomass has been receiving great attention in recent years and is expected to develop evermore due to its advantages as simplifying the process and improving the quality of bio-oil, which uses a catalyst to directly penetrate into biomass textures and enhance reactions that include cracking, decarboxylation, decarboxylation (Liu *et al.*, 2014).

Another expectation includes pyrolysis in a fixed bed reactor. A recent study carried out pyrolysis of rice straw using fixed bed reactor under a CO_2 environment at temperatures ranging from 300°C to 450°C. The maximum oil yield (34.5 wt.%) was obtained at 400°C. The solid residue yield decreased when the temperature increased from 300°C to 450°C, while the gas yields increased (Biswas, Singh, *et al.*, 2017).

2.6.4 Enzymatic, acid/alkaline, and sub/supercritical water hydrolysis

Lignocellulose can be broken down into simple sugars either enzymatically by hemicellulolytic enzymes or chemically by sulfuric or other acids (Zhang *et al.*, 2012). Generally, bioethanol production from lignocellulosic biomass consists of three major steps: pretreatment, enzymatic hydrolysis, and fermentation. The second step is the hydrolysis process (enzymatic, for example), that involves the conversion of cellulose into glucose, and hemicelluloses into several pentoses and hexoses (Taherzadeh e Niklasson, 2004). The cellulose and hemicelluloses fraction of rice coproducts can be converted to ethanol by enzymatic hydrolysis or sub/supercritical hydrolysis with sequential fermentation processes.

2.6.4.1 Reality

The reality of enzymatic, acid/alkaline and sub/supercritical water hydrolysis indicates the selection of processes that yield the highest content of substrate (mainly sugars) for biofuels and bioproducts production. NaOH solutions, H_2SO_4 solutions, and reactions with cellulases and xylanase are the main routes used nowadays for converting lignocellulosic biomass. Within these routes, it is interesting to highlight the use of NaOH solution (0.5 M) to hydrolyze rice straw. There was a remarkable increase in conversion to ethanol by 350% over the untreated straw (Hou *et al.*, 2014).

In relation to subcritical hydrolysis, the trends indicate the use of this technology for the breakdown of biopolymers into biochemicals and fermentable sugars by heated and pressurized water. The molecular mechanism of hydrolysis is comprised of three steps: the conjugated acid is formed by adding a proton to one oxygen molecule and two sugar molecules; the C-O bond is divided, and a carbon ion is formed. Finally, the water is transferred to the molecule of glucose (Zabot *et al.*, 2018).

When evaluating the reality of non-conventional processes, it is interesting to present the application of subcritical water hydrolysis in rice straw and rice husk for obtaining sugars and bioproducts (Abaide, Ugalde, *et al.*, 2019; Abaide, Mortari, *et al.*, 2019). Parameters as temperature (180°C, 220°C, and 260°C) and liquid/solid mass ratios of 7.5 g water/g straw and 15 g water/g straw were evaluated on the reducing sugar yield (Y_{RS}) and efficiency of conversion (E). For both biomasses, the condition with temperature of 220°C and liquid/solid mass ratios of 7.5 was the one that obtained the best values for the Y_{RS} and E. Values of Y_{RS} of 33.4 ± 4.3 g/100 g dry straw and 18.0 ± 2.9 g/100 g dry husks were obtained for straw and husks, respectively. Likewise, values of E of 72.1 ± 4.6 g sugar equivalents in glucose per 100 g of carbohydrates and 39.5 ± 1.7 g sugar equivalents in glucose per 100 g of carbohydrates for rice husk were obtained for straw and husks, respectively (Abaide, Ugalde, *et al.*, 2019; Abaide, Mortari, *et al.*, 2019).

2.6.4.2 Expectations

When evaluating the expectations for improving technological routes to obtain value-added products by hydrolysis of rice coproducts, some recent researches that achieved promising results are highlighted. When discussing subcritical hydrolysis process, this process degrades fewer sugars than acid and alkali hydrolysis, it is extremely fast when compared to both acid and enzymatic routes, and it may avoid the pretreatment step required for the enzymatic process. Subcritical hydrolysis is not widespread yet, but there is one industrial plant that uses this technology to process 70 tons of biomass per day to obtain products of interest (REMATEC Corp. Sakai SC Factory).

With respect to pilot plants to carry out hydrolysis of biomass, SCF Technologies A/S Danish Company has such pilot plant. The process operates with water at subcritical conditions in continuous mode with 30 L/h (temperature ranging from 280°C to 350°C; pressure ranging from 22.5 MPa to 25.0 MPa), and it converts wet low-value feeds such as sludge, algae, manure, and residues from food production (Toor *et al.*, 2012). As expectations, coproducts of rice, such as straw, husks, and bran could be used in such pilot plant. **Figure 8** depicts an experimental apparatus of sub/supercritical water hydrolysis in a semi-continuous mode, which can be used for hydrolysis of rice coproducts.

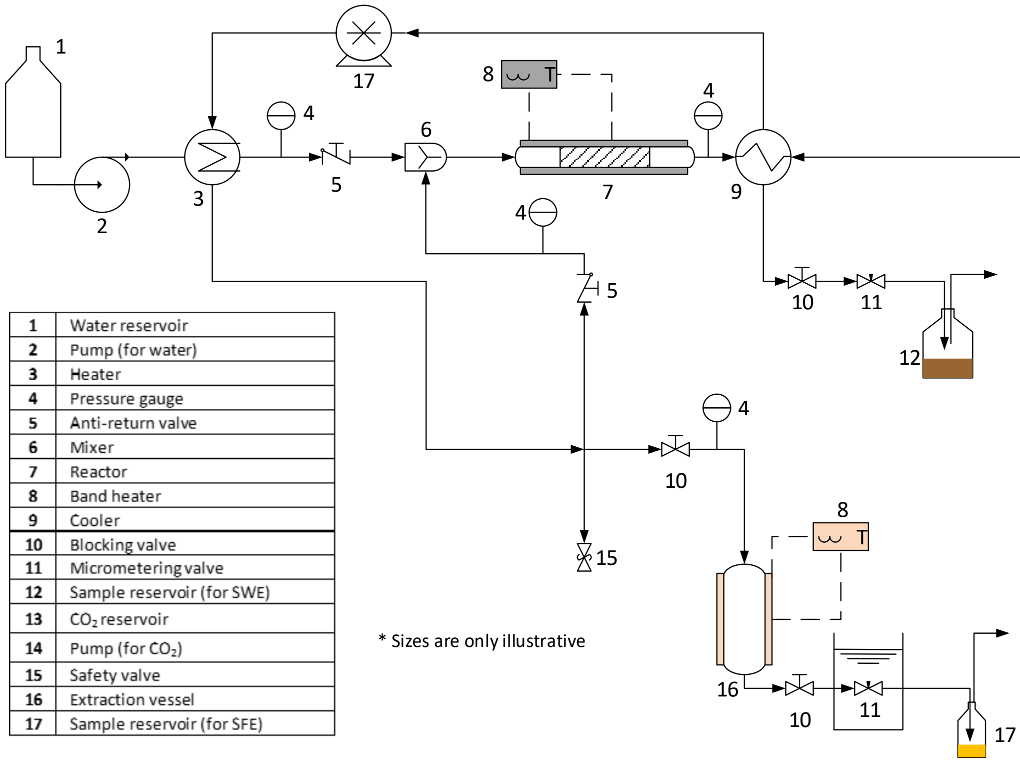


Figure 8 - Schematic flowsheet for subcritical hydrolysis coupled to an extraction system: a possible route for efficient use of rice coproducts

It is also interesting to evaluate the scientific production in the last 7 years related to the hydrolysis of rice coproducts (**Fig. 9**) for ethanol production.

The search was done in the Scopus database with the following keywords: enzymatic hydrolysis / ethanol / rice straw; acid hydrolysis / ethanol / rice straw; alkaline hydrolysis / ethanol / rice straw; subcritical water hydrolysis / ethanol / rice straw; enzymatic hydrolysis / ethanol / rice bran; acid hydrolysis / ethanol / rice bran; alkaline hydrolysis / ethanol / rice bran; subcritical water hydrolysis / ethanol / rice bran; enzymatic hydrolysis / ethanol / rice husks; acid hydrolysis / ethanol / rice husks; alkaline hydrolysis / ethanol / rice husks; subcritical water hydrolysis / ethanol / rice husks.

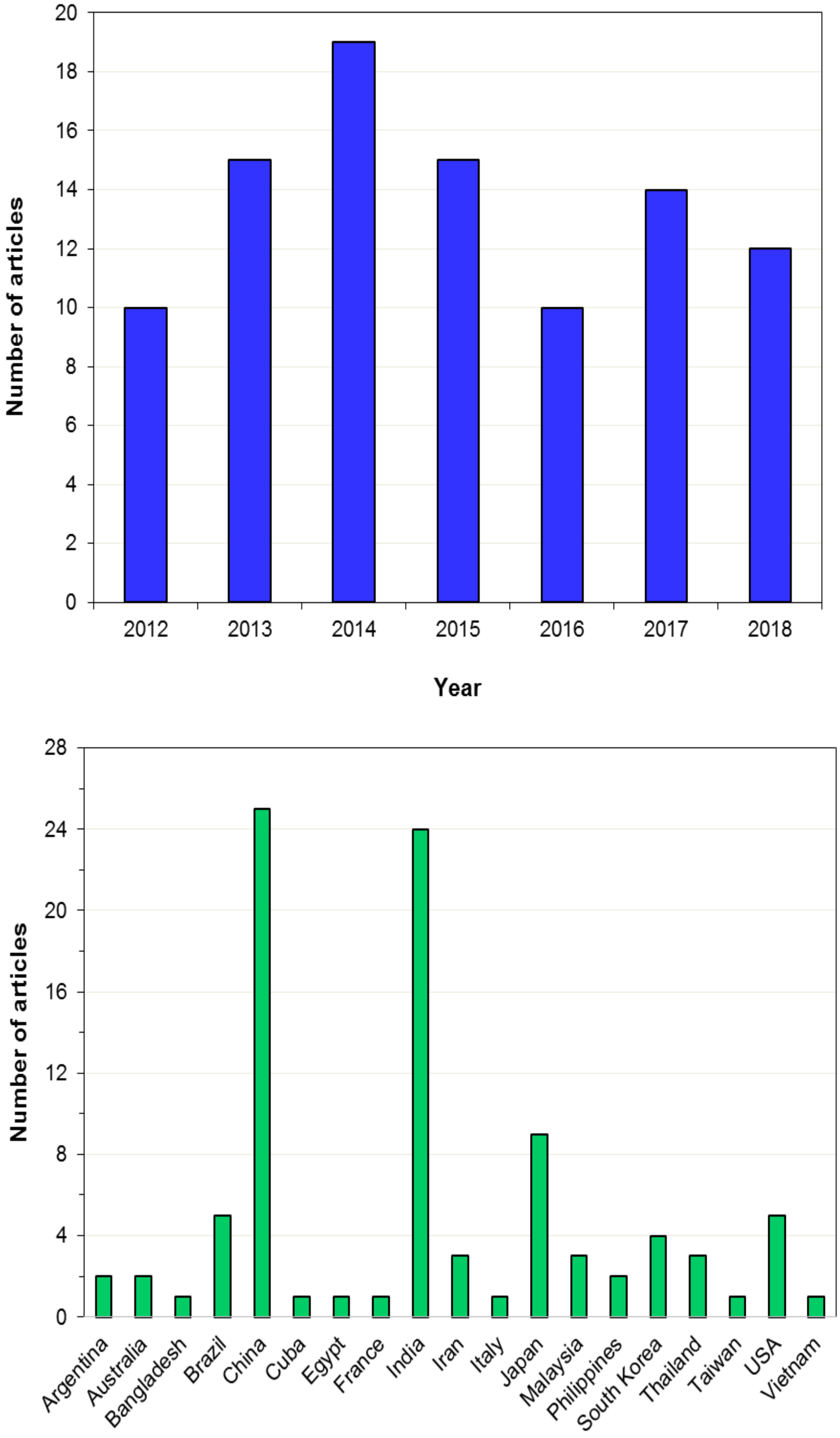


Figure 9 - Worldwide production of scientific articles on hydrolysis dedicated to ethanol production from 2012 to 2018 (until October) divided by year (a) and by country (b); the

search was done in the Scopus database with the following keywords: enzymatic hydrolysis / ethanol / rice straw; acid hydrolysis / ethanol / rice straw; alkaline hydrolysis / ethanol / rice straw; subcritical water hydrolysis / ethanol / rice straw; enzymatic hydrolysis / ethanol / rice bran; acid hydrolysis / ethanol / rice bran; alkaline hydrolysis / ethanol / rice bran; subcritical water hydrolysis / ethanol / rice bran; enzymatic hydrolysis / ethanol / rice husks; acid hydrolysis / ethanol / rice husks; alkaline hydrolysis / ethanol / rice husks; subcritical water hydrolysis / ethanol / rice husks

The highest number of reports related to hydrolysis of rice coproducts focused on ethanol production occurred in 2014 (**Fig. 9a**). China, India, Japan, South Korea, USA, Malaysia, and Taiwan are the countries that studied and reported most of the findings in this subject (**Fig. 9a**). This may be related to the fact that Asia is the world's largest producer of rice, which generates many coproducts from this lignocellulosic biomass. It is worth mentioning that some studies are being developed in other countries, such as Brazil, Iran, Argentina, Egypt, Australia, Cuba, The Philippines, Bangladesh, France, and Italy. Overall, there are a plenty number of reports on rice coproducts hydrolysis. However, for having an idea, the behavior displayed in **Figure 9** only depicts the hydrolysis exclusively for ethanol production.

2.7 PROCESSING OF RICE COPRODUCTS: REALITY, FUTURE TRENDS, AND EXPECTATIONS

The reality shows a high worldwide production of rice coproducts (husks, straw, and bran), accounting for approximately 490 million tons per year. Approximately 38% of each ton of rice harvested is the straw, which generally remains in the field (although it is not indicated). The other coproducts generated during rice processing are the husks (20%) and bran (8%). In common for both coproducts, a high content of cellulose (20-40 wt.%) and hemicelluloses (15-28 wt.%) is highlighted. Consequently, the effective utilization of the cellulosic material would play a significant role in the economic viability of ethanol processing.

Currently, there is a growing trend of studies focusing on renewable and environmentally friendly resources for obtaining biofuels, bioproducts, and energy. Nowadays, there is a worldwide concern about replacing fossil fuels by other alternative fuels. Therefore, production of biofuels and energy generation from lignocellulosic biomass is a topic at the forefront of innovation for a novel economy.

Regarding the current applications and studies within the biorefinery concept, we point out the reuse of rice coproducts for preparing building materials, carbon-based and silica-based materials, animal feed and fertilizers, extractive compounds, fermentable sugars, and adsorbent materials. For example, adsorption by activated carbon obtained from rice coproducts has the potential to improve pollutants removal from water. Furthermore, blends of crude rice bran biodiesel can be used as fuel in a diesel engine without making any modification to the diesel engine.

Therefore, after a critical and detailed review of the literature, the expansion of the holistic biorefinery is progressing forward. With it, the know-how should be improved, especially regarding the optimization of phytochemicals’ recoveries and specific compounds’ separation/fractionation. Based on several studies on processing technologies of rice coproducts, technological routes such as gasification, pyrolysis, combustion, sub/supercritical hydrolysis, supercritical and pressurized liquid extraction appear as future trends to be applied in large scale. Semi-continuous and continuous operations are also a highlighted trend in this area. The subject is in the strategic plan of development and expansion in several countries. Consequently, the number of companies dedicated to processing a pool of vegetal raw materials (including rice coproducts) is expected to grow rapidly, thus requiring a highly trained and specialized human resource.

Companies located in Japan, for example, have a special focus on subcritical water hydrolysis. Combustion, pyrolysis, and gasification processes can be applied to convert the remaining carbonaceous material in rice husks into energy. Likewise, countries with larger agricultural areas, such as the USA, Canada, and China, have companies that process agroindustrial wastes directly through thermochemical routes such as combustion and gasification. The Renmatix Company, located in Montreal (Canada) and with subsidiaries around the world, works with water-based technology platform developed to convert the lignocellulosic material into biobased ingredients and sustainable products. Another company that uses subcritical water technology is the Rematec Corp. Sakai SC Factory located in Osaka (Japan), which recycles waste oil and waste wood into reclaiming fuel.

Based on the whole context discussed in this study and considering the maximum reuse of biomass into a biorefinery concept, we can infer that the most promising routes for processing rice coproducts are hydrolysis for obtaining fermentable sugars and bioproducts and pyrolysis for obtaining bio-oil or gasification for obtaining syngas, tars, and biochar. The biochar is also a valuable product to be used in adsorption of specific compounds, as pharmaceutical substances, dies, and pesticides. Therefore, a way forward is suggested for increasing the use of rice coproducts produced in larger quantities in several countries. In this sense, the reality and expectations for processing rice coproducts are summarized in **Table 4** according to the explanations provided in this review. Fermentable sugars, adsorbent materials, heat, electricity, bio-oils, biochar, syngas, and compounds with antioxidant activity are highlighted.

Table 4 - Summary of reality and expectations on rice coproducts processing for obtaining energy and other derivatives

Coproduct	**Technology**	**Platform / Building block / Product / Derivative**	**Reality**	**Expectations**
Husks	Subcritical water hydrolysis	Fermentable sugars; adsorbent materials	A few studies dealing with the subject in batch and semi-continuous mode in laboratory scale	Identification of optimal processing conditions; studies in continuous mode; applications in the pilot and industrial scales; definition of economic feasibility
Husks	Direct combustion power system	Heat; electricity	Projects with direct combustion in fixed and fluidized beds	Projects with the TORBED reactor in industrial scale
Husks	Pyrolysis and gasification	Bio-oils; biochar; syngas	Projects in fixed and fluidized beds	Investigation with metal catalysts in pyrolysis; use of CO_2 in high temperatures
Straw	Direct combustion power system	Heat; electricity	Projects with direct combustion in fixed and fluidized beds	Identification of optimal process conditions using jetting-fountain configuration; assessment of the reduction of acoustic effects and explosions of burning bubbles
Straw	Subcritical water hydrolysis	Fermentable sugars; adsorbent materials	Tests in laboratory scale and in batch mode	Investigations in continuous mode; optimization of processing conditions; applications in the pilot and industrial scales; definition of economic feasibility

Table 4 - *Continued*

Coproduct	**Technology**	**Platform / Building block / Product / Derivative**	**Reality**	**Expectations**
Straw	Pyrolysis and gasification	Bio-oils; biochar; syngas	Projects in a fixed bed	Studies with metal catalysts in the pyrolysis
Bran	Ultrasonic assisted extraction	Antioxidant activity compounds; phenols; α-tocopherol	Studies that evaluate the percentage of solvent and temperature at laboratory scale in a batch system	Investigations in continuous mode; investigations of the influence of ultrasonic power and frequency
Bran	Microwave-assisted extraction	Antioxidant activity compounds; phenols; α-tocopherol;	Studies that evaluate the percentage of solvent or a mixture of solvents	Investigations of effects of microwave power and frequency; investigation of effects of microwave exposure time; evaluation of the process by performing more than one step (multiple steps)
Bran	Supercritical and pressurized liquid extractions	Bulk oil; compounds with antioxidant activity; phenols; α- tocopherol	A few studies dealing with semi-continuous mode using CO_2 in the supercritical state and evaluating the influence of solvent flow rate, temperature, and pressure	Comparisons using compressed liquefied petroleum gas and supercritical CO_2 as solvents; reduction of extraction time; increasing yields and productivity; use of cosolvents; operation in continuous mode

TORBED: toroidal bed

Conflict of interest

The authors declare that there are no conflicts of interest.

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REFERENCES

A. Abraham, A.K. Mathew, R. Sindhu, A. Pandey, P. Binod, Potential of rice straw for bio-refining: An overview, Bioresource Technology 215 (2016) 29-36.

A. Anukam, S. Mamphweli, P. Reddy, E. Meyer, Pre-processing of sugarcane bagasse for gasification in a downdraft biomass gasifier system: A comprehensive review Renewable Sustainable Energy Rev. 66 (2016) 775-801.

A.B.C.R.H.P. Project, Project 0363 - Cambodia, 2016. (Accessed January 2018).

A.C.R. Lim, B.L.F. Chin, Z.A. Jawad, K.L. Hii, Kinetic Analysis of Rice Husk Pyrolysis Using Kissinger-Akahira-Sunose (KAS) Method, Proced. Eng 148 (2016) 1247-1251.

A. Koopmans, J. Koppejan, Agricultural and forest residues generation, utilization and availability, Regional consultation on modern applications of biomass energy 10 (1997) 1-23.

A. Limayem, S.C. Ricke, Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects, Prog. Energy Combust. Sci. 38(4) (2012) 449-467.

A.M. Abdel-Hamid, J.O. Solbiati, I.K. Cann, Insights into lignin degradation and its potential industrial applications, Advances in Applied Microbiology 82 (2013) 1-28.

A.P. Hasan, M.A. Wakil, M.A. Kafy, Prospect of rice bran for biodiesel production in Bangladesh, Procedia Engineering 90 (2014) 746-752.

A. Rafe, A. Sadeghian, Stabilization of Tarom and Domesiah cultivars rice bran: Physicochemical, functional and nutritional properties, Journal of Cereal Science 74 (2017) 65-71.

A.R. Morais, R. Bogel-Lukasik, Green chemistry and the biorefinery concept, Sustainable Chem. Processes 1 (2013) 18-19.

A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy 38 (2012) 68-94.

A. Yank, M. Ngadi, R. Kok, Physical properties of rice husk and bran briquettes under low pressura densification for rural applications, Biomass Bioenergy 84 (2016) 22-30.

B. Biswas, N. Pandey, Y. Bisht, R. Singh, J. Kumar, T. Bhaskar, Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk, Bioresource Technology 237 (2017) 57-63.

B. Biswas, R. Singh, J. Kumar, R. Singh, P. Gupta, B.B. Krishna, T. Bhaskar, Pyrolysis behavior of rice straw under carbon dioxide for production of bio-oil, Renewable Energy In Press, Corrected Proof (2017).

B. Gadde, S. Bonnet, C. Menke, S. Garivait, Air pollutant emessions from rice straw open field burning in India, Thailand and the Philippines, Environ. Pollut 157 (2009) 1554-1558.

Bijay-Singh, Y.H. Shan, S.E. Johnson-Beebout, Yadvinder-Singh, R.J. Buresh, Crop Residue Management for Lowland Rice-Based Cropping Systems in Asia, Advances in Agronomy2013.

B.S. Sidhu, V. Beri, Effect of crop residue management on yields of different crops and soil properties, Biological wastes 27(1) (1989) 15-27.

B. Zhang, X. Han, P. Gu, S. Fang, J. Bai, Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desilicated rice husk, Journal of Molecular Liquids 238 (2017) 316-325.

C. Branca, A. Galgano, C. Blasi, M. Esposito, C. DiBlasi, H_2SO_4 Catalyzed Pyrolysis of Corncobs, Energy Fuels 25 (2011) 359-369.

C. Chen, C. Yu, H. Zhang, X. Zhai, Z. Luo, Investigation on K and Cl release and migration in micro-spatial distribution during rice straw pyrolysis, Fuel 167 (2016) 180-187.

C. Chou, S. Lin, w. Lu, Preparation and characterization of solid biomass fuel made from rice straw and rice bran, Fuel Process. Technol 90 (2009) 980-987.

C. Dodson, Toroidal bed reactor, Mortimer Tech Holdings Ltd United States, 2011.

C. Loha, S. Gu, J.D. Wilde, P. Mahanta, P.K. Chatterjee, Advances in mathematical modeling of fluidized bed gasification, Renewable & Sustainable Energy Reviews 40 (2014) 688-715.

C. Moliner, B. Bosio, E. Arato, A. Ribes, Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes, Fuel 180 (2016) 71-79.

CONAB, Follow-up of brazilian safra 2015/2016 - grains - eleventh survey, National supply company 11 (2016) 1-176.

C. Zhou, X. xia, C. Lin, D. Tong, J. Beltramini, Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels Chemical Society Reviews 40(11) (2011) 5588-5617.

C. Wang, W. Chen, H. Liu, J. Lai, C. Hsu, B. Wan, Process development for producing a food-grade glucose solution from rice straws, Chinese Journal of Chemical Engineering In Press (2017) Accepted Manuscript.

C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, Catalytic fast pyrolysis of lignocellulosic biomass, Chemical Society Reviews 43(22) (2014) 7594-7623.

D.B. Bevilaqua, S. Montipó, G.B. Pedroso, A.F. Martins, Sustainable succinic acid production from rice husks, Sustainable Chemistry and Pharmacy 1 (2015) 9-13.

D.C. Taylor, M.A. Smith, P. Fobert, E. Mietkiewska, R.J. Weselake, Plant systems - Metanolic engineering fo higher plants to produce bio-industrial oils, Comprehensive biotechnology 4 (2011) 67-85.

D.P. Wong, R. Suriyaprabha, R. Yuvakumar, V. Rajendran, Y.T. Chen, B.J. Hwang, L.C. Chen, K.H. Chen, Binder-free rice husk-based silicon-graphene composite as energy efficient Li-ion battery anodes, Journal of Materials Chemistry A 2 (2014) 13437-13441.

E.A. Dechere, O. Korver, Minor constituents of rice bran oil as function as functional foods, J. of Nut and Food Sci 54 (1996) 120-126.

E.D. Jong, A. Higson, P. Walsh, M. Wellisch, Bio-based Chemicals: Value Added Products from Biorefineries, IEA Bioenergy, Task 42 Biorefinery, 2012.

E.L. Iye, P.E. Bilsborrow, Assesment of the availability of agricultural residues on zonal basis for medium to large-scale bioenergy production in Nigeria, Biomass Bioenergy 48 (2013) 66-74.

E.M. Bezerra, A.P. Joaquim, J.H. Savastano, V.M. John, V. Agopyan, The effect of different miniral additions and synthetic fiber contents on properties of cement based composites, Cement and Concrete Composites 28 (2006) 555-563.

E. Natarajan, A. Nordin, A. Rao, Overview of combustion and gasification of rice husk in fluidized bed reactors, Biomass and Bioenergy 14 (1998) 533-546.

E.R. Abaide, G. Ugalde, M.D. Luccio, R.F.P.M. Moreira, M.V. Tres, G.L. Zabot, M.A. Mazutti, Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode, Bioresour. Technol 272 (2019) 510-520.

E.R. Abaide, S.R. Mortari, G. Ugalde, A. Valério, S.M. Amorim, M.D. Luccio, R.F.P.M. Moreira, R.C. Kuhn, W.L. Priamo, M.V. Três, G.L. Zabot, M.A. Mazutti, Subcritical water hydrolysis of rice straw in a semi-continuous mode, J. Clean. Prod 209(1) (2019) 386-397.

FAO, Rice market monitor, Food and Agriculture Organization of the United Nations 19(2) (2016) 1-35.

F. Adam, N. Appaturi, R. Thankappan, M.A.M. Nawi, Silica-tin nanotubes prepared from rice husk ash by sol-gel method: characterization and its photocatalytic activity, Applied Surface Science 257 (2010) 811-816.

F. Adam, H.K. Fua, Production of silica from biogenic material, in: M. Patent (Ed.) Malaysian Patent, Malaysian, 2008.

F. Arab, I. Alemzadeh, V. Maghsoudi, Determination of antioxidant component and activity of rice bran extract, Transactions C: Chemistry and Chemical Engineering 18 (2011) 1402-1406.

F. Cherubini, A.H. Stromman, Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems, Biofuel, Bioproducts and Biorefining 5(5) (2011) 548-561.

F.H. Isikgor, C.R. Becer, Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers, Polymer Chemistry 6 (2015) 4497-4559.

F. Okasha, G. Zaater, S. El-Emam, M. Awad, E. Zeidan, Co-combustion of biomass and gaseous fuel in a novel configuration of fluidized bed: Combustion characteristics, Fuel 133 (2014) 143-152.

G. Kaur, S. Sharma, H.P.S. Nagi, B.N. Dar, Functional properties of pasta enriched with variable cereal brans, Journal of Food Science and Technology 49 (2012) 467-474.

G.L. Zabot, E.R. Abaide, M.V. Tres, M.A. Mazutti, Subcritical hydrolysis contribution in the holistic biorefinery concept: obtaining bioproducts and biofuels from renewable natural resources for a novel bioeconomy, in: M. Hosseini (Ed.), Advanced Bioprocessing for Alternative Fuels, Biobased Chemicals, and Bioproducts, Cambridge: Woodhead Publishing, 2018, pp. 25-60.

G. Ningbo, L. Baoling, L. Aimin, L. Juanjuan, Continuous pyrolysis of pine sawdust at different pyrolysis temperatures and solid residence times, J. Anal. Appl. Pyrolysis 114 (2015) 155-162.

H. Acharya, S.K. Dutta, H. Banerjee, Production of magnesium silicide and silane from rice husk ash, Solar Energy Materials 3 (1980) 441-445.

H. Chen, X. Chen, Y. Qin, J. Wei, H. Liu, Effect of torrefaction on the properties of rice straw high temperature pyrolysis char: Pore structure, aromaticity and gasification activity, Bioresource Technology 228 (2017) 241-249.

H. Kanno, N. Tachibana, M. Fukushima, Optimization of conditions for thermal treatment of rice bran using an accelerator including an organo-iron compound, Bioresource Technology 102 (2011) 3430-3436.

H. Huang, X. Yuan, G. Zeng, Y. Liu, H. Li, J. Yin, X. Wang, Thermochemical liquefaction of rice husk for bio-oil production with sub- and supercritical ethanol as solvent, Journal of Analytical and Applied Pyrolysis 102 (2013) 60-67.

H.S. Heo, H.J. Park, J.I. Dong, S.H. Park, S. Kim, D.J. Suh, S. Young-Woong, K. Seung-Soo, P. Young-Kwon, Fast pyrolysis of rice husk under different reaction conditions, Journal of Industrial and Engineering Chemistry 16 (2010) 27-31.

H. Wu, Y. Ku, H. Tsai, Y. Kuo, Y. Tseng, Rice husk as solid fuel for chemical looping combustion in an annular dual-tube moving bed reactor, Chemical Engineering Journa 280(15) (2015) 82-89.

H. Zabed, J.N. Sahu, A.N. Boyce, G. Faruq, Fuel ethanol production from lignocellulosic biomass: An overview on feedstocks and technological approaches, Renewable Sustainable Energy Rev 66 (2016) 751-774.

I. Eom, J. Kim, S. Lee, T. Cho, H. Yeo, J. Cho, Comparison of pyrolytic products produced from inorganic-rich and memineralized rice straw (*Oryza sativa L.*) by fluidized bed pyrolyzer for future biorefinery approach, Bioresour. Technol 128 (2013) 664-672.

I.G. Zigoneanu, L. Williams, Z. Xu, C.M. Sabliov, Determination of antioxidant components in rice bran oil extracted by microwave-assisted method, Bioresource Technology 99 (2008) 4910-4918.

J. Cai, Y. He, X. Yu, S.W. Banks, Y. Yang, X. Zhang, Y. Yu, R. Liu, A.V. Bridgwater, Review of physicochemical properties and analytical characterization of lignocellulosic biomass, Renewable and Sustainable Energy Reviews 76 (2017) 309-322.

J.F. Soares, V.D. Prá, M. Souza, F.C. Lunelli, E. Abaide, J.R.F. Silva, R.C. Kuhn, J. Martínez, M.A. Mazutti, Extraction of rice bran oil using supercritical CO_2 and compressed liquefied petroleum gas, J. Food Eng. 170 (2016) 58-63.

J. Liu, Z. Ma, H. Zhu, Q. Caiyin, D. Liang, H. Wu, X. Huang, J. Qiao, Improving xylose utilization of defatted rice bran for nisin production by overexpression of a xylose transcriptional regulator in Lactococcus lactis, Bioresource Technology 228 (2017) 690-697.

J.M. Prado, L.A. Follegati-Romero, T. Foster-Carneiro, M.A. Rostagno, F. Maugeri-Filho, M.A.A. Meireles, Hydrolysis of sugarcane bagasse in subcritical water, J. Supercrit. Fluids 86 (2014) 15-22.

J.M. Shin, J.W. Gwak, P. Kamarajan, J.C. Fenno, A.H. Rickard, Y.L. Kapila, Biomedical applications of nisin, Journal of Applied Microbiology 120 (2015) 1449-1465.

J.M.D. Paye, A. Guseva, S.K. Hammer, E. Gjersing, M.F. Davis, B.H. Davison, J. Olstad, B.S. Donohoe, T.Y. Nguyen, C.E. Wyman, S. Pattathil, M.G. Han, L.R. Lynd, Biological lignocellulose solubilization:comparative evaluation of biocatalysts and enhancement via cotreatment, Biothechnology for Biofuels 8 (2016) 1-13.

J. Park, Y. Lee, C. Ryu, Y.K. Park, Slow pyrolysis of rice straw: analysis of product properties, carbon and energy yield., Bioresource Technology 155 (2014) 63-70.

J. Park, J.J. Wang, S. Kim, J. Cho, S. Kang, R.D. Delaune, K. Han, D. Seo, Recycling of rice straw through pyrolysis and its adsorption behaviors for Cu and Zn ions in aqueous solution, Colloids and Surfaces A: Physicochemical and Engineering Aspects 533(20) (2017) 330-337.

J.S. Tumuluru, C.T. Wright, J.R. Hess, K.L. Kenney, A review of biomass densification systems to develop uniform feedstock commodities for bioenergy application, Biofuels, Bioproducts and Biorefining 5(6) (2011) 683-707.

K. Chiang, C. Liao, C. Lu, The effects of prepared iron-based catalyst on the energy yield in gasification of rice straw, International Journal of Hydrogen Energy 41 (2016) 21747-21754.

K. Gul, B. Yousuf, A.K. Singh, P. Singh, A.A. Wani, Rice bran: Nutritional values and its emerging potential for development of functional food—A review, Bioactive Carbohydrates and Dietary Fibre 6 (2015) 24-30.

K. Ishii, T. Furuichi, A. Fujiyama, S. Watanabe, Logistics cost analysis of rice straw pellets for feasible production capacity and spatial scale in heat utilization systems: A case study in Nanporo town, Hokkaido, Japan, Biomass and Bioenergy 94 (2016) 155-166.

K. Kotarska, A. Świerczynska, W. Dziemianowicz, Study on the decomposition of lignocellulosic biomass and subjecting it to alcoholic fermentation, Renewable Energy 75 (2015) 389-394.

K. Majeed, M. Jawaid, A. Hassan, A. AbuBakar, H.P.S. AbdulKhalil, A.A. Salema, I. Inuwa, Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater. Des. 46, 391e410., Materials and Desgign 46 (2013) 391-410.

K.R. Bhattacharya, Rice quality: A guide to rice properties and analysis, Food Sci. Technol. Nutr Publishing Limited Series (2011).

K. Tomita, S. Machmudah, Wahyudiono, R. Fukuzato, H. Kanda, A.T. Quitain, M. Sasaki, M. Goto, Extraction of rice bran oil by supercritical carbon dioxide and solubility consideration, Separation and Purification Technology 125 (2014) 319-325.

K. Xu, C. Liu, K. Kang, Z. Zheng, S. Wang, Z. Tang, W. Yang, Isolation of nanocrystalline cellulose from rice straw and preparation of its biocomposites with chitosan: Physicochemical characterization and evaluation of interfacial compatibility, Composites Science and Technology 154 (2018) 8-17.

K.W. Chan, M.H. Khong, S. Iqbal, M. Ismail, Isolation and antioxidative properties of phenolics-saponins rich fraction from defatted rice bran, Journal of Cereal Science, 57 (2013) 480-485.

L. Calvo, M. Gil, M. Otero, A. Morán, A. Garcia, Gasification of rice straw in fluidized-bed gasifier for syngas application in close-coupled boiler-gasifier systems, Bioresour.Technol 109 (2012) 206-214.

L. Ding, Y. Gong, Y. Wang, F. Wang, G. Yu, Characterisation of the morphological changes and interactions in char, slag and ash during CO2 gasification of rice straw and lignite, Applied Energy 195 (2017) 713-724.

M. Ahiduzzaman, A.K.M.S. Islam, Energy Yield of Torrefied Rice Husk at Atmospheric Condition, Procedia Engineering 105 (2015) 719-724.

M.A. Brand, R.C. Jacinto, R. Antunes, A.B. Cunha, Production of briquettes as a tool to optimize the use of waste from rice cultivation and industrial processing, Renewable Energy 111 (2017) 116-123.

M. Chhabra, A. Sharma, G. Dwivedi, Performance evaluation of diesel engine using rice bran biodiesel, Egyptian Journal of Petroleum 26 (2017) 511-518.

M. Ghosh, Review on Recent Trends in Rice Bran Oil Processing, Journal of the American Oil Chemists' Society 84 (2007) 315-324.

M.K. Sharif, M.S. Butt, F.M. Anjum, S.H. khan, Rice bran: a novel functional ingredient, Food Sci. Nutr 38 (2014) 1184-1192.

M. Kordowska-wiater, A. Kubk-komar, Z. Targonski, Application of response surface methodology for the optimization of arabinose biotransformation to arabitol by Candida parapsilosis, Central European Journal of Biology 8 (2013) 835-842.

M.J. Taherzadeh, C. Niklasson, Ethanol from lignocellulosic materials: pretreatment, acid and enzymatic hydrolyses, and fermentation, Lignocellulose Biodegradation2004, pp. 49-68.

M.L. Chitawo, A.F.A. Chimphango, A synergetic integration of bioenergy and rice production in rice farms, Renewable and Sustainable Energy 75 (2017) 58-67.

M.P. Sharma, S.V. Bali, Effect of rice residue management in wheat yield and soil properties in rice-wheat cropping system, The Indian Journal of Agricultural Sciences 68 (1998) 695-696.

M.S. Hossain, M.R. Islam, M.S. Rahman, M.A. Kader, H. Haniu, Biofuel from co-´pyrolysis of solid tire waste and rice husk, Energ. Proced 110 (2017) 453-458.

M.Y.A. Fuad, Z. Ismail, Z.A.M. Ishak, A.K.M. Omar, Application of rice husk ash as fillers in polypropylene: Effect of titanate, zirconate and silane coupling agents, European Polymer Journal 31 (1995) 885-893.

M.Z. Abdullah, Z. Husia, S.L.Y. Pong, Analysis of cold flow fluidization teste results for various biomass fuels, Biomass and Bioenergy 24 (2003) 487-494.

N.J. Bozell, G.R. Petersen, Thecnology development for the production of biobased products from biorefinery carohydrates Gree Cemistry 12 (2010) 539-544.

N. Johar, I. Ahmad, A. Dufresne, Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk, Industrial Crops and Products 37 (2012) 93-99.

N. Sarkar, S.K. Ghosh, S.Bannerje, K. Aikat, Bioethanol production from agricultural wastes: An overview, Renewable Energy 37 (2012) 19-27.

N. Soltani, A. Bahrami, M.I. Pech-Canul, L.A. González, Review on the physicochemical treatments of rice husk for production of advanced materials, Chemical Engineering Journal 264 (2014) 899-935.

P.E. Bacon, Effect of nitrogen fertilization and rice stubble management techniques on soil moisture content, soil nitrogen status, and nitrogen uptake by wheat. , Field Crops Research 17(1) (1987) 75-90.

P.K. Mehta, N. Pitt, Energy and industrial materials from crop residues, Resource Recovery and Conservation 2(1) (1976) 23-28.

P. Lu, Y. Hsieh, Highly pure amorphous silica nano-disks from rice straw, Powder Technology 225 (2012) 149-155.

P. Mishra, A. Chakraverty, H. Banerjee, Production and purification of silicon by calcium reduction of rice-husk white ash, Journal of Materials Science 20 (1985) 4387-4391.

R. Blissett, R. Sommerville, N. Rowson, J. Jones, B. Laughlin, Valorisation of rice husk usgin TORBED® combustion process, Fuel Processing Technology 159 (2017) 247-255.

P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, Energy 25 (2000) 493-513.

R.C.A. Castro, B.G. Fonseca, H.T.L, Santos, I.S. Ferreira, S.I. Mussato, I.C. Roberto, Alkaline deacetylation as a strategy to improve sugars recovery and ethanol production from rice straw hemicellulose and cellulose, Ind. Crops Prod. 106(1) (2016) 65-73.

R.C. Brown, Introduction to Thermochemical Processing of Biomass into Fuels, Chemicals and Power, in: R.C. Brown (Ed.), Thermochemical processing of biomass, John Wiley & Son, United Kingdom, 2011, pp. 47-74.

R. Khonde, A. Chaurasia, Rice husk gasification in a two-stage fixed-bed gasifier: Production of hydrogen rich syngas and
kinetics, International Journal of Hidrogen Energy xx (2016) 1-10.

R.M. Carlos, K.D. Ba, Characterization of biomass energy projects in South-east Asia, Biomass and Bioenergy 32 (2008) 525-532.

R. Pandey, S.L. Shrivastava, Comparative evaluation of rice bran oil obtained with two-step microwave assisted extraction and conventional solvent extraction, Journal of Food Engineering 218 (2018) 106-114.

R. Pode, Potential applications of rice husk ash waste from rice husk biomass power plant, Renew. Sustain. Energy Rev. 53 (2016) 1468-1485.

R. Potumarthi, R.R. Baandlhe, P. Nayak, A. Jetty, Simultaneous pretreatment and sacchariffication of rice husk by *Phanerochete chrysosporium* for improved production of reducing sugars, Bioresour. Technol 128 (2013) 113-117.

R. Singh, A. Prakash, S.K. Dhiman, B. Balagurumurthy, A.K. Arora, S.K. Puri, T. Bhaskar, Hidrothermal conversion of lignin to substituted phenol and aromatic ethers, Bioresour. Technol 165 (2014) 319-322.

R. Singh, B.B. Krishna, G. Mishra, J. Kumar, Strategies for selection of thermo-chemical process for the valorisation of biomass, Renewable energy 98 (2016) 1226-237.

R. Suxia, X. Haiyan, Z. Jinling, L. Shunquing, H. Xiaofeng, L. Tingzhou, Furfural production from rice husk using sulfuric acid and a solid acid catalyst through a two-stage process, Carbohydrate Research 359 (2012) 1-6.

R. Tabaraki, A. Nateghi, Optimization of ultrasonic-assisted extraction of natural antioxidants from rice bran using response surface methodology, Ultrasonics Sonochemistry 18 (2011) 1279-1286.

R. Zerbino, G. Giaccio, G.C. Isaia, Concrete incorporating rice-husk ash without processing, Construction and Building Materials 25(1) (2011) 371-378.

S. Sayasoonthorn, S. Kaewreng, P. Patharasathapornkul, Rice Bran Oil Extraction by Screw Press Method: Optimum Operating Settings, Oil Extraction Level and Press Cake Appearance, Rice Science 19 (2012) 75-78.

S.A. Shah, M. Soomar, A. Hussain, Comparative Emission Analysis Of Bituminous Coal, Sugarcane Bagasse and Rice Husk Journal of Sindh University Research 48(3) (2016) 685-688.

S.K. Meher, Kinetic study of rice bran by thermogravimetric analysis Chemical Engineering, National Insitute of Technology, India, 2015.

S. Karagoz, T. Bhaskar, A. Muto, Y. Sakata, Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment, Fuel 84 (2005) 875-884.

S.M. Shafie, T.M. IMahlia, H.H. Masjuki, Life cycle assesment of rice straw co-firing with coal power generation in Malaysia, Energy 57 (2013) 284-294.

S.L. Moraes, C.P. Massola, E.M. Saccoccio, D.P. Silva, Y.B. Guimarães, Brazilian scenario of production and use of densified biomass, Revista IPT | Tecnologia e Inovação 1 (2017) 58-73.

S. Rani, M.L. Joy, K.P. Nair, Evaluation of physiochemical and tribological properties of rice bran oil – biodegradable and potential base stoke for industrial lubricants, Industrial Crops and Products 65 (2015) 328-333.

S. Sangon, A.J. Hunt, T.M. Attard, P. Mengchang, Y. Ngernyen, N. Supanchaiyamat, Valorisation of waste rice straw for the production of highly effective carbon based adsorbents for dyes removal, Journal of Cleaner Production 172(20) (2017) 1128-1139.

S.S. Toor, L. Rosendahl, M.P. Nielsen, M. Glausius, A. Rudolf, S.B. Iversen, Continuous production of bio-oil by catalytic liquefaction from wet distiller’s grain with solubles (WDGS) from bioethanol production, Biomass and Bioenergy 36 (2012) 327-332.

S. Sun, H. Tian, Y. Zhao, R. Sun, H. Zhou, Experimental and numerical study of biomass flash pyrolysis in an entrained flow reactor, Bioresource Technology 101 (2010) 3678-3684.

T. Chen, C. Wu, R. Liu, W. Fei, S. Liu, Effect of hot vapor filtration on the characterization of bio-oil from rice husk with fast pyroysis in fluidized-bed reactor, Bioresource Technology 102 (2011) 6178-6185.

T.I. Mohammed, T.O. Olugbade, Characterisation of briquettes from Rice Bran and Palm Kernel Shell, International Journal of Material Science Innovations 3(2) (2015) 60-67.

T. Kawai, M. Suveen, R. Michael, Husk-to-Home: A Sustainable Building Material for the Philippines, in: U.S.E.P. Agency (Ed.) 2018.

T. Lin, G. Guo, W. Hwang, S. Huang, The addition of hydrolyzed rice straw in xylose fermentation by Pichia stipitis to increase bioethanol production at the pilot-scale, Biomass and Bioenergy 91 (2016) 204-209.

T.N. Indira, A.V. Narayan, R.S. Barhate, K.S. Raghavaro, S. Khatoon, G. Channaiah, A. Rao, V. Prakash, Production of oryzanol-enriched fraction useful in the treatment of melanin related disorders and for minimizing wrinkles involves saponification; dehydration and leaching of RBO soapstock., japanCouncil of Scientific and Industrial Research (CSIR) Indian, 2005.

T. Yang, J. Wang, B. Li, X. Kai, R. Li, Effect of residence time on two-step liquefaction of rice straw in CO_2 atmosphere: differences between subcritical water and supercritical ethanol, Bioresour. Technol 229 (2017) 143-151.

U. Isaara, S. Rawdkuen, Rice bran: a potential of main ingredient in healthy beverage, International Food Research Journal 23(6) (2016) 2306-2318.

USDA, Food Price policy in an era of market instability, Colorado, United States, 2015.

V.K. Jain, S.N. Srinivas, Empowering Rural India the RE way- Inspiring Success Stories, in: N.D. MNRE. (Ed.) 2012.

V. VanHoed, G. Depaemelaere, J.V. Ayala, P. Santiwattana, R. Verhe, W. deGreyt, Influence of chemical refining on the major and minor components of rice bran oil, J. Amer. Oil Chemst. Society 83 (2006) 315-321.

W.N. Stacey, D.L. Rankins, Rice mill feed as a replacement for broiler litter in diets for growing beef cattle., Journal of Animal Science 82 (2004) 2193-2199.

W.V. Hancock, P. Chandramouli, Comparative properties of rice-husk board, particle board, and wafer board, Journal of the Indian Academy of Wood Science, 5(1) (1974) 18-27.

W.T. Tsai, M.K. Lee, Y.M. Chang, Fast pyrolysis of rice husk: Product yields and compositions, Bioresour. Technol 98 (2007) 22-28.

Wuxi Teneng Power Machinery Co., Powermax rice husk gasification power plant 2018. (Accessed January 2018).

X. Gao, W. Ma, C. Ma, F. Zhang, Y. Wang, Analysis on current status of utilization of crop straw in China, Journal Huazhong Agricultural University 21 (2002) 242-247.

X. Hou, J. Xu, N. Li, M. Zong, Effect of anion structures on cholinium ionic liquids pretreatment of rice straw and the subsequent enzymatic hydrolysis, Biofuels and Environmental Biotechnology 112(1) (2014) 65-73.

X. Wang, W. Lv, L. Guo, M. Zhai, P. Dong, G. Qi, Energy and exergy analysis of rice husk high-temperature pyrolysis, International Journal of Hydrogen Energy 41(46) (2016) 21121-21130.

Y.C. Rotliwala, P.A. Parikh, Thermal degradation of rice-bran with high density polyethylene: A kinetic study, Korean Journal of Chemical Engineering 28(3) (2011) 788-792.

Y. Guo, J. Zhao, H. Zhang, S. Yang, J. Qui, Z. Wang, H. Xu, Use of rice husk-based porous carbon for adsorption of Rhodamine B from aqueous solutions, Dyes and Pigments 66(2) (2005) 123-128.

Y. Liu, Y. Wang, F. Guo, X. Li, T. Li, C. Guo, J. Chang, Characterization of the gas releasing behaviors of catalytic pyrolysis of rice husk using potassium over a micro-fluidized bed reactor, Energy Conversion and Management 136 (2017) 395-403.

Y. Qian, J. Zhang, J. Wang, Pressurized pyrolysis of rice husk in an inert gas sweeping fixed-bed reactor with a focus on bio-oil deoxygenation, Bioresour. Technol 174 (2014) 95-102.

Y. Shen, L. Jarboe, R. Brown, Z. Wen, A thermochemical-biochemical hybrid processing of lignocellulosic biomass for producing fuels and chemicals, Biotecnol Adv 33(8) (2015) 1799-1813.

Y. Tsuchiya, T. Yoshida, Pelletization of brown coal and rice bran in Indonesia: Characteristics of the mixture pellets including safety during transportation, Fuel Processing Technology 156 (2017) 68-71.

Y. Wang, D. Cai, M. He, Z. Wang, P. Qin, T. Tan, Open fermentative production of L-lactic acid using white rice bran by simultaneous saccharification and fermentation, Bioresource Technology 198 (2015) 665-672.

Y. Zhang, Y. Zhao, X. Gao, B. Li, J. Huang, Energy and exergy analyses of syngas produced from rice husk gasification in an entrained flow reactor, Journal of Cleaner Production 95(15) (2015) 273-280.

Z. Li, J. Lu, Z. Yang, L. Han, T. tan, Utilization of white rice bran for production of L-lactic acid, Biomass and Bioenergy 39 (2012) 53-58.

Z. Zhang, B. Liu, Z. Zhao, Efficient acid-catalyzed hydrolysis of cellulose in organic electrolyte solutions. Polymer Degradation and Stability 97 (2012) 573-577.

- CAPÍTULO 3 -

HIDRÓLISE COM ÁGUA SUBCRÍTICA DA PALHA DE ARROZ

Subcritical water hydrolysis of rice straw in a semi-continuous mode

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Abstract

Rice straw is an agricultural residue rich in cellulose and hemicelluloses. Therefore, the objective of this study was to obtain fermentable sugars and bioproducts from this biomass by subcritical water hydrolysis (SWH) in a scaleable semi-continuous mode. Temperatures of 180°C, 220°C and 260°C, and liquid/solid mass ratios of 7.5 g water/g straw and 15 g water/g straw were evaluated on the reducing sugar yield (Y_{RS}), efficiency of conversion (E), kinetic profiles, composition of inhibitors and bioproducts, and physicochemical characteristics of remaining solid material. The pressure was set at 25 MPa and the reaction time was evaluated up to 15 minutes. The thermogravimetric analysis and Fourier Transform Infrared Spectroscopy provided additional information on the bulk and surface modification of the residual biomass. The highest Y_{RS} (33.4 ± 4.3 g/100 g dry straw) and E (72.1 ± 4.6 g sugar equivalents in glucose per 100 g of carbohydrates) were obtained at 220°C and liquid/solid mass ratio of 7.5 g water/g straw. The analysis of the hydrolyzed solution indicated xylose (0.29 - 7.81 wt.%), arabinose (0.35 - 4.85 wt.%), cellobiose (0.04 - 3.41 wt.%), glucose (0.05 - 1.54 wt.%), and levulinic acid (0.04 - 0.77 wt.%). The fermentable sugars and bioproducts can be applied in several industrial fields, especially for the production of bioethanol and other higher value-added chemical compounds. Furthermore, SWH performed in semi-continuous mode is a green technology within the biorefinery concept that can be operated at industrial scale for processing lignocellulosic biomass.

Keywords: Biomass, Cleaner Production, Biorefinery, Sugar, Xylose, Levulinic Acid.

3.1 INTRODUCTION

Production of rice around the world has increased in the last years, from 660 million tons (2007) to 746 million tons (2014). Consequently, the amount of rice straw generated from rice crop has increased as well (0.38 tons for each ton of harvested rice) (FAO, 2016). Brazil is the largest producer of rice outside the Asian continent. In the harvest of 2017, the cultivated area in Brazil was approximately 1.9 million hectares and the production was approximately 11.6 million tons (CONAB, 2018). Large quantities of rice straw are produced annually in farms. In the soil, this biomass undergoes a gradual biodegradation process that releases methane (Zalengera et al., 2014), which is not a friendly substance to the environment. The incorporation of rice straw in the soil influences the immobilization of inorganic nitrogen and reduces its decomposition, affecting the yields of other crops, such as wheat (Sidhu and Beri, 1989).

Overall, rice straw is not nutritive and could not be used directly in animals feed. Although rice cultivation is different from each country, the burning of straw is a common practice. However, the burning of open-pit waste contributes to the emission of hydrocarbons aromatics and dioxins that are harmful to the environment and human health because of their potential carcinogen (Gadde et al., 2009; Maraseni et al., 2018). One alternative to rice coproducts that are burned in open fields is to use them as compact biomass briquettes for power generation. This kind of pellets was first commercially produced in Nanporo town, Hokkaido, Japan (Ishii et al., 2016). In another example, rice straw is collected in Karonga district in Malawi from the rice farms and processing could generate approximately 16.64 GW.h in the base year 2016 (Chitawo and Chimphango, 2017).

Accompanying the increasing of agricultural biomass produced, the increase of energy and fuel requirements is encouraging the development of researches for using lignocellulosic biomass as a sustainable source of bioproducts and renewable energy. Specifically, conversion of biomass to high-performance biofuels like bioethanol and biogas has recently received special interest (Faba et al., 2015; Ozbek et al., 2018). Considering the high cellulose and hemicelluloses contents in rice straw, it can be potentially used for biofuel production through fermentation or as precursors for producing other bioproducts, as levulinic acid and dimethyl-furan (Bevilaqua et al., 2013; Serrano-Ruiz and Dumesic, 2011). However, to obtain fermentable sugars and bioproducts from rice straw, the complex lignocellulosic structure should be broken down.

Some techniques have been proposed to dissociate cellulose and hemicelluloses, as the use of acid or enzymatic catalysts (Li et al., 2018; Silveira et al., 2015). Each one of these methods presents drawbacks, which influences the feasibility of hydrolysis of lignocellulosic biomass at industrial scale. The main drawbacks can be summarized as diluted acid hydrolysis affects the subsequent microbial fermentation due to the high levels of inhibitors produced during the reaction and due to the need of solvent removal (An et al., 2015) while enzymatic hydrolysis is a high-cost technology and presents high reaction time (Shen et al., 2018). In this context, a special attention has been focused on the development of more sustainable and greener technologies of biomass processing (Getachew and Chun, 2017; Silva et al., 2018), especially those technologies are scaleable and reproducible under larger scales, as using a continuous or a semi-continuous mode.

Within the biorefinery concept and as a clean technology, subcritical water hydrolysis (SWH) is being used as an efficient alternative for dissociating lignocellulosic biomass. A wide variety of biomass as white wine grape pomace, wheat straw, sugarcane bagasse, bamboo, sugarcane straw, coffee industry residues, and rice husk is completely processed into fermentable sugars and bioproducts by SWH treatment within a few minutes. Therefore, SWH is a promising technology because it has the potential for breaking down biopolymers of cellulose and hemicelluloses into simple sugars like xylose and glucose, and into small molecules for downstream fermentation or gasification. The SWH requires short time intervals when compared to enzymatic hydrolysis and does not require steps of separation of solvents such as those required by acid hydrolysis (Li et al., 2016; Pourali et al., 2009). Subcritical water has low viscosity and high diffusivity, which facilitates its penetration into the complex structure of the lignocellulosic matrix. The low dielectric constant, similar to non-polar organic solvents, enhances the solubility of organic compounds. Physical properties of water (such as density, ionic product, dielectric constant) can be finely tuned by varying temperature and pressure (Cocero et al., 2018).

In a global context, the SWH is applied on a pilot scale using the technology developed and commercialized by the SCF Technologies A/S Danish Company. The process can operate with water (30 L/h) at subcritical conditions in continuous mode (temperature 280°C; pressure ranging from 22.5 MPa to 25.0 MPa). The SWH is able to convert wet low-value feeds such as sludge, algae, manure, and residues from food production (Toor et al., 2012). The Renmatix Company, located in Montreal (Canada) and with subsidiaries around the world, works with water-based technology platform developed to convert woody material into biobased ingredients and sustainable products. Another company that uses subcritical water technology is the Rematec Corp. Sakai SC Factory, which recycles waste oil and waste wood into reclaiming fuel (Ozaki, 2008). However, the application of SWH in large scale for processing rice residues has not become a reality up to now. Only a few studies on SWH in laboratory scale have been conducted with rice straw (Lin et al., 2015; Syaftika and Matsumura, 2018; Yang et al., 2017), which most of them were conducted in batch mode. In both works, the yield of reducing sugars was the main response. These studies are important, but the compositions of sugars, bioproducts, and inhibitors have not been presented. Furthermore, none study could be found that reported the integrated evaluation of SWH of rice straw on hydrolyzed liquid solution and on solid residue (coproduct). Therefore, the focus of this work was the valorization of rice straw using the SWH as a clean and practical technology for converting cellulose and hemicellulose aiming at producing reducing sugars (RS) (e. g., xylose, glucose, arabinose and cellobiose) and bioproducts (e. g., levulinic acid) in a scaleable semi-continuous mode.

3.2 MATERIALS AND METHODS

3.2.1 Rice straw

Rice straw was obtained from crops in the central region of the state of Rio Grande do Sul/Brazil (29° 41’ 03’’S, 53° 48’ 25’’W), from 2016/2017 harvest. The biomass was oven dried for 24 h at 60°C. Afterward, it was ground in a Willey Knife Mills (SL 30, Solab, Brazil) with a 20 mesh separation grid. The milled biomass was frozen at -5°C until the experimental assays (maximum 3 months of storage).

3.2.2 Rice straw characterization

Moisture, ash and total extractives contents were determined directly on an unextracted sample according to the methodologies of Association of Official Analytical Chemists and National Renewable Energy Laboratory (AOAC, 1997; NREL, 2018). In all cases, the composition of rice straw was measured by three independent experiments, where average values and standard deviations are reported.

For moisture determination, 5 g of rice straw was prepared in Petri dishes. The samples were placed in an oven at 105°C for 4 h and weighed. Then samples were placed in the oven for another 1 h and weighed again. This procedure was repeated until having a constant mass. For ash determination, 5 g of rice straw was weighed and placed in melting pots (AOAC, 1997). The samples were calcined in an oven (MDS 15X15X30, Fornitec, Brazil) at 400°C for 1 h and at 800°C for 2 h. The ash was determined by mass difference. A flowchart of the main experimental procedures, including the straw characterization, is presented in Figure 10.

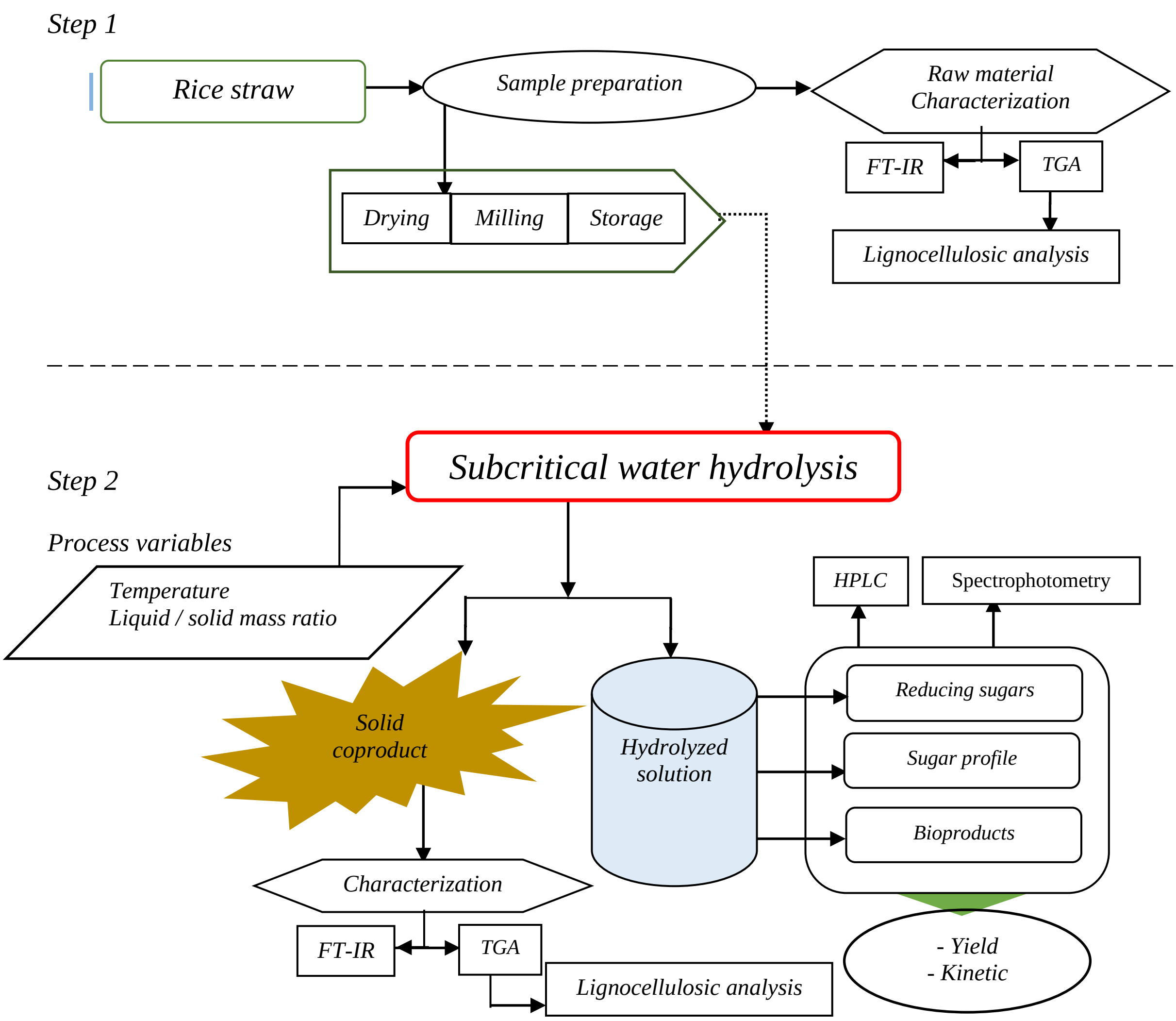
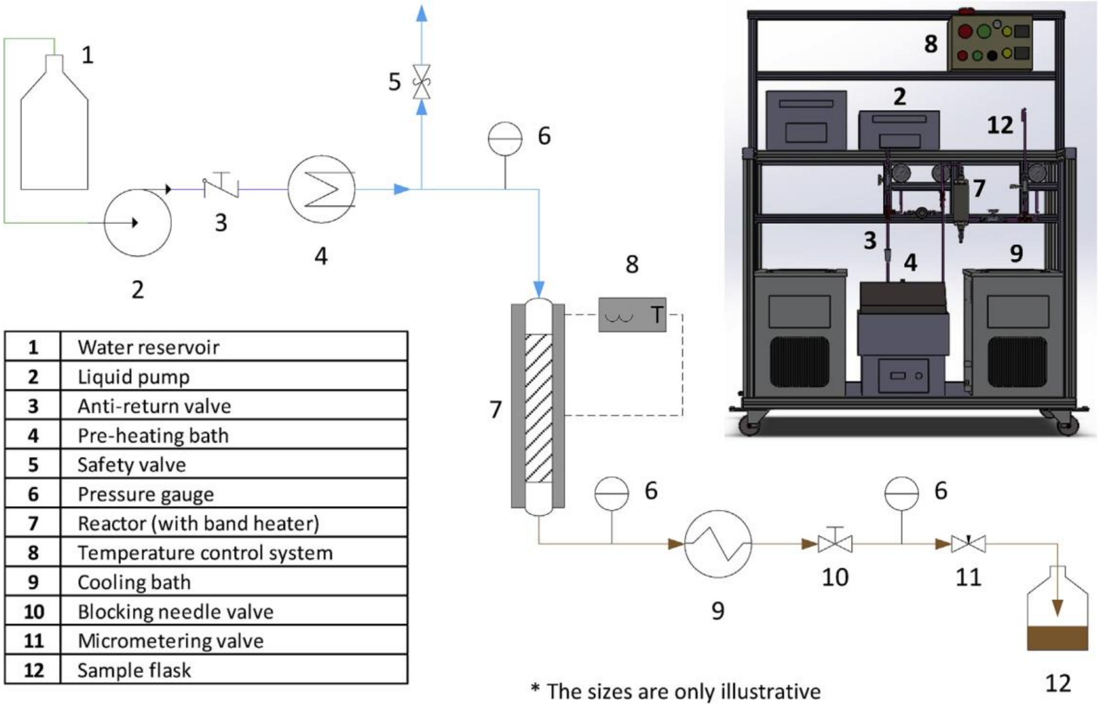


Figure 10 - Flowchart of the main experimental procedures performed in this research; FT-IR: Fourier-Transform Infrared; TGA: thermogravimetric analysis; HPLC: high-performance liquid chromatography

For determination of extractives, 2.5 g of rice straw was placed in a cartridge in a Soxhlet apparatus (MA491/6, Marconi, Brazil) with 195 mL of 90% ethanol in the extractor vessel (with glass beads) (NREL, 2018). The total reflux time was approximately 24 h with solvent exchange each 12 h. After this time, the cartridges were removed from the extractor vessel and rinsed thoroughly with running water. After washing, the cartridge was placed again in the extractor vessel with 195 mL of distilled water. The same procedure of reflux time and solvent exchange was repeated. Thereafter, the cartridges were washed with running water and dried at 105°C until constant weight. The extractable content was determined by mass difference.

3.2.3 Equipment for subcritical water hydrolysis in a semi-continuous mode

A schematic diagram of the equipment used in the study is shown in Figure 11. The system consists of a high-pressure pump (PU4087, Jasco, Japan) for pumping water, thermostatic baths (SL-152, Solab, Brazil) for water preheating and hydrolyzed solution cooling, a flow non-return valve, a stainless steel reactor with a useful volume of 50 mL, a ceramic band heater (1500 W) equipped with a thermocouple for temperature measurement (with a control panel) 316L stainless steel pipes (3.175 mm external diameter), pressure gauges, blocking valves and a micrometering valve (3125GY, Hoke, USA).



1	Water reservoir
2	Liquid pump
3	Anti-return valve
4	Pre-heating bath
5	Safety valve
6	Pressure gauge
7	Reactor (with band heater)
8	Temperature control system
9	Cooling bath
10	Blocking needle valve
11	Micrometering valve
12	Sample flask

Figure 11 **-** Flowchart of SWH process in semi-continuous mode and schematic representation of the equipment

3.2.4 Subcritical water hydrolysis of rice straw

For each assay, rice straw (20 g) was loaded in the reactor vessel and distilled water was pumped with a constant mass flow rate. Immediately after the system was pressurized with water (pipes and reactor vessel), the pump was turned off and the micrometering valve was closed. The band heater was turned on for increasing the temperature to the desired value (according to each assay) and, consequently, the pressure, which was fixed in 25 MPa based on studies reported elsewhere (Prado et al., 2016). The initial water pumping time in the reactor vessel was approximately 5 minutes.

Firstly, a transient assay was performed for evaluating the influence of temperature on the semi-continuous SWH of rice straw. From 100°C to 260°C, 9 samples were collected during the temperature increase for measuring RS. Based on this transient assay, the levels of temperature were selected (180°C, 220°C and 260°C) for the subsequent assays. All assays were completely randomized. In such case, the flow rate was set at 10 mL/minute and 20 mL/minutes to satisfy the liquid/solid ratios (R) of 7.5 g water/g straw and 15 g water/g straw, respectively, for a total reaction time of 15 minutes. Samples of the hydrolyzed solution were collected at intervals of 0.5 minutes (first 2 minutes) and at 1 minute (2-10 minutes). A final sample was collected during the interval of 10-15 minutes. The samples were stored under refrigeration for determination of pH, RS, sugars composition, inhibitors and bioproducts. In all cases, the compositions of hydrolyzed solutions were measured in duplicate and the average values and standard deviations are reported. The time intervals of collection and maximum running time were defined based on studies reported in the scientific literature (Cardenas-toro et al., 2014; Prado et al., 2016). The remaining solid residue at the end of the hydrolysis process for each condition was collected and dried at 105°C until constant weight for further characterization.

3.2.5 Analyses of hydrolyzed solution

3.2.5.1 pH

The pH of the hydrolyzed solutions was determined using a digital pHmeter (DM-22, Digimed, Brazil). Prior to the measurements, the pHmeter was calibrated using technical buffer solutions of pH 4.01 ± 0.02 and 7.00 ± 0.02.

2.5.2 Reducing sugars

The RS content was analyzed by the dinitrosalicylic (DNS) colorimetric method (Miller, 1959) using D-glucose as a standard. For every 1 mL of sample, 1 mL of DNS reagent was added. The mixture was heated by placing in boiling water (100°C) for 5 minutes until developing the red-brown color. Thereafter, 8 mL of 15.1 g/L of potassium sodium tartrate solution was added to stabilize the color and the mixture was cooled to 25°C in a water bath. The absorbance was measured with a spectrophotometer (UV-2700, Shimadzu, Japan) at 575 nm. For each experimental assay of hydrolysis, the RS yield (Y_{RS}, g sugar equivalents in glucose per 100 g of raw material) was calculated according to equation 1 and the efficiency (E, g sugar equivalents in glucose per 100 g of carbohydrates (hemicelluloses and celluloses)) was calculated according to equation 2.

$$Y_{RS}=\frac{m_{RS}}{m_{SA}}\times 100 \tag{1}$$

$$E=\frac{m_{RS}}{m_{CA}}\times 100 \tag{2}$$

Where: m_{RS} is the mass (g) of RS in the hydrolyzed solution, m_{SA} is the initial mass (g) of rice straw placed inside the reactor vessel at the beginning of the process, and m_{CA} is the initial mass (g) of carbohydrates (hemicelluloses + cellulose).

The Tukey's test was applied to determine the significant differences of Y_{RS} and E among the assays after 15 min of reaction using the software Statistica 7.0® (StatSoft, Inc.).

3.2.5.3 Sugars and bioproducts

Each sample of the hydrolyzed solution was conditioned in 2 mL microtubes and centrifuged at 14,000 rpm for 3 minutes. The supernatant was filtered on a 0.22 μm polytetrafluoroethylene (PTFE) membrane for chromatographic analysis. The contents of cellobiose, glucose, xylose, arabinose, formic acid, acetic acid, and levulinic acid were analyzed by high-performance liquid chromatography (HPLC) (Proeminence UFLCXR, Shimadzu, Japan) equipped with a refractive index detector (RID 10A, Shimadzu, Japan). An Aminex HPX-87H column (300 mm × 7.8 mm) (Bio-Rad, USA) was used at 30°C. As the mobile phase, a solution of H_2SO_4 45 mM (pH 2.6) prepared with ultrapure water was used, which was obtained from a Mili-Q ultrapure water system (Milipore, USA). After preparation, the mobile phase was filtered under vacuum using 0.45 μm and 47 mm diameter porosity cellulose esters (Milipore, USA) and degassed in an ultrasonic bath (USC-1400, Unique, São Paulo). The volumetric flow rate of the mobile phase was 0.6 mL/minutes and the volume of injection of samples was 15 μL. The compounds were separated in the stationary phase and monitored with a refractive index (IR) detector at 30°C for a run time of 25 minutes. The concentrations of each component were obtained by the correlation between the areas of the chromatograms and standard curves previously determined by standards of cellobiose, D-glucose, D-xylose and D-arabinose, formic acid, acetic acid and levulinic acid.

3.2.5.4 Furfural and hydroxymethylfurfural inhibitors

For the furfural and hydroxymethylfurfural analyses, the previously filtered samples were analyzed on an HPLC system (Proeminence UFLCXR, Shimadzu, Japan) equipped with a photodiode array detector (PDA 20-A, Shimadzu, Japan). A Shim-Pak ODS C18 column

(Shimadzu, Japan) was used. A solution of acetonitrile: water (1:8 with 1% (v/v) acetic acid) filtered on 0.45 μm and 47 mm diameter porosity cellulose esters (Milipore, USA) and degassed in an ultrasound bath (USC - 1400, Unique, São Paulo) was used as mobile phase. The conditions for the analysis were: 10 μL of injection volume, flow rate of 0.80 mL/minute, column temperature of 30°C, wavelength of 280 nm, detector temperature of 30°C, and run time of 10 minutes. The concentrations of each component were obtained by the correlation between the areas of the chromatograms and standard curves previously determined by furfural and hydroxymethylfurfural (HMF) standards (Sigma, Brazil). The areas of the peaks corresponding to furfural and HMF were used to calculate their concentration in the samples. These procedures were based on the methodology of Fleig et al. (2018).

3.2.6 Analysis of solid coproduct

3.2.6.1 Solid coproduct

After SWH, the residual solids contained in the reactor vessel were transferred to a Petri dish, taking care to prevent loss. The amount of solid coproducts was determined by the difference between the initial amount of dried biomass and the final dried mass remaining in the reactor at the end of the process, using a digital analytical balance (AY-220, Marte, Brazil).

3.2.6.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) of fresh rice straw and solid coproducts was performed in a thermogravimetric analyzer (DTG60 / 60H, Shimadzu, Japan). The analysis consisted of heating the samples at 10°C/minute from room temperature (25°C) to 850°C in a non-oxidizing atmosphere (N_2, 99.997% purity) at 100 mL/minute. Thermogravimetric data were converted into derivative thermograms (DTG).

3.2.6.3 Fourier-transform infrared (FT-IR) spectroscopy

Samples of fresh rice straw and solid coproducts were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy (IR Prestige 21, Shimadzu, Japan) to have the degradation of the major constituents. The spectra were obtained with a nominal resolution of 4 cm^{-1} and within the spectral range between 4000 and 400 cm^{-1}. All disks were made in the KBr tablet die accessory, using a press (Hand press SSP-10a press Shimadzu, Japan). For the preparation of the disks, 100 mg of KBr and 1 mg of the sample were used, which are thoroughly macerated and mixed into a smooth agate gravel and after pressing under 8 tons, resulting in thin transparent disks (less than 1 mm thick) with 13 mm in diameter.

3.3 RESULTS AND DISCUSSION

3.3.1 Raw material characterization

The moisture, ash, extractives, cellulose, hemicelluloses, and lignin content are shown in Table 5. The ash that constitutes the structure of rice straw may be a factor affecting the SWH process because it is constituted mainly by inorganic refractory compounds that can hinder the access of water to cellulose and hemicelluloses, undesirably acting as a barrier.

Table 5 **-** Chemical composition of fresh rice straw

	Moisture[a]	**Ash**[a]	**Extractives**[a]	**Cellulose**[b]	**Hemicelluloses**[b]	**Lignin**[b]
Composition (wt.%)	9.0 ± 0.1	12.2 ± 0.6	17.5 ± 1.1	22.4	24.6	9.4

[a] Mean ± standard deviation.

[b] by DTG analysis.

Although the composition can vary depending on climatic conditions of cultivation, the extractive content is closer to that one (17.8%) reported by He et al. (2009). Extractives are composed of organic compounds of low molecular weight, such as phenolic compounds, terpenes, saturated and unsaturated fatty acids, proteins and flavonoids and may affect SWH process (Marabezi, 2009; Zabot et al., 2018).

3.3.2 Transient heating on the RS yields

The transient hydrolysis during the heating indicated that the amount of sugars begins to increase expressively after 21 minutes, where the temperature was higher than 180°C (Fig.12). For example, the RS yield at 220°C was 7 g/100 g rice straw.

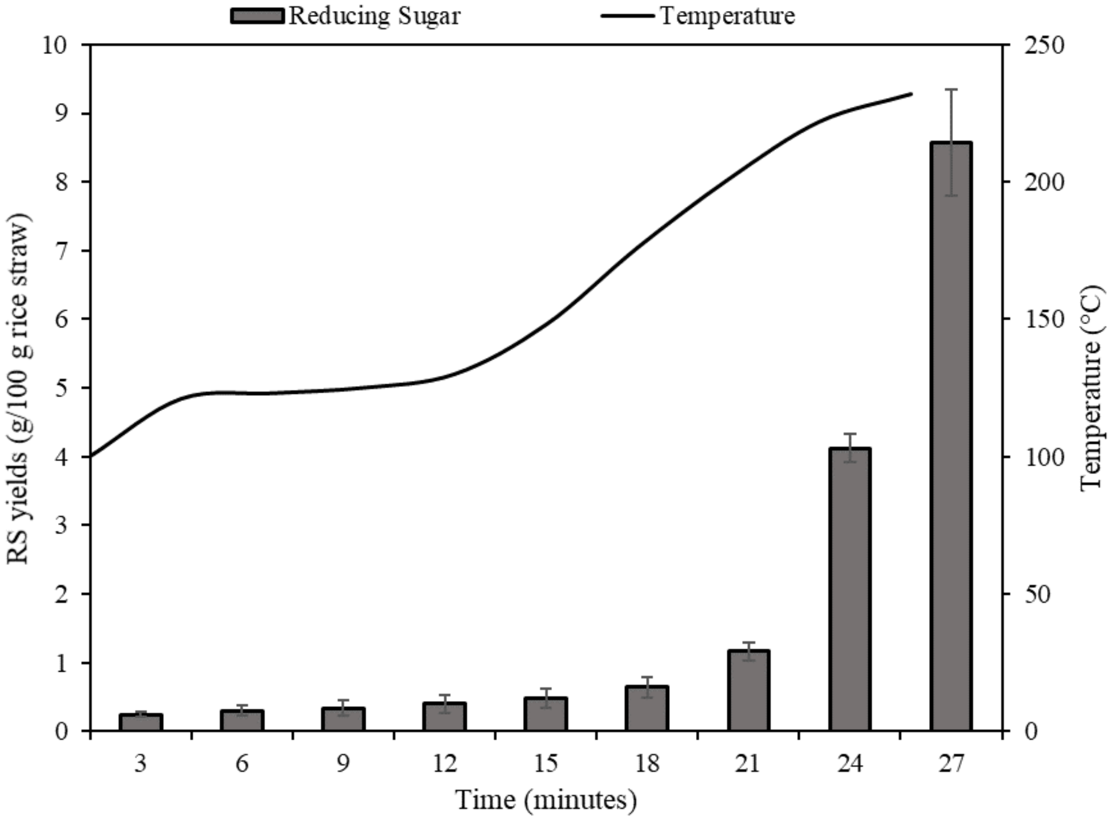


Figure 12 - Kinetic profile of RS in hydrolyzed samples from rice straw at 25 MPa and at different temperatures according to the reactor heating (transient assay)

When evaluating the scientific literature, the sugar yields for SWH of wheat straw at 180°C and 220°C were approximately 4 wt.% and 16 wt.%, respectively (Abdelmoez et al., 2014). This behavior can be explained by the effects of temperature on hydrolysis rates.

Hemicelluloses are hydrolyzed at 190–230°C (Allen et al., 1996), while cellulose hydrolysis takes place above 230°C (Yu and Wu, 2011). Based on the transient assay, the levels of temperature of 180°C, 220°C and 260°C (Table 6) were selected for performing the SWH of rice straw under constant temperature.

3.3.3 Influence of temperature and liquid/solid ratio on the efficiency and RS yields of SWH in a semi-continuous mode

The Y_{RS} and E obtained at different conditions of temperature and liquid/solid ratio after 15 minutes of reaction are shown in Table 6. A statistical analysis (Tukey's test) was done for comparing the means. According to the analysis, the highest Y_{RS} was obtained at 220°C / R-7.5 (33.6 ± 4.3 g/100g rice straw), which was statistically different ($p < 0.05$) when compared with the value obtained in the assay 4 (20.0 ±0.3 g/100g rice straw; the second highest Y_{RS}). No statistical differences were observed for the assays 1, 2, and 6, where the lowest values of Y_{RS} were obtained. Regarding the values of E, the behavior was similar to that one presented for Y_{RS}. The highest E was obtained at 220°C / R-7.5 (72.1 ± 4.6 g sugar equivalents in glucose per 100 g of carbohydrates), which was statistically different ($p < 0.05$) when compared with the values obtained in the other assays.

The RS efficiency in SWH process at different temperatures and R are shown in Figure 13. When analyzing the kinetic profiles, the reaction rate does not follow a same pattern for the different conditions. For 220°C / R-7.5 condition, there was an increase on yields of RS up to 10 minutes of reaction. After this time, the conversion rate became approximately zero and the maximum value of 33.5 ± 4.3 g/100 g rice straw was reached. For the 220°C / R-15 condition, the yield of RS became constant after 4 minutes of reaction (20 ± 0.3 g/100 g rice straw).

Table 6 - Influence of parameters (temperature and solid ratio) on the RS yield (Y_{RS}) and efficiency (E) of SWH of rice straw in a semi-continuous mode (at 25 MPa)

Assay^a	**Code**	**Liquid/solid mass ratio (g water/g straw)**	**Temperature (°C)**	**Y_{RS} (g/ 100 g rice straw)**	**E (g/ 100 g carbohydrates)**
1	180°C / R-7.5	7.5	180	2.6 ± 0.2^{cd}	5.7 ± 0.3^{c}
2	180°C / R-15	15	180	0.8 ± 0.2^{d}	5.4 ± 4.9^{c}
3	220°C / R-7.5	7.5	220	33.6 ± 4.3^{a}	72.1 ± 4.6^{a}
4	220°C / R-15	15	220	20.0 ± 0.3^{b}	43.1 ± 0.7^{b}
5	260°C / R-7.5	7.5	260	11.1 ± 4.1^{bc}	23.9 ± 8.8^{bc}
6	260°C / R-15	15	260	7.0 ± 2.1^{cd}	19.3 ± 1.1^{c}

* All assays were performed in duplicate, totalizing 12 assays; all assays were completely randomized.

$^{a-d}$ Different letters in the same column represent a significant difference at 95% ($p < 0.05$ – Tukey's test) among the assays for each response.

The RS yield increased as the temperature increased from 180°C to 220°C (Fig. 13(a)). This result was attributed to the increase of ionization constant of water at high temperature. The concentrations of H^+ and OH^- increased, thereby facilitating the hydrolysis of cellulose and hemicelluloses into monosaccharides (Akiya and Savage, 2002). Cellulose and hemicelluloses are hydrolyzed into fermentable sugars with high efficiencies at short residence times, but the RS efficiency was reduced when 260°C was used (Fig. 13(b)). The lower RS yield at 260°C was attributed to the enhanced thermal degradation of compounds, with the formation of volatile and non-recovered substances (Pinto et al., 2017). The SWH process was also applied to hydrolyze white wine grape pomace (Pedras et al., 2017). The authors evaluated the effect of temperature (170, 190 and 210°C) at 10 MPa on RS efficiency.

When increasing the temperature from 170 to 190 and 210°C, the RS efficiency increases from 40.1 ± 1.2 to 41.2 ± 1.1 and 49.3 ± 2.1 g/ 100 g carbohydrates, respectively.

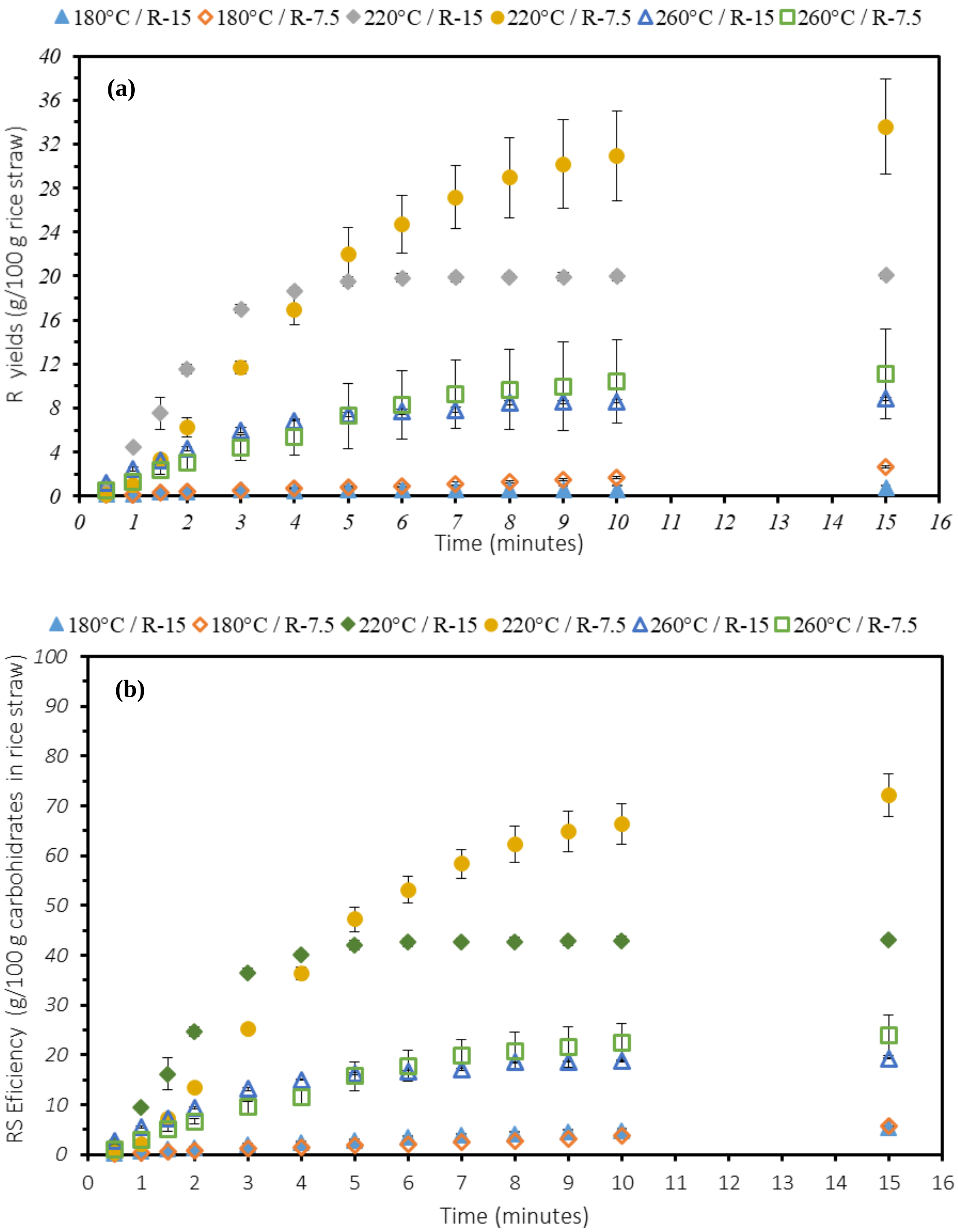


Figure 13 - Kinetic profile of RS yield (a) and efficiency (b) (accumulated samples) in hydrolyzed samples from rice straw at 25 MPa under different experimental conditions; the bars represent the standard deviation

At temperatures near to 250°C, the cellulose is dissolved but not hydrolyzed. Therefore, it is possible to obtain a high degree of polymeric molecules. However, the process is limited by the amount of amorphous cellulose available. In these cases, reaction times in the order of hours are required, which implies the operation in batch and semi-continuous reactors (Mohan, M. et al., 2015).

When evaluating the RS efficiency for SWH at 220°C, it was higher (72 g/100 g carbohydrates) for the lowest R. This can be attributed to the longer residence time when the values of R of 7.5 and 15 g water/g straw (both at 220°C) are compared. With respect to studies reported elsewhere, the SWH process was applied to hydrolyze defatted pressed palm fiber (Cardenas-toro et al., 2014). The authors evaluated the influence of residence time on RS efficiency at 180 and 280°C at 25 MPa. At 180°C, when increasing the residence time from 1.25 to 2.5 minutes, the RS efficiency increases from 4.8 to 7.5 g/ 100 g carbohydrates. At 280°C, when increasing the residence time from 1.25 to 2.5 minutes, the RS efficiency increases from 12.5 to 22 g /100 g carbohydrates.

SWH was also applied to dissociate lignocellulosic biomass from defatted grape seed, pressed palm fiber and coconut husk (Prado et al., 2014b). In the kinetic profiles, the RS yields continued increasing after 15 minutes of reaction, but at a small rate. The profiles demonstrated that the maximum rice straw hydrolysis rate (4 g/minute) was higher (in the best condition) than the maximum rates of hydrolysis for the defatted grape seed (0.26 g/minute), pressed palm fiber (0.66 g/minute), and coconut husk (0.9 g/minute) (Prado et al., 2014b). It is important to mention that the ratio between the mass of solid and the liquid flow rate was similar to this work since Prado et al. (2014b) used 34 g of biomass with a flow rate of 33 mL/minute. In this study, 20 g of dry rice straw was used, with a flow rate of 20 mL/minute. The different rates are attributed to the different physicochemical compositions of each biomass, with different proportions in crystalline and amorphous structures. It implies to higher or lower solvent accessibility to the glycosidic bonds of hemicelluloses and cellulose (Cocero et al., 2018).

A pre-treatment with dilute acid and enzymatic hydrolysis was applied to dissociate rice straw into fermentable sugars (Lee et al., 2017). The best result obtained for RS was 22 g/100 g rice straw using 1% (v/v) sulfuric acid solution for 60 minutes and enzymatic hydrolysis for 48 h. This result is equivalent to a rice straw hydrolysis rate of 0.0075 g/minute, which is much lower (533 times) than that obtained in this work.

The advantages of using SWH in a semi-continuous mode (industrial purposes, as used in this work) can be better identified when comparing our responses with other works that have used SWH in a batch mode (Lin et al., 2015). The authors obtained an RS yield of 34 g / 100 g rice straw in a batch reactor for 8 minutes at 280°C and 20 MPa. The yield is close to that one obtained in the present study (33.5 wt.%), but with a reaction time two times higher.

3.3.4 Composition of the hydrolyzed solutions

The hydrolyzed solutions were analyzed in terms of sugars, inhibitors, and bioproducts (Table 7). Xylose was the predominant monosaccharide present in the hydrolyzed solutions, followed by arabinose. Under conditions where the temperature was 220°C and 260°C, the highest values for xylose were obtained, with only one exception: 260°C / R-15 (higher flow). The sugars content for the 260°C / R-15 condition is associated with the degradation of xylose in acetic acid, since it is possible to visualize that the value for acetic acid is high, being 2.38 g/100 g rice straw. Xylose and arabinose originate from hemicelluloses hydrolysis (Zhu et al., 2013). For the 220°C and 260°C conditions, there was a higher concentration of inhibitors (furfural and HMF) and bioproducts (acetic, formic and levulinic). Inhibitors and bioproducts most likely result from cellulose degradation, with the only one exception of acetic acid, which was probably obtained from the degradation of hemicelluloses (Cocero et al., 2018).

Table 7 - Yields of sugars, inhibitors, and bioproducts (g/100 g biomass; dry basis) obtained by SWH of rice straw for 15 minutes

	180°C / R-7.5[a]	**180°C / R-15[a]**	**220°C / R-7.5[a]**	**220°C / R-15[a]**	**260°C / R-7.5[a]**	**260°C / R-15[a]**
Sugars (g/100 g rice straw)						
Glucose	0.05 ± 0.01	0.11 ± 0.03	0.49 ± 0.14	1.54 ± 0.32	0.49 ± 0.05	0.18 ± 0.01
Cellobiose	0.04 ± 0.02	0.05 ±0.01	0.67 ± 0.21	3.41 ± 0.06	0.67 ± 0.11	0.09 ± 0.03
Xylose	0.31 ± 0.06	0.29 ±0.11	2.85 ± 0.33	7.81 ± 0.42	2.85 ± 0.54	0.33 ± 0.07
Arabinose	0.35 ± 0.11	0.55 ±0.16	0.54 ± 0.19	4.85 ± 0.24	0.53 ± 0.4	0.74 ± 0.21
Total	0.75 ± 0.20	1.00 ±0.30	4.55 ± 0.87	17.61 ± 104.	4.54 ± 1.10	1.34 ± 0.32
Inhibitors (g/100 g rice straw)						
HMF	0.00	0.00	0.11 ± 0.02	0.19 ± 0.05	0.57 ± 0.17	0.28 ± 0.08
Fufural	0.00	0.00	0.39 ± 0.21	0.70 ± 0.37	0.10 ± 0.03	0.17 ± 0.09
Total	0.00	0.00	0.50 ± 0.23	0.89 ± 0.42	0.67 ± 0.20	0.45 ± 0.17
Bioproducts (g/100 g rice straw)						
Formic	0.16 ± 0.10	0.22 ± 0.14	0.90 ± 0.25	3.44 ± 0.63	1.57 ± 0.12	1.10 ± 0.23
Acetic	0.30 ± 0.08	0.44 ± 0.03	1.14 ± 0.56	3.85 ± 0.44	2.92 ± 0.37	2.38 ± 0.15
Levulinic	0.04 ± 0.02	0.04 ± 0.01	0.20 ± 0.07	0.77 ± 0.33	0.71 ± 0.10	0.44 ± 0.18
Total	0.50 ± 0.20	0.70 ± 0.18	2.24 ± 0.88	8.06 ± 1.44	5.20 ± 0.59	3.92 ± 0.56

[a] R: liquid/solid mass ratio (g water/g straw).

The assays were performed in duplicate.

When the xylose content (7.81 g/100 g dry rice straw; Table 7) is evaluated, its value is slightly lower than that obtained in the hydrolysis of dry rice straw using 1% (v/v) nitric acid over 1 h of reaction (Krishania et al., 2018). This occurs because at temperatures near to 220°C, the H^+ content increases, thus increasing the acid content in water and the destruction of hemicelluloses into the monomeric sugar xylose (Hong-Jia et al., 2014). In terms of acids, high values were obtained for acetic acid (3.85 g/100 g rice straw), formic acid (3.44 g/100 g rice straw) and levulinic acid (0.77 g/100 g rice straw) under the condition 220°C / R-15. The high yield for these bioproducts at this temperature (220°C) is related to the increased sugar degradation rate when the temperature increases from 180 to 220°C (Lin et al., 2015). When the temperature is set at 260°C, these bioproducts can bind to volatile compounds that do not remain in the hydrolyzed solution (Pinto et al., 2017). As a bioproduct, levulinic acid can be used as a chemical platform for the production of other higher value-added chemical compounds, such as methyl vinyl ketone and olefins. In the pharmaceutical industry, levulinic acid is used to produce aminolevulinic acid and benzoazepinones (Bevilaqua et al., 2013). For levulinic and formic acids, one way of recovering such bioproducts from the hydrolyzed solution is through the esterification reaction with butane, producing hydrophobic esters, which can be separated from the solution by distillation (Sen et al., 2012).

Rice straw hydrolyzed solutions were also analyzed in terms of fermentable sugars, inhibitors and bioproducts at different intervals for 15 minutes (Figs. 14 and 15). These results are important because it is possible to optimize the SWH process by maximizing the yield of fermentable sugars and minimizing the yields of inhibitors.

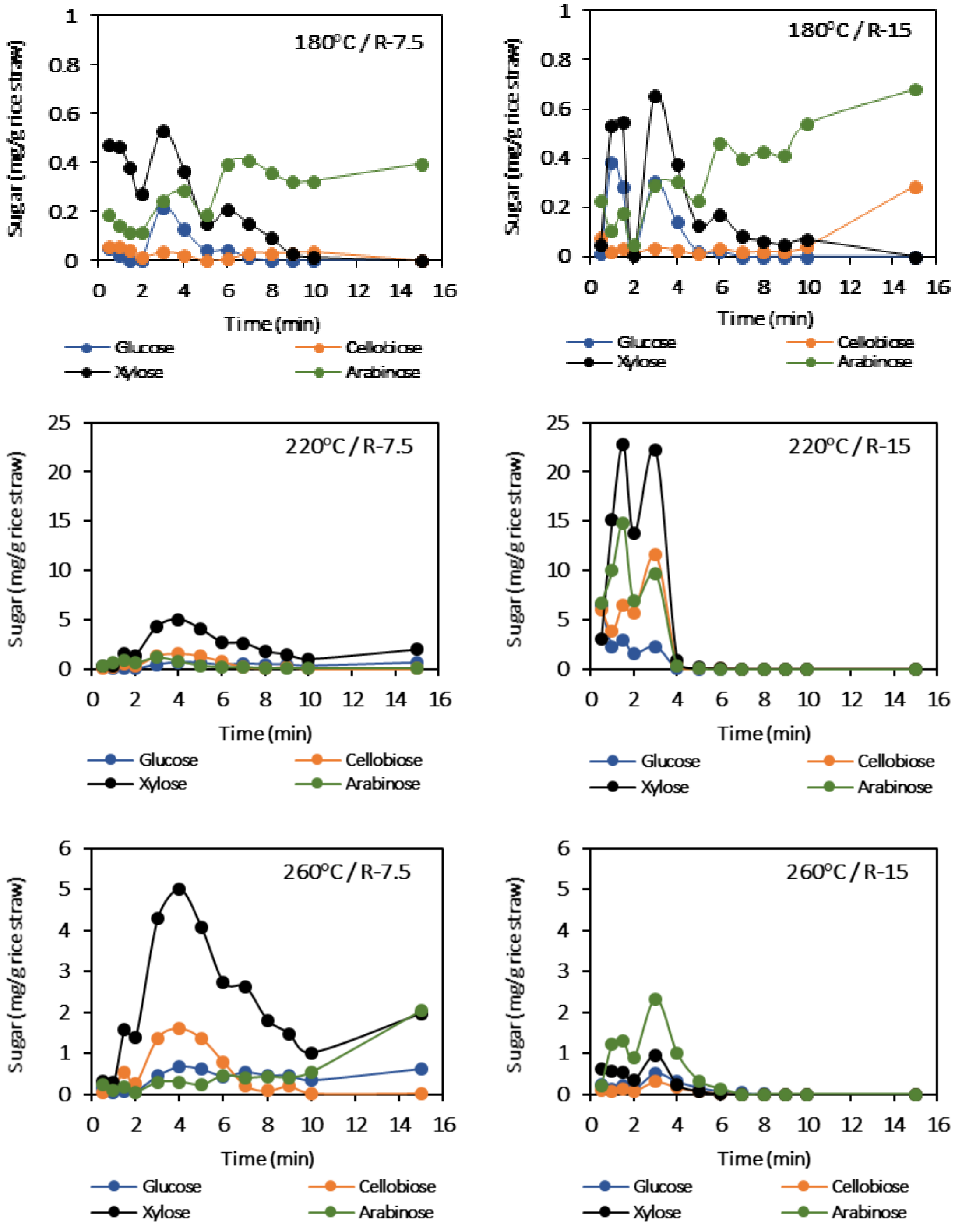


Figure 14 - Yield of fermentable sugars (non-accumulated samples) in hydrolyzed samples from rice straw at 25 MPa under different experimental conditions; R: liquid/solid mass ratio (g water/g straw)

Lower levels of sugars and inhibitors are obtained for samples obtained under the conditions 180°C / R-7.5 and 180°C / R-15. This is attributed to the non-occurrence of cellulose hydrolysis and low hemicelluloses hydrolysis at this temperature (Cocero et al., 2018). In this study, for the condition with the highest sugars (220°C / R-15), the yields are related to xylose and arabinose in the first 4 minutes of hydrolysis. Approximately 22 mg xylose/g rice straw is obtained in the range of 1.5 minutes and 3 minutes and 14 mg arabinose/g rice straw is obtained in the range of 1.5 minutes. Similar behavior was observed in SWH of sugarcane bagasse (Prado et al., 2014a). Xylose (8 mg xylose/g sugarcane bagasse) and glucose (6 mg xylose/g sugarcane bagasse) yields were obtained at 4 minutes using 290°C, 20 MPa, and flow rate of 33 mL/minutes.

When the conditions 220°C / R-15 and 220°C / R-7.5 are compared, there was a large difference in the sugars yield obtained, whereas in the condition R-7.5 the quantity of sugars is 5 times smaller. This behavior can be attributed to the fact that the flow rate in the 220°C / R-15 assay is higher and, as a consequence of the shorter residence time in the reactor vessel, less degradation can occur (Tanaka et al., 2012). This assertion can be confirmed by results presented in Figure 16. When the R increased, the amount of solid coproducts increased because there was lower cellulose and hemicelluloses dissociation. As the temperature increased, the amount of residual solids became smaller due to larger dissociation of lignocellulosic structure. This type of behavior was also reported in the SWH of coffee residue (Mayanga-Torres et al., 2017) and sugarcane straw (Lachos-Perez et al., 2017).

In the 220°C / R-15 condition, the highest yields of furfural were also achieved. Approximately 2.25 mg furfural / g rice straw was obtained in 3 minutes (Fig. 15). High levels of bioproducts (levulinic, acetic and formic acid) are observed in the first 4 minutes, reducing after 6 minutes. There is rapid degradation of cellulose (high formic acid content) and hemicelluloses (high acetic acid content) in the first 2 to 3 minutes for the 220°C / 15 condition. These results are similar to those reported in the SWH of sugarcane bagasse (Pinto et al., 2017; Prado et al., 2014a).

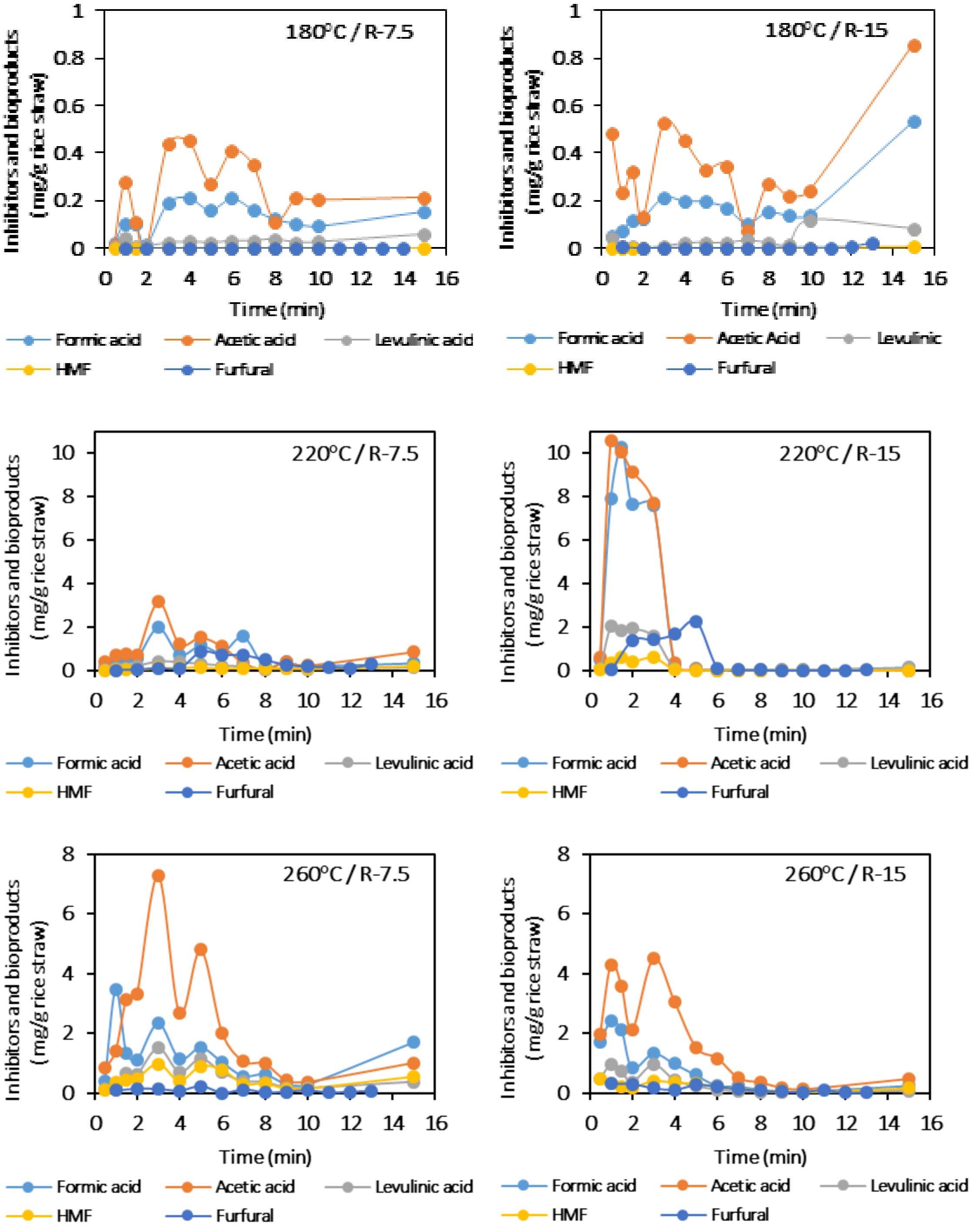


Figure 15 - Yield of bioproducts and inhibitors (non-accumulated samples) in hydrolyzed samples from rice straw at 25 MPa under different experimental conditions; R: liquid/solid mass ratio (g water/g straw)

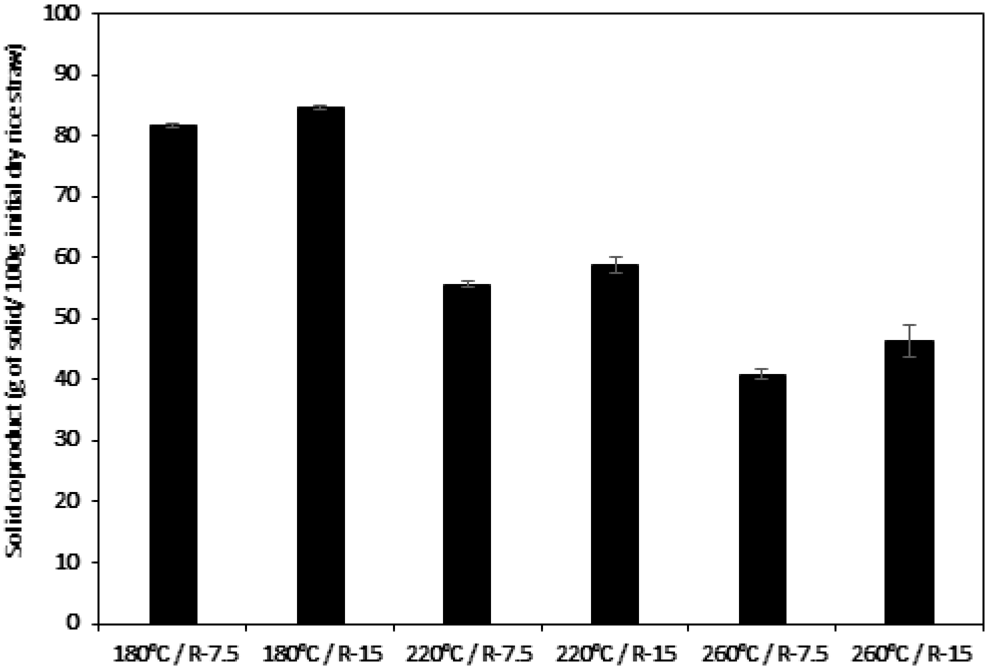


Figure 16 - Solid coproduct after SWH of rice straw under different experimental conditions

The content of inhibitors and bioproducts for conditions with temperature of 220°C and 260°C are in accordance with the results for the pH (Figure 17). In the first 3 minutes of reaction, the concentrations of inhibitors and acetic and formic acids are raised for higher temperatures, resulting in a reduction of pH in those first minutes. This behavior was also verified for different biomass (Lachos-Perez et al., 2016; Prado et al., 2014b).

The pH of hydrolyzed solutions became increasingly acidic with increasing temperature. The lower values of pH indicate the presence of acidic materials, most likely organic acids in the aqueous solutions. The organic acids provide acidic protons to catalyze the subsequent hydrolysis of monomers and oligomers as an autocatalytic process (Pourali et al., 2010). The weakly acidic pH shown in Figure 17 for temperature of 180°C is consistent with the fact that lower temperatures are insufficient for hydrolysis of the lignocellulosic matrix (Cocero et al., 2018).

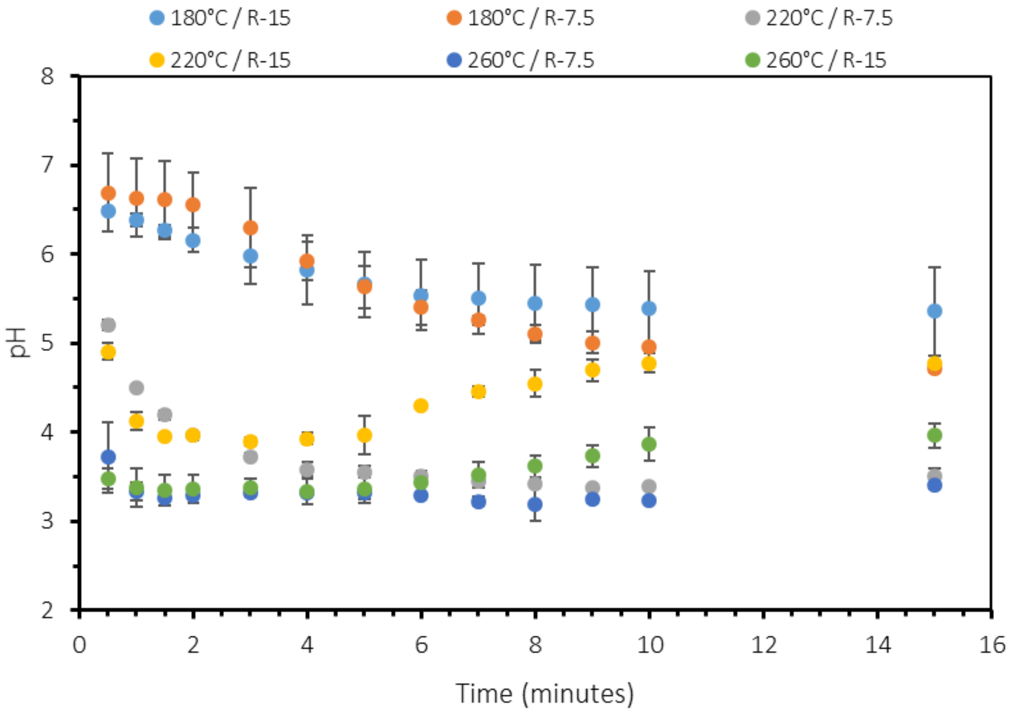


Figure 17 - Kinetic profile of pH of hydrolyzed samples from rice straw

3.3.5 Solid coproduct

3.3.5.1 FT-IR spectroscopy

The chemical composition of fresh rice straw and solid coproducts was characterized for functional group content using FT-IR. The FT-IR spectra of fresh rice straw and coproducts (solid remaining after SWH process) presented a similar profile, but with different peak intensities. SWH removed certain components in different quantities when comparing the experimental conditions. In Figure 18, the bands in the 3336 cm^{-1} region represent the -OH stretch present in the lignin structures (Xu et al., 2013), while the bands near to 900 cm^{-1} (e. g., 913 cm^{-1}) indicate the CH stretch of the sugar units of cellulose (Basberg, 2010). The peak with the highest intensity at 1600 cm^{-1} is related to the highest temperature (260°C). This behavior can be attributed to higher biomass dissociation and coke formation, since the C = C bond appears at 1600 cm^{-1} (Möller et al., 2013).

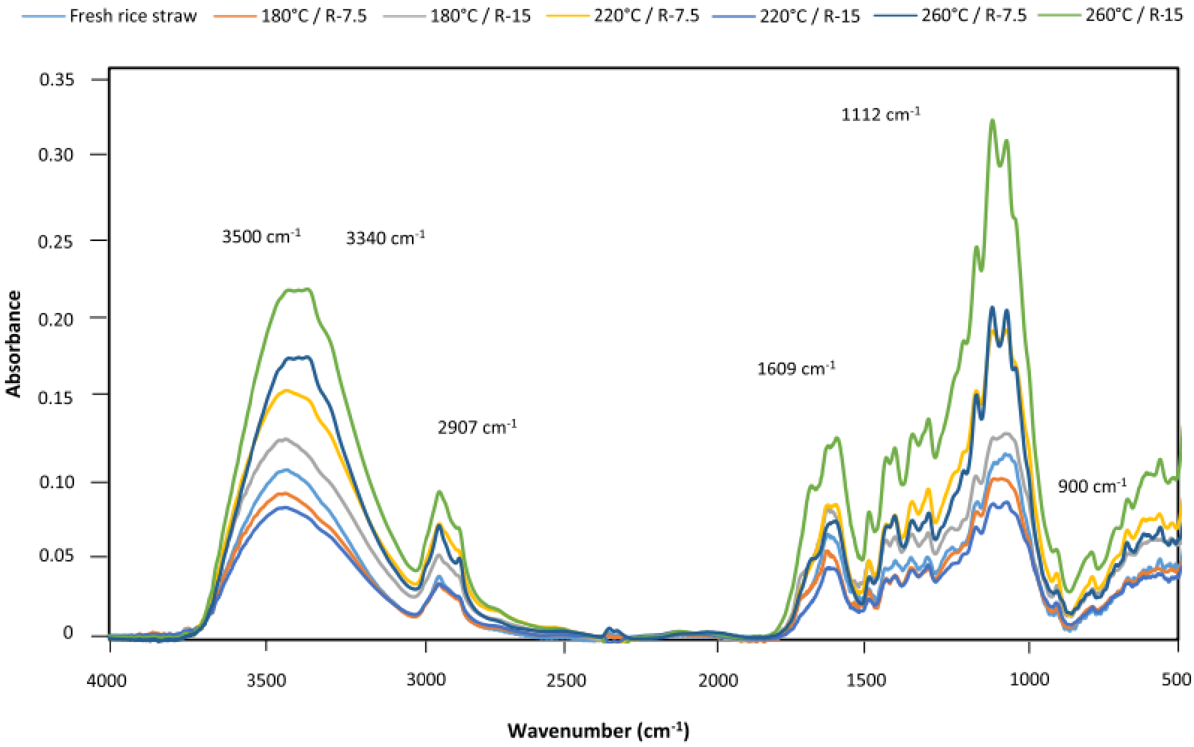


Figure 18 - FT-IR spectroscopy analysis of fresh rice straw and solid coproducts after SWH process

As the temperature in SWH assays increased, the peak corresponding to the range of 3500 to 3000 cm^{-1} also increased. This increasing can also be attributed to the larger hemicelluloses dissociation, leaving more exposed lignin with its vibration bands in –OH (Lachos-Perez et al., 2016). Furthermore, there is a reduction in the peak corresponding to the range of 3500 to 3000 cm^{-1}. As the R increases, the lignin vibration bands appear with less intensity, either by its dissociation or due to its masking by other components such as cellulose and hemicelluloses. At approximately 1100 cm^{-1}, the peaks with the highest intensities are related to rice solid coproduct after hydrolysis at 260°C and 220°C. These types of bonds in such coproducts can be explained with the help of Figure 19(b) (DTG), because the increase of temperature favored decreasing the amount of hemicelluloses.

3.3.5.2 TGA

The fresh rice straw and solid coproducts were analyzed by TGA to determine the thermal degradation of these materials. Derivative thermograms (DTG) were fit using the methods recommended in the literature (Cai et al., 2013; Lachos-Perez et al., 2017) to determine mass composition for hemicelluloses, cellulose, lignin, and char. The contributions of individual components were determined by integration and normalized to a unity shown in Figure 19(b). The average temperatures were attributed to each one of the components in the DTG curves.

For cellulose, hemicelluloses, lignin, and char the temperature range of the base of the peak by the DTG is specified in the literature. For the thermal decomposition of cellulose, the range of 330-370°C (Cai et al., 2013) was used. For hemicelluloses, the temperature range was 175-350°C (Peng and Wu, 2010). For lignin and coal, the temperature ranges were 370-550 and 550-770°C, respectively (Fisher et al., 2002; Watkins et al., 2015). Only 26 wt.% of fresh rice straw remained after heating the samples at 800°C under a nitrogen chamber. For solid coproducts processed at 260°C, the remaining mass was 33%. Therefore, for the coproduct obtained by SWH at 260°C, an amount of 7% of solid may be in the carbonized form.

For fresh rice straw, two peaks appeared: one from 250°C to 320°C and the other from 320°C to 400°C. The peaks appearing within the ranges of 200-320°C and 320-400°C refer to hemicelluloses (Peng and Wu, 2010) and cellulose (Fisher et al., 2002; Peng and Wu, 2010), respectively. When rice straw was subjected to SWH process at 180°C, the peak of hemicelluloses is reduced and the peak of cellulose is increased. Therefore, part of hemicelluloses must have been dissociated in that condition. For SWH at 220°C and 260°C, the presence of hemicelluloses in the solid coproducts was not observed because no peak was observed. The peak that appears for these conditions is in the 320°C to 400°C range (Figure

19), where cellulose dissociation is observed (Fisher et al., 2002). The peak representing the assay at 260°C overlaps the peak representing the assay performed at 220°C. However, the peak representing the assay performed at 260°C shows lower intensity and the area on the curvature is smaller (Table 8). This behavior is consistent with the expected results, as there is a larger cellulose dissociation at temperatures near to 250°C (Mohan, D. et al., 2015).

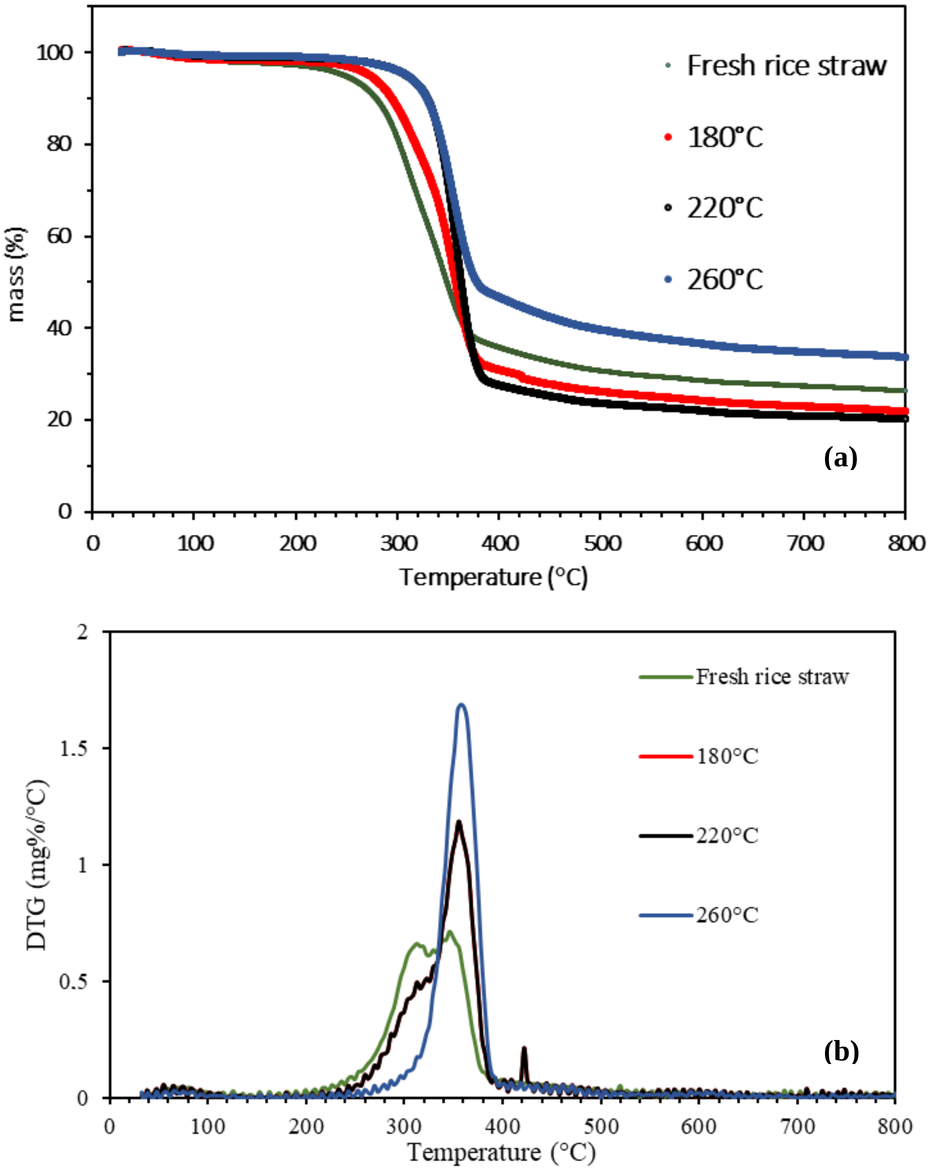


Figure 19 - TGA of fresh rice straw and solid coproducts after SWH process: (a) degradation profile and (b) derivative thermogravimetric analysis (DTG)

According to results presented in Table 8, the highest dissociation of hemicelluloses occurs at 260°C. SWH using temperatures in the range 180-250°C is sufficient to hemicelluloses dissociation, but not cellulose (Cantero et al., 2015; Cocero et al., 2018). The lignin content increased as the temperature increased in the SWH process. Due to the hemicelluloses and cellulose dissociation, the remaining solid is richer in lignin and char. The results presented in Table 8 favor understanding of how long dissociation of the major constituents of rice straw have occurred in sugars, inhibitors, and bioproducts. Increasing the temperature from 180°C to 220°C, the amount of inhibitors and bioproducts increased (Table 7), as a consequence of dissociation of cellulose.

Table 8 **-** Composition (dry mass basis) of rice straw obtained through the areas of peaks in the DTG analysis referring to cellulose, hemicelluloses, lignin, and char

	Hemicellulose (%)	**Cellulose (%)**	**Lignin (%)**	**Char (%)**
Fresh rice straw	24.62	22.40	9.44	2.86
180°C	24.40	36.40	12.13	3.30
220°C	24.40	36.40	12.13	3.31
260°C	9.32	50.25	16.76	2.62

3.4 CONCLUSIONS

Rice straw was processed by a green process (subcritical water hydrolysis) in a semi-continuous mode to have fermentable sugars and bioproducts. The highest reducing sugar yields (33.5 ± 4.3 wt.%) were obtained at 220°C with a liquid/solid ratio of 7.5 g water/g straw. The highest content of levulinic acid was obtained at 220°C with a liquid/solid ratio of 15 g water/g straw. TGA and FT-IR analyses provided information on the solid coproducts, as changes in its composition. The results obtained are in accordance with the literature in terms of dissociation of the lignocellulosic structure at different temperatures. The values for the pH of the hydrolyzed solutions at different time intervals are in agreement with the results obtained for the organic acids.

In this context, subcritical water technology is opening a new perspective on the future of agricultural waste recycling business. This technique is strongly nominated to be an alternative route for sugar and bioproducts conversion from cellulose and hemicelluloses found in agricultural biomass, following the biorefinery concept. Therefore, the subcritical water hydrolysis shows a clean technology for the production of products of high-added value. In this study, rice straw was assessed, but a wide range of biomass could be processed, including wastes from agricultural, chemical, pharmaceutical and food industries.

Conflict of interest

The authors inform that there are no conflicts of interest.

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REFERENCES

Abdelmoez, W., Nage, S.M., Bastawess, A., Ihab, A., Yoshida, H., 2014. Subcritical water technology for wheat straw hydrolysis to produce value added products. J. Clean. Prod 70, 68-77.

Akiya, N., Savage, P.E., 2002. Roles of Water for Chemical Reactions in High-Temperature Wate. Chem. Rev 102(8), 2725-2750.

Allen, S.G., Kam, L.C., Zemann, A.J., Antal, M.J., 1996. Fractionation of sugar cane with hot, compressed liquid wate. Ind. Eng. Chem. Researc 35, 2709-2715.

An, Y.X., Zong, M.H., wu, H., Li, N., 2015. Pretreatment of lignocellulosic biomass with renewable cholinium ionic liquids: Biomass fractionation, enzymatic digestion and ionic liquid reuse. Bioresour. Technol 192, 165-171.

AOAC, 1997. Association of Official Analytical Chemists – AOAC, 16th ed. Of.Analys, Washington, USA.

Basberg, S., 2010. Prediction of Vibrational Spectra of Polysaccharides; Simulated IR Spectrum of Cellulose Based on Density Functional Theory (DFT). J. Physic. Chem 114(36), 11703-11708.

Bevilaqua, D.B., Rambo, M.K.D., Cardoso, T.M., Martins, A.L., 2013. Cleaner production: levulinic acid from rice husks. J. Clean. Prod 47, 96-101.

Cai, J., Wu, W., Liu, R., Huber, G.W., 2013. A distributed activation energy model for the pyrolysis of lignocellulosic biomass. Green Chem 15(5), 1331-1340.

Cantero, D.A., Bermejo, M.D., Cocero, M.J., 2015. Reaction engineering for process intesification of supercritical waterbiomass refining. J. Supercrit. Fluids 96, 21-35.

Cardenas-Toro, F.P., Foster-Carneiro, T., Rostagno, M.A., Petenate, A.J., Filho, F.M., Meireles, M.A.A., 2014. Integrated supercritical extraction and subcritical water hydrolysis for the recovery of bioactive compounds from pressed palm fiber. J. Supercrit. Fluids 93, 42-48.

Chitawo, M.L., Chimphango, A.F.A., 2017. A synergetic integration of bioenergy and rice production in rice farms. Renewable Sustainable Energy Rev 75, 58-67.

Cocero, M.J., Cabeza, A., Abad, N., Adamovic, T., Vaquerizo, L., Martínez, C.M., Pazo-Cepeda, M.V., 2018. Understanding biomass fractionation in subcritical & supercritical water. J. Supercrit. Fluids 133, 550-565.

CONAB, 2018. Monitoring of the Brazilian crop. National Supply Company 5, 1-142.

Faba, L., Diaz, E., Ordóñez, S., 2015. Recent developmentes on the catalytic technologies for the transformation of biomass into biofuels: A patent survey. Renewable Sustainable Energy Rev 51, 273-287.

FAO, 2016. Rice market monitor. Food and Agriculture Organization of the United Nations 19(2), 1-35.

Fisher, T., Hajaligol, M., Waymack, B., Kellogg, D., 2002. Pyrolysis behavior and kinetics of biomass derived materials. J. Anal. Appl. Pyrol 62(2), 331-349.

Fleig, O.P., Lopes, E.S., Rivera, E.C., Filho, R.M., Tovar, L.P., 2018. Concept of rice husk biorefining for levulinic acid production integrating three steps: Multi-response optimization, new perceptions and limitations. Process. Biochem 65, 146-156.

Gadde, B., Bonnet, S., Menke, C., Garivait, S., 2009. Air pollutant emessions from rice straw open field burning in India, Thailand and the Philippines. Environ. Pollutat 157, 1554-1558.

Getachew, A.T., Chun, B.S., 2017. Influence of pretreatment and modifiers on subcritical water liquefaction of spent coffee grounds: A green waste valorization approach. J. Clean. Prod 142, 3719-3727.

He, Y., Pang, Y., Li, X., Liu, Y., Li, R., Zheng, M., 2009. Investigation on the Changes of Main Compositions and Extractives of Rice Straw Pretreated with Sodium Hydroxide for Biogas Production. Energy Fuels 23(4), 2220-2224.

Hong-Jia, Z., Xiao-Guang, F., Xue-Liang, Q., Qiu-Xiang, Z., wen-Ya, W., Shuang-Xi, S., Li-Hong, D., Mattheos, A.G.K., Dong-Sheng, W., Qi-Peng, Q., 2014. A novel cleaning process for industrial production of xylose in pilot scale from corncob by using screw-steam-explosive extruder. Bioprocess and Biosystem 37, 2425-2436.

Ishii, K., Furuichi, T., Fujiyama, A., Watanabe, S., 2016. Logistics cost analysis of rice straw pellets for feasible production capacity and spatial scale in heat utilization systems: A case study in Nanporo town, Hokkaido, Japan. Biomass and Bioenergy 94, 155-166.

Krishania, M., Kumar, V., Sangwan, R.S., 2018. Integrated approach for extraction of xylose, cellulose, lignin and silica from rice straw. Bioresour. Technol. Reports 1, 89-93.

Lachos-Perez, D., Martinez-Jimenez, F., Rezende, C.A., Tompsett, G., Timko, M., Foster-Carneiro, T., 2016. Subcritical water hydrolysis of sugarcane bagasse: An approach on solid residues characterization. J. Supercrit. Fluids 108, 69-78.

Lachos-Perez, D., Tompsett, G.A., Guerra, P., Timko, M.T., Rostagno, M.A., Martínez, J., Foster-Carneiro, T., 2017. Sugars and char formation on subcritical water hydrolysis of sugarcane straw. Bioresour.Technol 243, 1069-1077.

Lee, V.J.Q., Salimi, M.N., Yusoff, A., 2017. Fermentable sugar production from paddy straw by two steps chemical pretreatment and hydrolysis process, in: Physics, A.I.o. (Ed.) AIP Conference Proceedings. Malaysia.

Li, F., Liu, L., An, Y., He, W., Themelis, N.J., 2016. Hydrothermal liquefaction of three kinds of starches into reducing sugars. J. Clean. Prod 112, 1049-1054.

Li, J., Lu, M., Guo, X., Zhang, H., Li, Y., Han, L., 2018. Insights into the improvement of alkaline hydrogen peroxide (AHP) pretreatment on the enzymatic hydrolysis of corn stover: Chemical and microstructural analyses. Bioresour. Technol 265, 1-7.

Lin, R., Cheng, J., Ding, L., Song, W., Qi, F., Zhou, J., Cen, K., 2015. Subcritical water hydrolysis of rice straw for reducing sugar production with focus on degradation by-products and kinetic analysis. Bioresour.Technol 186, 8-14.

Marabezi, K., 2009. Systematic study of the reactions involved in the determination of lignin and holocellulose contents in samples of sugarcane bagasse and straw (in Portuguese), Institute of Chemistry of São Carlos. University of Sao Paulo (USP), São Carlos.

Maraseni, T.N., Deo, R.C., Qu, J., Gentle, P., Neupane, P.R., 2018. An international comparison of rice consumption behaviours and greenhouse gas emissions from rice production. J. Clean. Prod 172, 2288-2300.

Mayanga-Torres, P.C., Lachos-Perez, D., Rezende, C.A., Prado, J.M., Ma, Z., Tompsett, G.T., Timko, M.T., Foster-Carneiro, T., 2017. Valorization of coffee industry residues by subcritical water hydrolysis: recovery of sugars and phenolic compounds. J. Supercrit. Fluids 120(1), 75-85.

Mohan, D., Banerjee, T., Goud, V.V., 2015. Hydrolysis of bamboo biomass by subcritical water treatment. Bioresour.Technol 191, 244-252.

Mohan, M., Timung, R., Deshavath, N.N., Banerjee, T., Goud, V.V., Dasu, V.V., 2015. Optimization and hydrolysis of cellulose under subcritical water treatment for the production of total reducing sugars RSC Advances. pp. 103265-103275.

Möller, M., Harnisch, F., Schröder, U., 2013. Hydrothermal liquefaction of cellulose in subcritical water—the role of crystallinity on the cellulose reactivity. Research Advances 27(3), 11035-11044.

NREL, 2018. Biomass Compositional Analysis Laboratory Procedures, in: Laboratory, N.R.E. L. USA.

Ozaki, J.W., 2008. Subcritical water technology opens a new way to the future of industrial waste recycling business, in: Center, J.i.w.i. (Ed.). Japan.

Ozbek, H.N., Fockink, D.H., Yanik, D.K., Gogus, F., Lukasik, R.M., 2018. The green biorefinery concept for the valorisation of pistachio shell by high-pressure CO_2/H_2O system. J.Clean.Prod 196, 842-851.

Pedras, B., Salema-Oom, M., Sá-Nogueira, I., Simões, P., Paiva, A., Barreiros, S., 2017. Valorization of white wine grape pomace through application of subcritical water: analysis of extraction, hydrolysis, and biological activity of the extracts obtained. J. Supercrit. Fluids 127, 68-74.

Peng, Y., Wu, S., 2010. The structural and thermal characteristics of wheat straw hemicellulose. J. Anal. Appl. Pyrol 88, 134-139.

Pinto, A.R.R., Antas, F., Santos, R.C.D., Bowra, S., Simões, P., Barreiros, S., Paiva, A., 2017. Effect of reactor configuration on the subcritical water hydrolysis of recycled paper mill sludge. J. Anal. Appl. Pyrol 127, 68-74.

Pourali, O., Asghari, F.S., Yoshida, H., 2009. Sub-critical water treatment of rice bran to produce valuable materials. Food. Chem 115, 1-7.

Pourali, O., Asghari, F.S., Yoshida, H., 2010. Production of phenolic compounds from rice bran biomass under subcritical water conditions. Chem. Eng. J. 160, 259-266.

Prado, J.M., Follegati-Romero, L.A., Foster-Carneiro, T., Rostagno, M.A., Maugeri-Filho, F., Meireles, M.A.A., 2014a. Hydrolysis of sugarcane bagasse in subcritical water. J. Supercrit. Fluids 86, 15-22.

Prado, J.M., Foster-Carneiro, T., Rostagno, M.A., Folegatti-Romero, L.A., Maugeri-Filho, F., Meireles, M.A.A., 2014b. Obtaining sugars from coconut husk, defatted grape seed, and pressed palm fiber by hydrolysis with subcritical water. J. Supercrit. Fluids 89, 89-98.

Prado, J.M., Lachos-Perez, D., Foster-Carneiro, T., Rostagno, M.A., 2016. Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugar: A review. Food. Bioprod. Process 98, 95-123.

Sen, S.M., Gürbüz, E.I., Wettstein, S.G., Alonso, D.M., Dumesic, J.A., Maravelias, C.T., 2012. Production of butene oligomers as transportation fuels using butene for esterification of levulinic acid from lignocellulosic biomass: process synthesis and technoeconomic evaluation. Green. Chem 14(12), 3289-3294.

Serrano-Ruiz, J.C., Dumesic, J.A., 2011. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuel. Energ. Environm. Sci 4, 83-99.

Shen, Z., Zhang, K., Si, M., Liu, M., Zhuo, S., Liu, D., Ren, L., Yan, X., Shi, Y., 2018. Synergy of lignocelluloses pretreatment by sodium carbonate and bacterium to enhance enzymatic hydrolysis of rice straw. Bioresour. Technol 249, 154-160.

Sidhu, B.S., Beri, V., 1989. Effect of crop residue management on yields of different crops and soil properties. Biological Wastes 27(1), 15-27.

Silva, E.K., Martelli-Tosi, M., Vardanega, R., Nogueira, G.C., Zabot, G.L., Meireles, M.A.A., 2018. Technological characterization of biomass obtained from the turmeric and annatto processing by using green technologies. J. Clean. Prod 189, 231-239.

Silveira, M.H., Morais, A.R., Lopes, A.M.C., Olekszyszen, D.N., Bogel-Łukasik, R., Andreus, J., Ramos, L.P., 2015. Current Pretreatment Technologies for the Development of Cellulosic Ethanol and Biorefineries. ChemSusChem 8, 3366-3390.

Syaftika, N., Matsumura, Y., 2018. Comparative study of hydrothermal pretreatment for rice straw and its corresponding mixture of cellulose, xylan, and lignin. Bioresour. Technol 255, 1-6.

Tanaka, M., Takamizu, A., Hoshino, M., Sasaki, M., Goto, M., 2012. Extraction of dietary fiber from Citrus Junos peel with subcritical wate. Food. Bioprod. Process 90, 180-186.

Toor, S.S., Rosendahl, L., Nielsen, M.P., Glausius, M., Rudolf, A., Iversen, S.B., 2012. In a global context, the SWH application is being used on a pilot scale by Danish Company SCF Technologies A / S has such pilot plant. Biomass and Bioenergy 36(102), 327-332.

Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, M., Jeelani, A., 2015. Extraction and characterization of lignin from different biomass resources. J. Mat. Res. Tech 4(1), 26-32.

Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D., 2013. Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: a mini-review. Appl. Energy 104, 801-809.

Yang, T., Wang, J., Li, B., Kai, X., Li, R., 2017. Effect of residence time on two-step liquefaction of rice straw in CO2 atmosphere: differences between subcritical water and supercritical ethanol. Bioresour. Technol 229, 143-151.

Yu, Y., Wu, H., 2011. Effect of ball milling on the hydrolysis of microcrystalline cellulose in hot-compressed water. AlChE Journal 57(3), 793-800.

Zabot, G.L., Moraes, M.N., Meireles, M.A.A., 2018. Process integration for producing tocotrienols-rich oil and bixin-rich extract from annatto seeds: A techno-economic approach. Food Bioprod. Process 109, 122-138.

Zalengera, C., Blanchard, R.E., Eames, P.C., Juma, A.M., Chitawo, M.L., Gondwe, K.T., 2014. Overview of the Malawi energy situation and a pestle analysis for sustainable developement of renewable energy. Renewable Sustainable Energy Rev 38, 335-347.

Zhu, G., Xiao, Z., Zhu, X., Yi, F., Wan, X., 2013. Reducing sugars production from sugarcane bagasse wastes by hydrolysis in subcritical water. Clean Technol. Env. Polic 15(1), 55-61.

- CAPÍTULO 4 -

HIDRÓLISE COM ÁGUA SUBCRÍTICA DAS CASCAS DE ARROZ

Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode

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Abstract

This work aimed at producing fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis at 25 MPa in a semi-continuous mode. The influences of temperature (180°C; 220°C; 260°C) and liquid/solid ratio (7.5 g water/g husks; 15 g water/g husks) on reducing sugar yields (Y_{RS}), efficiency (E), kinetic profiles (0-15 min), composition of sugars, inhibitors and organic acids, and physicochemical characteristics of the remaining solid material were evaluated and discussed in the work. The highest Y_{RS} (18.0 ± 2.9 g/100 g husks) and E (39.5 ± 1.7 g sugars/100 g carbohydrates) were obtained at 220°C and 7.5 g water/g husks. In such condition, the hydrolyzed solutions presented cellobiose (18.0 g/L), xylose 17.7 g/L), arabinose (3.6 g/L), glucose (1.5 g/L), and levulinic acid (0.7 g/L). The fermentable sugars and bioproducts can be applied in several industrial fields, especially for the production of bioethanol and other higher value-added chemical compounds.

Keywords: Biomass, Biorefinery, Reducing Sugars, Levulinic Acid, TGA.

4.1 INTRODUCTION

The use of lignocellulosic biomass within the concept of biorefinery is gaining significant interest, not only for the minimization of environmental impact but also for the rational utilization of natural biomass resources (Faba et al., 2015). The increasing of energy and fuel requirements are encouraging researches for using lignocellulosic biomass as a sustainable source of bioproducts and renewable energy, as bioethanol (Ozbek et al., 2018). Cellulose and hemicelluloses from several feedstocks can be converted into sugars and ethanol through the appropriate selection of processing technologies (Rastogi & Shrivastava, 2017). As an agroindustrial biomass waste, rice husk is an abundant, inexpensive and readily available waste with an annual global quantity of 149 million tons, which 70% is used for energy production by its burning (FAO, 2016). Brazil is the largest producer of rice outside the Asian continent. In the harvest of 2017, the cultivated area in Brazil was approximately 1.9 million hectares and the production was approximately 11.6 million tons (CONAB, 2018).

Rice husks contain cellulose, hemicelluloses, and lignin with some amount of proteins, starch, extractives and inorganics (Potumarthi et al., 2013). The most frequent use of rice husks is as a fertilizer additive and in the rice processing plants for the production of thermal and electric energy through steam boilers. The use of rice husks in combustion system is not the best alternative due to the high content of alkali metals, alkaline earth metals, and silica, which causes boiler operation problems, such as the formation of deposits, incrustations, and corrosion. Furthermore, the high concentrations of lignin and silica in this biomass cause a slow rate of decomposition in the soil (Bijay-Singh et al., 2013). Therefore, considering the high contents of cellulose (28.6 wt.%) and hemicelluloses (20 wt.%) (Potumarthi et al., 2013), rice husks can be potentially used for biofuel production (Lau et al., 2015). However, it is important to emphasize that it is necessary to hydrolyze rice husks to enhance the production of biofuels through fermentation.

Several processes have been continuously developed to dissociate cellulose and hemicelluloses from lignocellulosic biomass. The processes commonly used are dilute acid, enzymatic hydrolysis, and ionic liquids (Martín et al., 2017; Zhang et al., 2018). Each one of these processes presents some advantages and drawbacks, which influences the feasibility of hydrolysis of lignocellulosic biomass at an industrial scale. The main problems can be summarized as diluted acid hydrolysis affects the subsequent fermentation due to the high levels of inhibitors produced during the reaction; ionic liquid has a high cost and complex synthesis process, which restrict its use in industrial applications (An et al., 2015); and enzymatic hydrolysis presents high cost and high reaction time (Shen et al., 2018). Therefore, special attention has been focused on the development of more sustainable technologies to improve biomass processing.

Subcritical water hydrolysis (SWH) is being used as an efficient alternative for dissociating lignocellulosic biomass. A wide variety of biomass from agroindustrial manufacture is completely processed into fermentable sugars and bioproducts by SWH treatment within a few minutes. Therefore, SWH is a promising technology because it has a potential for breaking down biopolymers of hemicelluloses into simple sugars like xylose and arabinose, and into small molecules for downstream fermentation (Prado et al., 2016). Depending on the processing conditions and biomass employed, the concentration of compounds (oligosaccharides, monosaccharides, acetic acid, and sugars decomposition products) in the liquid phase may differ (Ciftci & Saldaña, 2015).

There are a few studies on the hydrolysis of rice husks using subcritical water technology (Gullón et al., 2011; Phaiboonsilpa et al., 2013). Furthermore, to the best of our knowledge, none study could be found in the main database (Scopus and ISI Web of Science, for instance) that reported the integrated evaluation of SWH of rice husks on yields of fermentable sugars and bioproducts in the hydrolyzed liquid solution. Therefore, the focus of this work was to obtain fermentable sugars (e. g., xylose, glucose, arabinose, and cellobiose) and bioproducts (e. g., levulinic acid) from such biomass using SWH as a green technology.

4.2 MATERIALS AND METHODS

4.2.1 Raw material

The rice husks were kindly donated by a rice manufacturing company located in the central region of the state of Rio Grande do Sul - Brazil. Immediately after the reception, the biomass was oven dried for 24 h at 60°C. Afterward, it was ground in Willey Knife Mills equipment (SL 30, Solab, Brazil) with a 20 mesh separation grid. The milled biomass was frozen at -5°C until the further experimental assays.

4.2.2 Rice husks composition analyses

Moisture and the contents of ash and total extractives were determined directly in the unextracted samples according to the methodologies of Association of Official Analytical Chemists and National Renewable Energy Laboratory (AOAC, 1997; NREL, 2018). The analyses were performed in triplicate and the responses are expressed as a mean ± standard deviation.

For moisture determination, 5 g of rice husks were prepared in Petri dishes. The samples were placed in an oven at 105°C for 4 h and weighed. The samples were placed in the oven for another 1 h and weighed again. This procedure was repeated until having a constant mass. For ash determination, 5 g of rice husks were weighed and placed in melting pots (AOAC, 1997). The samples were calcined in an oven (MDS 15X15X30, Fornitec, Brazil) at 400°C for 1 h and at 800°C for 2 h. The ash was determined by mass difference.

For determination of extractives, 2.5 g of rice husks were placed in a cartridge in a Soxhlet apparatus (MA491/6, Marconi, Brazil) with 195 mL of 90% (volume basis) ethanol in the extractor vessel (with glass beads) (NREL, 2018). The total reflux time was approximately 24 h with a solvent exchange each 12 h. After this time, the cartridges were removed from the extractor vessel and rinsed thoroughly with running water. After washing, the cartridge was placed again in the extractor vessel with 195 mL of distilled water. The same procedure of reflux time and solvent exchange was repeated. Thereafter, the cartridges were washed with running water and dried at 105°C until constant weight. The extractable content was determined by mass difference. Cellulose, hemicelluloses, and lignin were determined by thermogravimetric analysis (TGA), and the data were converted into derivative thermograms (DTG) and peaks were integrated (Lachos-Perez et al., 2016).

4.2.3 Experimental procedure of hydrolysis

The experimental system used in the study consists of a high-pressure pump (PU4087, Jasco, Japan) for pumping water, thermostatic baths (SL-152, Solab, Brazil) for water preheating and hydrolyzed solution cooling, a flow non-return valve, a 316L stainless steel reactor (internal volume of 50 mL), a ceramic band heater (1500 W) equipped with a thermocouple for temperature measurement (with a control panel), 316L stainless steel pipes (3.175 mm external diameter), pressure gauges, blocking valves, and a micrometering valve (3125GY, Hoke, USA).

For each assay, dried and milled rice husks (30 g) were loaded in the reactor vessel and distilled water was pumped with a constant mass flow rate (according to each assay). Immediately after the system was pressurized with water (pipes and reactor vessel), the pump was turned off and the micrometering valve was closed. The band heater was turned on for increasing the temperature to the desired value (according to each assay) and, consequently, the pressure, which its final value was fixed at 25 MPa based on studies reported elsewhere (Prado et al., 2016). The initial water pumping time in the reactor vessel was approximately 5 min.

Firstly, a transient assay was performed for 27 min to evaluate the influence of temperature on the semi-continuous SWH of rice husks. From 100 to 260°C, 9 samples were collected with a flow rate as 15 mL/min for measuring reducing sugars (RS) and inhibitors (hydroxymethylfurfural (HMF) and furfural). Based on the transient assay, the levels of temperature were selected (180°C, 220°C, and 260°C) for the subsequent assays. All assays were completely randomized. In such case, the flow rates were set as 15 mL/min and 30 mL/min to satisfy the liquid/solid ratios (R) of 7.5 g water/g husks and 15 g water/g husks, respectively, for a total reaction time of 15 min. Samples of the hydrolyzed solution were collected at intervals of 0.5 min (first 2 min) and at 1 min (2-10 min). A final sample was collected during the interval of 10-15 min. The samples were stored under refrigeration for determination of pH, RS, sugars composition, inhibitors, and organic acids. In all cases, the compositions of hydrolyzed solutions were measured in duplicate and the average values and standard deviations are reported. The time intervals of collection and maximum running time were defined based on studies reported in the scientific literature (Lin et al., 2015; Mayanga-Torres et al., 2017) and on preliminary assays. The remaining solid residue at the end of the hydrolysis process for each condition was collected and dried at 105°C until constant weight for further characterization.

4.2.4 Analytical methods

4.2.4.1 pH

The pH of the hydrolyzed solutions was determined using a digital pH meter (DM-22, Digimed, Brazil). Prior to the measurements, the pH meter was calibrated using technical buffer solutions of pH 4.01 ± 0.02 and 7.00 ± 0.02.

4.2.4.2 Reducing sugars (RS)

The RS content was analyzed by the dinitrosalicylic (DNS) colorimetric method (Miller, 1959) using ᴅ-glucose as a standard. Briefly, 1 mL of sample and 1 mL of DNS reagent were mixed and the mixture was heated by placing in boiling water (100°C) for 5 min until developing the red-brown color. Thereafter, 8 mL of 15.1 g/L of potassium sodium tartrate solution was added to stabilize the color and the mixture was cooled to 25°C in a water bath. The absorbance was measured with a spectrophotometer (UV-2700, Shimadzu, Japan) at 575 nm. For each experimental assay of hydrolysis, the reducing sugar yield (Y_{RS}; g sugar equivalents in glucose per 100 g of raw material) was calculated according to equation 1 and the efficiency (E; g sugar equivalents in glucose per 100 g of carbohydrates (hemicelluloses and celluloses)) was calculated according to equation 2.

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

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

Where: m_{RS} is the mass (g) of RS in the hydrolyzed solution, m_{SA} is the initial mass (g) of rice husks loaded inside the reactor vessel at the beginning of the process, and m_{CA} is the initial mass (g) of carbohydrates (hemicelluloses + cellulose).

The Tukey’s test was applied to determine the significant differences ($p < 0.05$) of Y_{RS} and E among the assays at 3 min and 15 min of reaction using the software Statistica 7.0® (StatSoft, Inc.).

4.2.4.3 Sugars and organic acids

The analytical methodology for the determination of sugars and organic acids was based on Fleig et al. (2018), which the procedures are described briefly in this section. Each sample of the hydrolyzed solution was conditioned in 2 mL microtubes and centrifuged at 14,000 rpm for 3 min. The supernatant was filtered on a 0.22 μm polytetrafluoroethylene (PTFE) membrane for chromatographic analysis. The contents of cellobiose, glucose, xylose, arabinose, formic acid, acetic acid, and levulinic acid were analyzed by high-performance liquid chromatography (HPLC) (Proeminence UFLCXR, Shimadzu, Japan) equipped with a refractive index detector (RID 10A, Shimadzu, Japan). An Aminex HPX-87H column (300 mm × 7.8 mm) (Bio-Rad, USA) was used at 30°C. As the mobile phase, a solution of H_2SO_4 45 mM (pH 2.6) prepared with ultrapure water (Milipore, USA) was used. After preparation, the mobile phase was filtered under vacuum using cellulose esters of 47 mm diameter with a porosity of 0.45 μm (Milipore, USA) and degassed in an ultrasonic bath (USC-1400, Unique, Brazil). The volumetric flow rate of the mobile phase was 0.6 mL/min and the volume of injection of samples was 15 μL. The compounds were separated in the stationary phase and monitored with a refractive index (IR) detector at 30°C for a run time of 25 min. The concentrations of each component were obtained by the correlation between the areas of the chromatograms and standard curves previously determined by standards of cellobiose, D-glucose, D-xylose and D-arabinose, formic acid, acetic acid, and levulinic acid.

4.2.4.4 Furfural and hydroxymethylfurfural inhibitors

The analytical methodology for the determination of inhibitors (furfural and hydroxymethylfurfural (HMF)) was based on Fleig et al. (2018), which the procedures are described briefly in this section. Filtered samples were analyzed in an HPLC system (Proeminence UFLCXR, Shimadzu, Japan) equipped with a photodiode array detector (PDA 20-A, Shimadzu, Japan). A Shim-Pak ODS C18 column (Shimadzu, Japan) was used. A solution of acetonitrile: water (1: 8 with 1% (v/v) acetic acid) filtered on cellulose esters of 47 mm diameter with porosity of 0.45 μm (Milipore, USA) and degassed in an ultrasound bath (USC - 1400, Unique, São Paulo) was used as mobile phase. The conditions for the analysis were: 10 μL of injection volume, flow rate of 0.8 mL/min, column temperature of 30°C, wavelength of 280 nm, detector temperature of 30°C, and run time of 10 min. The concentrations of each component were obtained by the correlation between the areas of the chromatograms and standard curves previously determined by furfural and HMF standards. The areas of the peaks corresponding to furfural and HMF were used to calculate their concentration in the samples.

4.2.5 Characterization of solid coproduct

After the SWH, the solids (coproduct) contained in the reactor vessel were transferred to properly identified vials and stored in a refrigeration system at 5°C for further characterization: Thermogravimetric Analysis (TGA), Fourier-Transform Infrared (FT-IR) Spectroscopy, and Scanning Electron Microscopy (SEM).

4.2.5.1 Thermogravimetric analysis

TGA of fresh rice husks and solid coproducts was performed using a thermogravimetric analyzer (Model DTG60 / 60H, Shimadzu, Japan). Samples (approximately 10 mg) were placed in an alumina crucible and held under a nitrogen (N_2, 99.997% purity) flow rate of 100 mL/min. The samples were heated from 25°C to 850°C (10°C/min). Raw thermogravimetric data were converted into derivative thermograms (DTG) using the vendor software.

4.2.5.2 Fourier-transform infrared spectroscopy

Samples of fresh rice husks and solid coproducts were analyzed by FT-IR spectroscopy (IR Prestige 21, Shimadzu, Japan). The spectra were obtained with a nominal resolution of 4 cm^{-1} and within the spectral range between 4000 and 400 cm^{-1}. All disks were made in the KBr tablet die accessory, using a press (Hand press SSP-10a press Shimadzu, Japan). For the preparation of the disks, 100 mg of KBr and 1 mg of the sample were used, which are thoroughly macerated and mixed into a smooth agate gravel and after pressing under 8 tons, resulting in thin transparent disks (less than 1 mm thick) with 13 mm in diameter.

4.2.5.3 Scanning electron microscopy

The morphology of the particles was determined by scanning electron microscopy (SEM) in the fresh rice husks and in the coproducts. The samples were placed in stubs and covered with gold. Afterward, the samples were analyzed at 15 kV acceleration voltage in a scanning electron microscope (TM3030, HITACHI, Japan).

4.3 RESULTS AND DISCUSSION

4.3.1 Raw material characterization

The moisture, ash, extractives, cellulose, hemicelluloses, and lignin content in fresh rice husks (mass wet basis) were 9.1 ± 0.5%, 16.6 ± 0.7%, 11.4 ± 1.1%, 18.5%, 28.0%, and 16.0%, respectively. The ash that constitutes the structure of rice husks may be a factor affecting the SWH process because it is constituted mainly by inorganic refractory, consisting mainly of silica compounds that can hinder the access of water to cellulose and hemicelluloses, undesirably acting as a barrier.

Although the composition can vary depending on climatic conditions of cultivation, the extractive content is closer to that one (11.0%) reported by Fleig et al. (2018). Extractives are composed of organic compounds of low molecular weight, such as phenolic compounds, terpenes, saturated and unsaturated fatty acids, proteins and flavonoids, and may affect the SWH process. The values obtained for cellulose and hemicelluloses were used to determine the amount of carbohydrates and to calculate the E.

4.3.2 Influence of transient heating on the Y_{RS}

The transient hydrolysis during the heating indicated that the amount of sugars and inhibitors begins to increase expressively after 18 min, where the temperature was higher than 180°C (Fig. 20). For example, the RS content at 220°C (21 min) was 5.8 ± 0.9 g/L, HMF was 0.6 ± 0.1 g/L, and furfural was 2.4 ± 0.2 g/L. When evaluating the scientific literature, the sugar content for SWH of rice husks at 240°C, 2 mL/min and 18 MPa was approximately 1.39 g/L. This behavior can be explained by the effects of flow rate on hydrolysis rates. There is an increase in the depolymerization and degradation of sugars with low flow rates due to the longer residence time (Prado et al., 2016).

The hydrolyzed solutions obtained after 24 min at temperatures above 240°C showed high contents of HMF and furfural, mainly at 260°C, with a content of 4.0 ± 0.2 and 6.5 ± 0.4 g/L, respectively. This concentration is sufficient to inhibit fermentation using *Saccharomyces cerevisiae* (2 g/L of HMF) or *Candida tropicalis* (3 g/L of furfural) for the production of ethanol (Wang et al., 2018). Based on the transient assay, the high Y_{RS} and the concentrations of HMF and furfural, the levels of temperature of 180°C, 220°C and 260°C (Table 9) were selected for performing the SWH of rice husks under constant temperature.

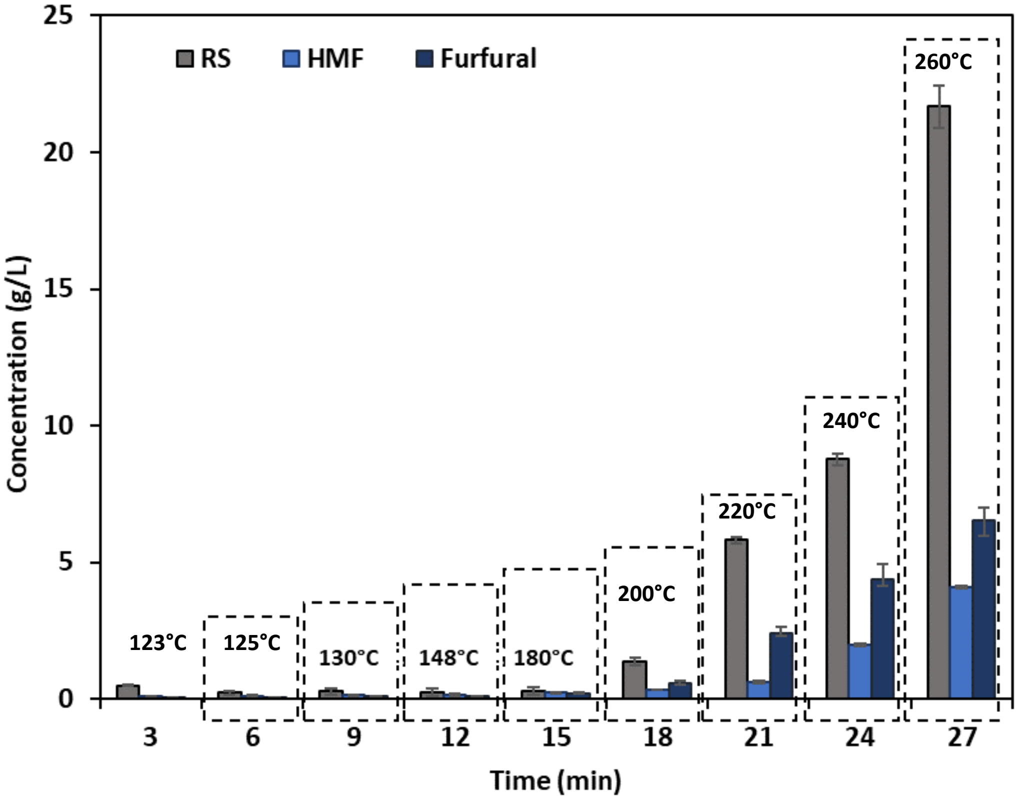

Figure 20 - Concentration of reducing sugars (RS) and inhibitors in the hydrolyzed samples from rice husks at 25 MPa and at different temperatures according to the reactor heating (transient assay)

4.3.3 Influence of temperature and liquid/solid ratio on E and Y_{RS}

The Y_{RS} and E obtained at different conditions of temperature and R at 3 min and 15 min by SWH from rice husks are shown in Table 9. A statistical analysis ($p < 0.05$) was performed for having a comparison of means for each response. When evaluating the Y_{RS} at 3 min, the Tukey's test indicated some significant differences. At 3 min, the highest value was obtained at 220°C / R-7.5 (15.3 ± 3.0 g/100 g rice husks), which this value was statistically different ($p < 0.05$) when compared with the value obtained in the condition of 220°C / R-15 (second highest Y_{RS} as 8.1 ± 0.7 g/100 g rice husks). Furthermore, in this reaction time (3 min), all assays performed at 180°C and 260°C do not differ from each other, regardless the R. When evaluating the Y_{RS} at 15 min, the behavior for the assays performed at 220°C was similar to 3 min. However, in such case, the responses of the assays performed at 180°C presented significant differences ($p < 0.05$) from the responses of the assays performed at 260°C (higher Y_{RS}). The findings clearly indicated the likely dependence of Y_{RS} on the temperature. The influence of R is mainly seen at the beginning of reaction (< 3 min), which is an indication that for longer times (> 3 min) the sugars conversion rate is low and do not depend on the amount of water in contact with the solid biomass.

Table 9 - Influence of temperature and liquid/solid mass ratio (R) on the Y_{RS} and E of SWH of rice husks in a semi-continuous mode at 3 min and 15 min of reaction times (accumulated samples)

Assay*	**Code**	**Y_{RS} (g/100 g rice husks)**		**E (g/100 g carbohydrates)**	
		3 min	**15 min**	**3 min**	**15 min**
1	180°C / R-7.5	0.5 ± 0.1^{c}	0.8 ± 0.1^{c}	1.2 ± 0.1^{c}	1.8 ± 0.1^{c}
2	180°C / R-15	0.8 ± 0.1^{c}	0.9 ± 0.1^{c}	1.7 ± 0.1^{c}	2.0 ± 0.1^{c}
3	220°C / R-7.5	15.3 ± 3.0^{a}	18.3 ± 2.1^{a}	33.1 ± 2.2^{a}	39.5 ± 1.7^{a}
4	220°C / R-15	8.1 ± 0.7^{b}	8.6 ± 0.6^{b}	18.2 ± 0.9^{b}	18.5 ± 0.9^{b}
5	260°C / R-7.5	5.0 ± 1.1^{bc}	5.5 ± 0.7^{b}	8.8 ± 0.7^{b}	11.8 ± 0.1^{b}
6	260°C / R-15	4.8 ± 0.4^{bc}	6.2 ± 1.1^{b}	13.3 ± 3.0^{b}	14.2 ± 2.5^{b}

* All assays were performed in duplicate, totalizing 12 assays; all assays were completely randomized.

$^{a\text{-}c}$ Different letters in the same column represent a significant difference at 95% ($p < 0.05$ – Tukey's test) among the assays for each response and for each reaction time.

Y_{RS}: reducing sugar yield.

E: efficiency.

Regarding the values of E (Table 9), the behavior was similar for both reaction times (3 min and 15 min). The highest value of E (39.5 ± 1.7 g sugar equivalents in glucose per 100 g of carbohydrates) was also obtained at 220°C / R-7.5, which was statistically different ($p < 0.05$) when compared with the values obtained in the other assays. For the values of E, the largest values were obtained in this order: 220°C, 260°C, and 180°C. The temperature presented more influence on E than the R. The E was only dependent on the R in the conditions of 220°C, where a lower value of R is preferable. These findings can be attributed to the residence time of water in the fixed reaction bed because the R is straightly related to water flow rate. When the R was the largest one (15 g water/g rice husks) at 220°C, the solvent flow rate for this laboratory scale was 30 g water/min. In such case, the residence time of water inside the reactor was lower than 1 min, which could not be sufficient for dissociating cellulose and hemicelluloses to a large degree. Indeed, the conversion efficiencies were larger at 220°C / R-7.5, which the values are potential outcomes for obtaining sugar-concentrated hydrolyzed solutions. In our viewpoint, it is not necessary to reach efficiencies near to 100% because there are larger quantities of rice husks available worldwide and values of E in the range of 20-40 g sugars per 100 g of carbohydrates are sufficient to yield larger quantities of RS.

The Y_{RS} and E of SWH process at different temperatures and R are also shown in Figure 21. When analyzing the kinetic profiles (Fig. 21a), the highest contents of sugars in hydrolyzed solutions were reached in the condition of 220°C / R-7.5. At 1 min and 5 min, the recovered sugars increased from 4.1 ± 0.1 g/100 g rice husks to 17.9 ± 2.6 g/100 g rice husks, with an average hydrolysis rate of 3.4 g/min in 100 g of rice husks. After this time (5 min), the conversion rate became approximately zero and the maximum value of 18.0 ± 2.9 g/100 g rice husks was reached. This rice husks hydrolysis rate (3.4 g/min; this work) was higher than the maximum rates of hydrolysis for wheat straw (1.6 g/min) submitted to SWH at 200°C (Abdelmoez et al., 2014).

For the 220°C / R-15 condition, the Y_{RS} became constant after 3 min of reaction (8.3 ± 0.3 g/100 g rice husks) with an average hydrolysis rate of 2.7 g/min in 100 g of rice husks. The 220°C / R-7.5 condition presented Y_{RS} of approximately 2.3 times higher than the 220°C / R-15 condition. As inferred, this behavior can be attributed to the longer residence time when the values of R of 7.5 and 15 g water/g husks (both at 220°C) are compared. With respect to studies reported elsewhere, the SWH process was applied to hydrolyze sugarcane bagasse (Prado et al., 2014a). At 180°C and 25 MPa, when decreasing flow rate from 33 mL/min to 22 mL/min (increase in residence time), the Y_{RS} changes from 14 g/100 g bagasse to 18 g/100 g bagasse.

Overall, the highest Y_{RS} (18.3 ± 2.1 g/100 g husks) obtained from the SWH of rice husks in the best operational condition (220°C / R-7.5) is generally higher than the results obtained by other processing technologies, like acid or enzymatic hydrolysis. For example, enzymatic hydrolysis of rice husks with cellulolytic complex from *Trichoderma reesei* (NS50013) was performed for 240 min to obtain reducing sugars (Moscon et al., 2014). In the best condition (55°C, 90 wt.% of moisture, reaction time of 240 min, and enzyme load of 5.5 wt.%), a Y_{RS} of 1.7 g/100 g rice husks was achieved. In another report, rice husks were hydrolyzed at 220°C using sulfuric acid solutions in an autoclave with volume of approximately 2 L (Megawati et al., 2011). With acid solutions of 0.37 N and 0.48 N, values of Y_{RS} of 14.6 g/100 g rice husks and 17.2 g/100 g rice husks were obtained, respectively. The authors suggested that a higher yield of sugar can be obtained by a higher concentration of acid (Megawati et al., 2011). However, in our viewpoint, a higher concentration of acid in the reaction media can cause some operational and environmental troubles, as reactor corrosion and the need for solvent removal/disposal.

When considering the results of RS in a volumetric basis, some comparisons with other scientific reports can also be done. In our study, the concentration of reducing sugars at 3 min of reaction was 113.6 g/L. Otherwise, in the study reported by Germec et al. (2016), only 25.5 g/L of fermentable sugar was obtained by dilute acid hydrolysis of rice husks at 131°C, 1:10.3 (w/v) of solid:liquid ratio, 1.5% (w/v) of acid ratio and 24 min. In another study, the concentration of RS obtained from rice husks was still lower: 0.9 g/L (Potumarthi et al., 2013). In such study, a white-rot fungus (*Phanerochete chrysosporium*) was used for delignification of rice husks and, thereafter, the pretreated biomass was used for RS production along with cellulase and xylanase. According to the authors, this method could be a good alternative to avoid operational costs associated with washing and the removal of inhibitors during the conventional pretreatment methods. However, the amount of sugar production should be enhanced to become attractive in larger scales.

The Y_{RS} increased as the temperature increased from 180 to 220°C (Fig. 21a). These findings are associated with the increase of ionization constant of water at high temperature. The concentrations of H^+ and OH^- increased, thus facilitating the hydrolysis of cellulose and hemicelluloses into monosaccharides (Cocero et al., 2018). Cellulose and hemicelluloses are hydrolyzed into fermentable sugars with high E at short residence times, but the E was reduced when 260°C was used (Fig. 21b). The lower E at 260°C was associated with the enhanced thermal degradation of compounds, with the formation of volatile and non-recovered substances (Pinto et al., 2017). The SWH was used to hydrolyze white wine grape pomace at 10 MPa and 170°C, 190°C and 210°C (Pedras et al., 2017). When increasing the temperature from 170°C to 190°C and 210°C, the RS efficiency increased from 40.1 ± 1.2 to 41.2 ± 1.1 and to 49.3 ± 2.1 g/100 g carbohydrates, respectively. A similar behavior was obtained in this work for the R-7.5. As the temperature changed from 180°C to 220°C, the E increased from 1.8 ± 0.1 to 39.4 ± 1.6 g/100 g carbohydrates.

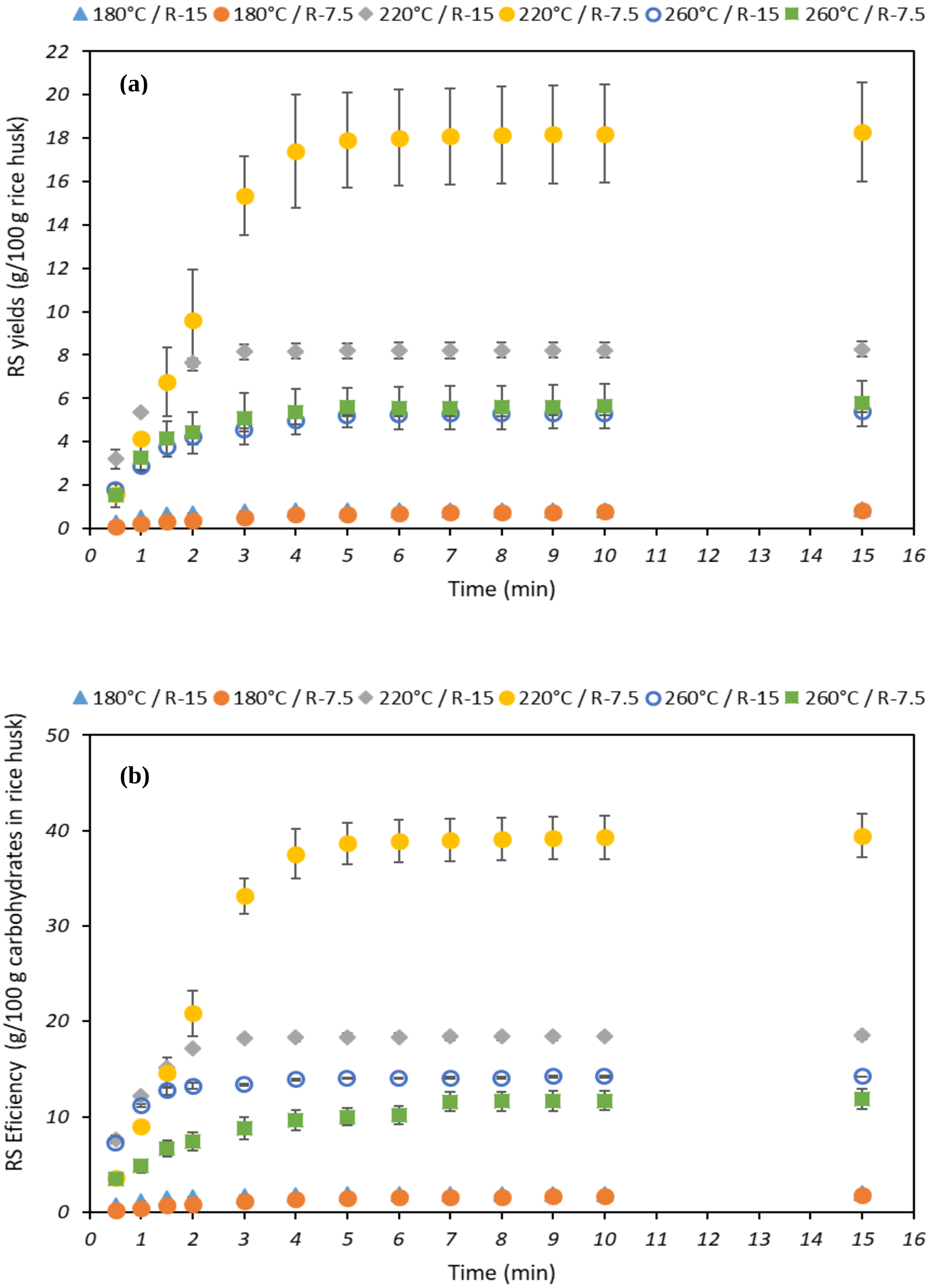

Figure 21 - Kinetic profile of Y_{RS} (a) and efficiency (b) (accumulated samples) of the hydrolyzed samples from rice husks at 25 MPa under different experimental conditions; the bars represent the standard deviation

SWH was also applied to dissociate lignocellulosic biomass from sweet blue lupin hull (Ciftci & Saldaña, 2015). At 180°C and 5 MPa, the increase of flow rate from 2 mL/min to 5 mL/min caused an increase of the hemicelluloses sugar efficiency from 81 g/100 g carbohydrates to 86 g/100 g carbohydrates. A similar behavior was also observed in this work. When comparing the E in the production of RS between the conditions 180°C / R-7.5 and 180°C / R-15, the values were 1.8 ± 0.1 g water/g husks and 2.1 ± 0.1 g water/g husks, respectively. This behavior is most likely attributed to the non-occurrence of cellulose hydrolysis and low hemicelluloses hydrolysis at this temperature, as suggested by Cocero et al. (2018).

4.3.4 Composition of hydrolyzed solution

The hydrolyzed solutions were analyzed in terms of sugars, inhibitors, and organic acids (Table 10). Cellobiose was the predominant monosaccharide present in the hydrolyzed solutions, followed by xylose. Under conditions where the temperature was 220°C (reaction for 3 min), the highest values of cellobiose (18.0 g/L) and xylose (17.7 g/L) were verified. The lower sugars content for the conditions at temperature 260°C when compared with 220°C is associated with the degradation of xylose into acetic acid, which the contents of this acid were 21.9 g/L and 14.7 g/L for the conditions 260°C / R-7.5 and 260°C / R-15, respectively. Xylose can be used to produce xylitol, which is a polyol possessing high sweetening power and lower calories than sucrose. Xylitol finds application as a nutraceutical substance due to its antidiabetic, antioxidant and anticarcinogenic properties (Kumar et al., 2018).

The total concentration of xylose and arabinose (21.3 g/L) obtained in the 220°C / R-7.5 condition for 3 min of hydrolysis is generally higher or similar than that obtained by other studies that used lignocellulosic biomass to obtain sugars in short reaction times. For example, enzymatic hydrolysis with xylanase and cellulase was performed in exhausted sugar beet cossettes to obtain bioproducts and sugars (Díaz et al., 2017).

Table 10 **-** Yields of sugars, inhibitors, and organic acids (g/L) obtained by SWH of rice husks in continuous mode at 3 min (accumulated samples)

	180°C / R-7.5	**180°C / R-15**	**220°C / R-7.5**	**220°C / R-15**	**260°C / R-7.5**	**260°C / R-15**
Sugars (g/L)						
Glucose	0.3 ± 0.1	0.6 ± 0.1	1.5 ± 0.2	4.2 ± 0.4	2.3 ± 0.2	1.7 ± 0.2
Cellobiose	0.8 ± 0.1	0.7 ± 0.1	18.0 ± 2.6	2.6 ± 0.3	1.6 ± 0.2	0.6 ± 0.1
Xylose	0.2 ± 0.1	0.2 ± 0.1	17.7 ± 2.2	13.4 ± 1.2	2.0 ± 0.3	2.7 ± 0.5
Arabinose	1.2 ± 0.2	0.0	3.6 ± 0.8	0.6 ± 0.1	3.2 ± 0.6	0.7 ± 0.2
Total	2.5 ± 0.2	1.5 ± 0.1	40.8 ± 4.9	20.8 ± 2.1	9.1 ± 1.0	5.7 ± 0.8
Inhibitors (g/L)						
HMF	0.0	0.0	0.9 ± 0.1	0.10 ± 0.01	0.8 ± 0.1	0.9 ± 0.1
Fufural	0.0	0.0	2.4 ± 0.5	0.50 ± 0.09	1.0 ± 0.2	0.9 ± 0.2
Total	0.0	0.0	3.3 ± 0.6	0.60 ± 0.10	1.8 ± 0.3	1.8 ± 0.3
Organic acids (g/L)						
Formic acid	0.24 ± 0.04	0.11 ± 0.02	4.1 ± 0.6	3.8 ± 0.8	2.8 ± 0.4	4.6 ± 0.6
Acetic acid	0.58 ± 0.11	0.21± 0.04	4.5 ± 0.5	7.1 ± 0.6	21.9 ± 1.7	14.7 ± 1.9
Levulinic acid	0.05 ± 0.01	0.04 ± 0.01	0.7 ± 0.1	0.9 ± 0.2	2.3 ± 0.3	1.8 ± 0.4
Total	0.87 ± 0.26	0.36 ± 0.07	9.3 ± 1.1	11.8 ± 1.4	27.0 ± 2.2	21.1 ± 2.8

R: liquid/solid mass ratio (g water/g husks).

In the best condition (6 g exhausted sugar beet cossettes, 220 filter paper unit (FPU)/mL of cellulase and 30 U/mL xylanase, hydrolysis time of 24 h; where U means the amount of the enzyme that converts 1 µmol of substrate per minute), a total concentration of xylose and arabinose of 12.5 g/L was obtained. In another work (Dagnino et al., 2013), the enzymatic hydrolysis of rice husks with an acid pretreatment was performed. With a pretreatment of 16 min using a concentration of 0.3% (w/v) H_2SO_4 and sequential enzymatic hydrolysis with 40 FPU/g of cellulase at 50°C for 48 h, the xylose concentration obtained was 37.4 g/L.

Regarding the glucose content, the condition 220°C / R-15 presented a value of 4.2 g/L (at 3 min of reaction). This value is lower than the findings in a work that reported homogeneous catalysis with H_2SO_4 (Fleig et al., 2018). At 180°C, 90 min, and 3% (w/v) H_2SO_4 concentration, the glucose content was 20.3 g/L. The solvent most likely dissociated most of the cellulose and hemicelluloses in the lignocellulosic structure. However, the SWH presented was performed in a shorter time: 15 min. Moreover, for such process, no purification is required for the removal of the solvent.

Regarding the inhibitors contents (HMF as 0.9 g/L and furfural as 2.4 g/L (Table 10), evaluated in the best condition of sugars (220°C / R-7.5), the values are high when analyzing the inhibitory effect for subsequent ethanol production by fermentation (Wang et al., 2018). However, when assessing the potential use of furfural by a purification step, it may be stated that it is also a key platform chemical produced in lignocellulosic biorefineries that could further be transformed into fuels and useful chemicals. Furthermore, it is a substance widely used in oil refining, plastics, pharmaceutical, and agrochemical industries. Furfural, identified as one of the top 12 value-added products, is a valuable product with a worldwide market of approximately 300,000 tons per year (Danon et al., 2014).

In terms of acids at 3 min of reaction, high values of acetic acid (21.9 g/L), formic acid (2.8 g/L) and levulinic acid (2.3 g/L) were obtained under the condition 260°C / R-7.5. These findings may indicate the low values of xylose (2.0 g/L) and (2.7 g/L) under 260°C / R-7.5 and 260°C / R-15, respectively. The acetic acid represents a well-known fermentation inhibitor but, if separated and purified, it can be sold as a chemical product. It is one of the carboxylic acids widely used to produce various acetic esters such as vinyl acetate, which is used to prepare polyvynilacetate, and ethyl acetate (Cebreiros et al., 2017). The separation of acetic acid from aqueous solutions by liquid-liquid extraction can be performed.

As a bioproduct, levulinic acid can be used as a chemical platform for the production of other higher value-added chemical compounds, such as methyl vinyl ketone and olefins. In the pharmaceutical industry, levulinic acid is used to produce aminolevulinic acid and benzoazepinones (Bevilaqua et al., 2013). Levulinic acid was also obtained in the acid hydrolysis (H_2SO_4) of rice husks (Fleig et al., 2018). In the condition with 3% (w/v) acid, 180°C and 60 min, 12.6 g/L of levulinic acid was obtained. For levulinic and formic acids, one way of recovering such bioproducts from the hydrolyzed solution is through the esterification reaction with butane, producing hydrophobic esters, which can be separated from the solution by distillation (Sen et al., 2012). Rice husks hydrolyzed solutions were also analyzed in terms of fermentable sugars, inhibitors and organic acids at different intervals for 15 min (Figs. 22 and 23). These results are important because it is possible to optimize the SWH process.

Lower levels of sugars and inhibitors are obtained for samples submitted to the conditions 180°C / R-7.5 and 180°C / R-15. In this study, for the condition with the highest sugars (220°C / R-7.5), the contents of cellobiose and xylose in the first 2 min of hydrolysis were approximately 68 g/L in 1 min and 29.8 g/L in 1.5 min, respectively.

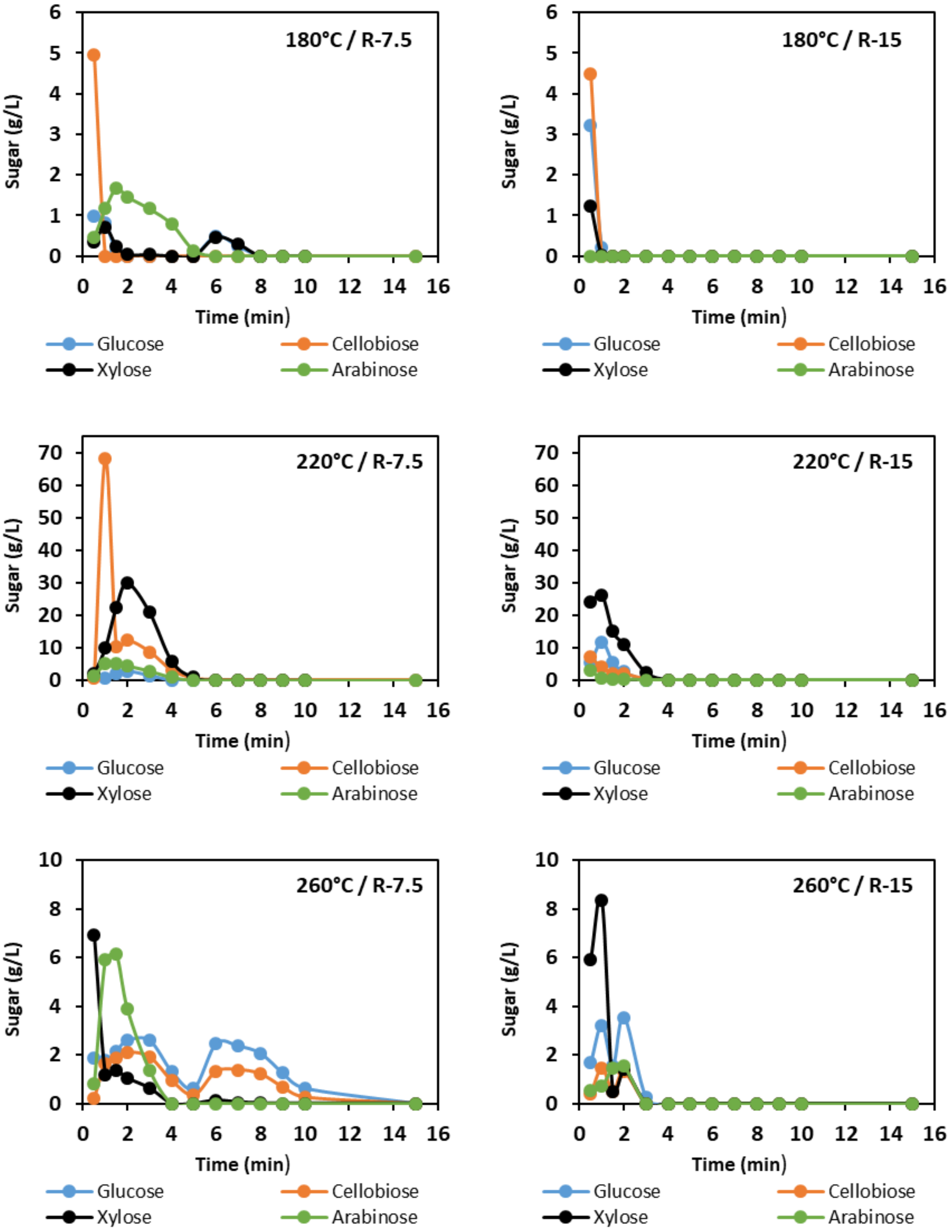

Figure 22 - Content of fermentable sugars (non-accumulated samples) in the hydrolyzed samples from rice husks at 25 MPa under different experimental conditions; R: liquid/solid mass ratio (g water/g husks)

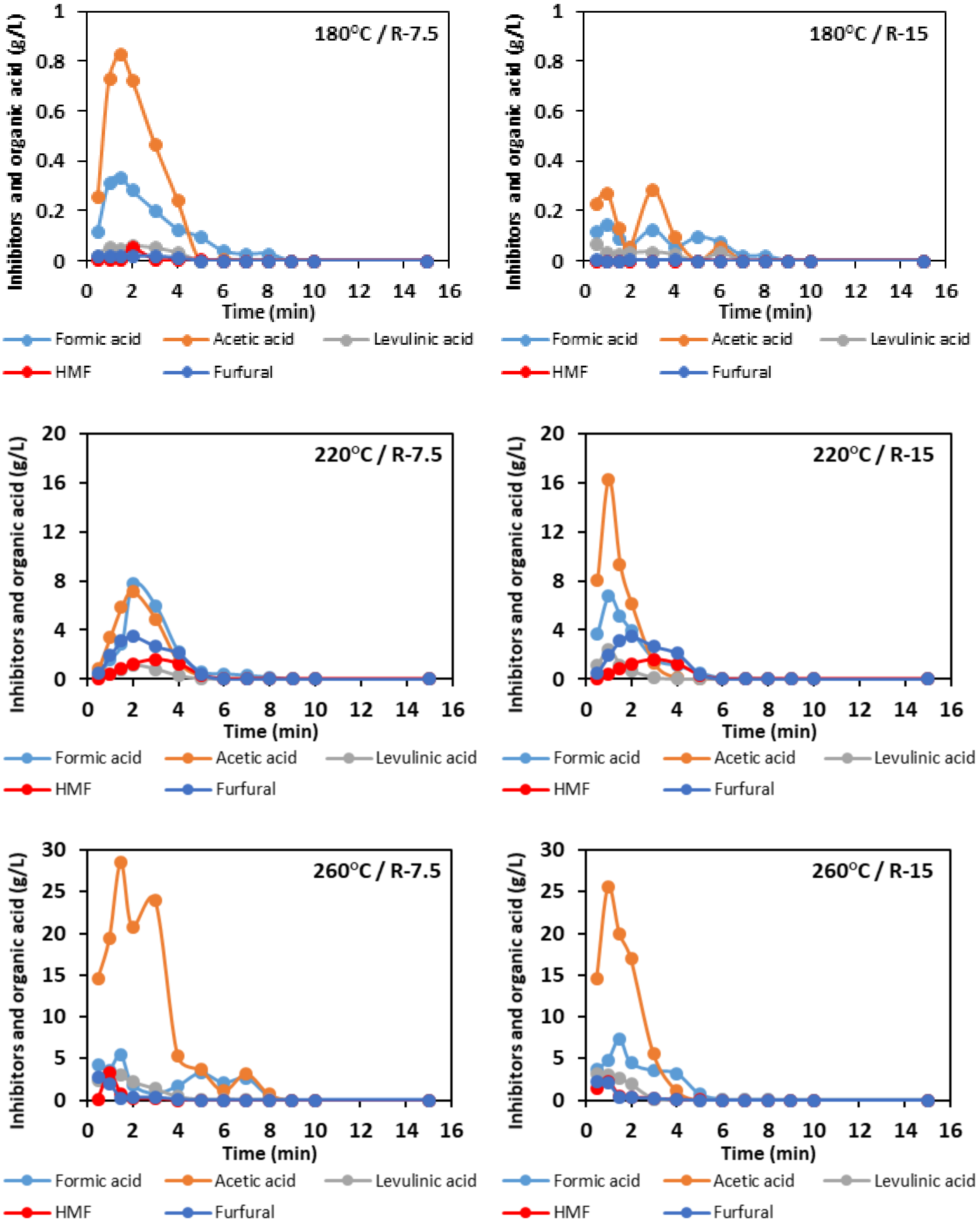

Figure 23 - Content of organic acids and inhibitors (non-accumulated samples) in the hydrolyzed samples from rice husks at 25 MPa under different experimental conditions; R: liquid/solid mass ratio (g water/g husks)

The high value found for cellobiose can be attributed to the dissociation of amorphous cellulose, which at approximately 220°C it is readily dissolved (Yu & Wu, 2011). With respect to the high contents of xylose at 220°C / R-7.5, they can be attributed to the rapid dissociation of hemicelluloses in the range from 190 to 230°C in (Prado et al., 2016). At temperatures near to 220°C, the H^+ content increases, thus increasing the acid content in water and the destruction of hemicelluloses into the monomeric sugar xylose.

When the conditions 220°C / R-15 and 220°C / R-7.5 are compared, there was a large difference in the sugars content. In the condition R-15, the quantity of glucose + cellobiose is 10 times smaller. This behavior can be attributed to the increase in the R, which suppresses the depolymerization of oligosaccharides and, consequently, decreases the concentration of sugars in the hydrolyzed solutions (Cardenas-toro et al., 2014).

SWH was also evaluated in terms of kinetic profile (0-15 min) of sugar composition. At 260°C, the xylose content is lower than at 220°C. At 260°C / R-7.5, the maximum xylose (6.9 g/L) and arabinose (6.1 g/L) contents were achieved in the first 2 min. There is a decrease in the content of these two sugars when the temperature was increased from 220 to 260°C. This behavior can be attributed to the increased degradation of sugars into organic acids, furfural and HMF when the temperature is increased (Peterson et al., 2008; Pinto et al., 2017). This assertion can be confirmed by results presented in Figure 23. The acetic acid contents were 28 g/L (260°C / R-7.5) for the first 1.5 min and 25 g/L (260°C / R-15) for the first 1 min. When the temperature increased from 220 to 260°C, the amount of acetic acid increased because there was a higher dissociation of hemicelluloses. The contents of formic and levulinic acids were low for all conditions, demonstrating that there was low degradation of sugars from cellulose (Fig. 23). The cellulose structure was dissociated mostly in cellobiose under conditions where the temperature was 220°C and 260°C (Fig. 22).

Hydrolysis with semi-flow hot-compressed water at 230°C/10 MPa/15 min (1st stage) and 270°C /10 MPa/30 min (2nd stage) was studied (Phaiboonsilpa et al., 2013). In the first stage (15 min), the contents of acetic and formic acids were 6.5 g/L (0.13 g/g rice husks) and

0.5 g/L (0.01 g/g rice husks), respectively, while the contents of xylose and arabinose were 17.5 g/L and 14.5 g/L, respectively. The differences in the contents of sugars and organic acids when comparing the present work and the study of Phaiboonsilpa et al. (2013) may be explained due to the difference in the value of R. In Phaiboonsilpa et al. (2013), 0.5 g of rice husks and a flow of 10 mL/min were applied for 60 min (R of 1200 g water/g husks). In our study, the values of R were 7.5 and 15 g water/g husks. Therefore, the R used in this study is up to 160 times lower. Therefore, a high R implies the suppression of the oligosaccharide depolymerization and a consequent reduction of concentrations of sugars and organic acids (Cardenas-toro et al., 2014).

The contents of inhibitors and organic acids for conditions with temperature at 220°C and 260°C are in accordance with the results for the pH (Fig. 24). In the first 2 min, the pH values are low (approximately 3). This behavior is related to the reaction and formation of inhibitors and organic acids, mainly acetic acid, which at 2 min it presents a high content, ranging from 7.1 (220°C / R-7.5) to 28 g/L (260°C / R-15) (Fig. 23). This type of behavior was also reported in the SWH of coconut husk, defatted grape seed and pressed palm fiber (Prado et al., 2014b), and sugarcane bagasse (Lachos-Perez et al., 2016).

The organic acids provide acidic protons to catalyze the subsequent hydrolysis of monomers and oligomers as an autocatalytic process. For the assay at 180°C, the pH is close to the neutral (Fig. 24). This is consistent with the fact that these lower temperatures are insufficient for the hydrolysis of the lignocellulosic matrix and thus not producing acidic hydrolyzed solutions (Cocero et al., 2018).

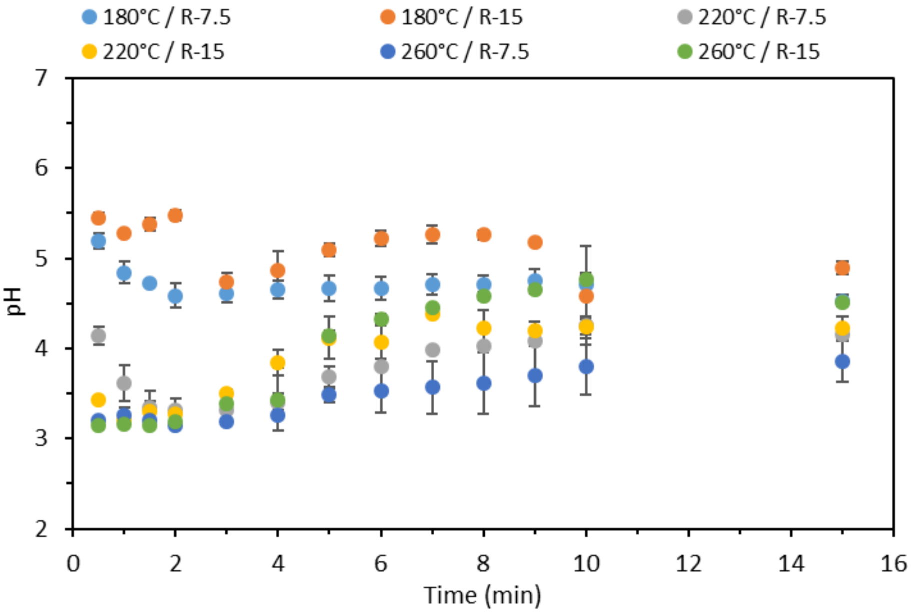

Figure 24 - Kinetic profile of pH of the hydrolyzed samples from rice husks at 25 MPa under different experimental conditions; the bars represent the standard deviation

4.3.5 Solid coproduct

4.3.5.1 FT-IR spectroscopy

The chemical composition of fresh rice husks and solid coproducts was characterized for functional group content using FT-IR (Fig. S.1) The FT-IR spectra of fresh rice husks and coproducts (solid remaining after SWH process) presented a similar profile, but with different band intensities. The SWH removed certain components in different quantities when comparing the experimental conditions. The bands in the 1600 cm^{-1} region represent the -OH stretch present in the silica structures (Möller et al., 2013), while the bands near to 1100 cm^{-1} (e. g., 913 cm^{-1}) indicate the C-O, C-C and C-OH stretches of the sugar units of cellulose (Xu et al., 2013). The band with the highest intensity at 1600 cm^{-1} is related to the highest temperature (260°C). This behavior can be attributed to cellulose dissociation and with the consequent exposure of silica.

As the temperature in SWH assays increased, the band corresponding to the range of 1100 cm^{-1} also increased. This increasing may also be attributed to the larger hemicelluloses dissociation, leaving more exposed cellulose with its vibration bands in –OH, -O, -C (Lachos-Perez et al., 2016). At approximately 1100 cm^{-1}, the bands with the highest intensities are related to rice solid coproduct after hydrolysis at 260°C and 220°C. These types of bonds in such coproducts can be explained with the assistance of Figure 25 (DTG) because the increase of temperature favored decreasing the amount of hemicelluloses.

4.3.5.2 TGA

The fresh rice husks and solid coproducts were analyzed by TGA to determine the thermal degradation of these materials. DTG was fitted using the methods recommended in the literature (Cai et al., 2013; Lachos-Perez et al., 2017) to determine mass composition for hemicelluloses, cellulose, lignin, and char. The contributions of individual components were determined by integration and normalized as shown in Figure 25b. The average temperatures were attributed to each one of the components in the DTG curves.

For cellulose, hemicelluloses, lignin, and char, the temperature range of the peak base by the DTG is specified in the literature. For the decomposition of cellulose, the range of 330-370°C (Cai et al., 2013) was used. For hemicelluloses, the temperature range was 175-350°C (Peng & Wu, 2010). For lignin and coal, the temperature ranges were 370-550 and 550-770°C, respectively (Watkins et al., 2015). Only 35 wt.% of fresh rice husks remained after heating the samples at 800°C under a nitrogen chamber. For solid coproducts processed at 260°C, the remaining mass was 50%. Therefore, for the coproduct obtained by SWH at 260°C, an amount of 18% of solid may be in the carbonized form.

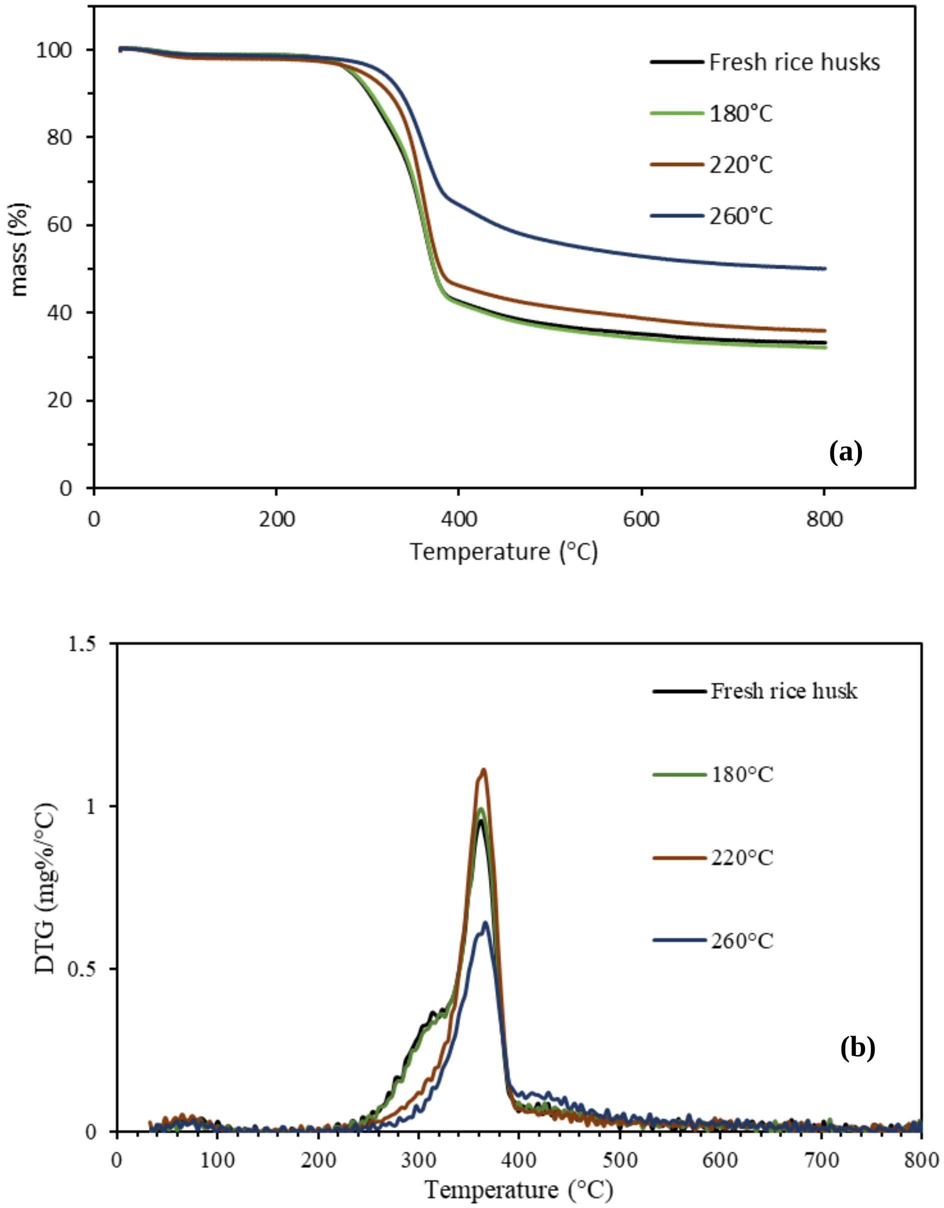

Figure 25 - TGA of fresh rice husks and solid coproducts after SWH process: (a) degradation profile and (b) derivative thermogravimetric analysis (DTG)

For fresh rice husks and coproducts at 180°C, a portion of the peak appeared from 250°C to 320°C (referring to hemicelluloses) and another appeared within the limits of 320-390°C (referring to celluloses) (Peng & Wu, 2010). When rice husks were processed at 220°C, the peak of hemicelluloses disappeared and the peak of cellulose increased. Therefore, hemicelluloses must have been dissociated in this condition. For SWH at 260°C, the peak of cellulose is reduced. The peak that appears for these conditions is in the 320°C to 400°C range (Figure 25b), where cellulose dissociation is observed (Watkins et al., 2015). However, the peak representing the assay performed at 260°C shows lower intensity and the area on the curvature is smaller (Table 11). This behavior is consistent with the expected results, as there is a larger cellulose dissociation at temperatures near to 250°C (Mohan et al., 2015).

According to the results presented in Table 11, the highest dissociation of hemicelluloses occurs at 220°C and 260°C. The SWH using temperatures in the range 180-250°C is sufficient to dissociate hemicelluloses, but not cellulose by a sufficient manner (Cantero et al., 2015). The lignin content increased as the temperature increased in the SWH process. Due to the hemicelluloses and cellulose dissociation, the remaining solid is richer in lignin and char. The results presented in Table 11 favor understanding of how long dissociation of the major constituents of rice husks have occurred in sugars, inhibitors, and organic acids. When increasing the temperature from 220°C to 260°C, the amount of inhibitors and organic acids increased (Table 10) as a consequence of dissociation of cellulose.

Table 11 **-** Composition (dry mass basis) of rice husks obtained through the areas of peaks in the DTG analysis referring to cellulose, hemicelluloses, lignin, and char

	Hemicelluloses (%)	**Cellulose (%)**	**Lignin (%)**	**Char (%)**
Fresh rice husks	18.5	28.0	15.9	2.8
180°C	18.0	29.9	16.6	3.2
220°C	9.6	30.7	17.9	4.1
260°C	6.5	19.0	19.2	4.6

4.3.5.3 Scanning Electron Microscopy (SEM)

The morphology of rice husks was a few influenced by the SWH process. The surface of fresh rice husks presented morphology consistent with the native cell wall (Fig. S.2). The surface of fresh husks has granules that are ruptured, which can be due to the grinding stage (sample preparation). Interestingly, in the SWH at 180°C, the surface does not seem to be modified, which is consistent with the results of sugars, inhibitors, and organic acids (low content) (Table 10). Under hydrolysis conditions where the operating temperature was 220°C and 260°C, a disruption of the granules is observed, which is in agreement with the content of sugars, inhibitors, and organic acids (dissociation of hemicelluloses and cellulose) (Table 10). This behavior (rupture of the granules with increasing temperature) was also visualized in the SWH of sugarcane bagasse (Lachos-Perez et al., 2016).

4.4 CONCLUSIONS

Rice husks have been processed by SWH. High Y_{RS} (18.0 ± 2.9 g/100 g dry rice husks) was found at 220°C with a liquid/solid ratio of 7.5 g water/g husks. For levulinic acid, the highest content was 2.3 g/L at 260°C / R-7.5. Dissociation of cellulose and hemicelluloses was observed by TGA and FT-IR analyses. Based on the conclusions and as recent and future perspectives, the fermentable sugars and bioproducts obtained from rice husks by SWH may be applied in several industrial fields, principally for the bioethanol production and for the production of other higher value-added chemical compounds.

Appendix A. Supplementary data

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

Conflict of interest

The authors inform that there are no conflicts of interest.

Acknowledgments

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REFERENCES

Abdelmoez, W., Nage, S.M., Bastawess, A., Ihab, A., Yoshida, H., 2014. Subcritical water technology for wheat straw hydrolysis to produce value added products. J. Clean. Prod. 70, 68-77.

An, Y.X., Zong, M.H., wu, H., Li, N., 2015. Pretreatment of lignocellulosic biomass with renewable cholinium ionic liquids: Biomass fractionation, enzymatic digestion and ionic liquid reuse. Bioresour. Technol. 192, 165-171.

AOAC. 1997. Association of official analytical chemists – AOAC. 16th ed. AOAC, Washington, USA.

Bevilaqua, D.B., Rambo, M.K.D., Cardoso, T.M., Martins, A.L., 2013. Cleaner production: levulinic acid from rice husks. J. Clean. Prod. 47, 96-101.

Bijay-Singh, Shan, Y.H., Beebout, S.E.J., Yadvinder-Singh, Buresh, R.J., 2013. Crop Residue Management for Lowland Rice-Based Cropping Systems in Asia, Cambridge.

Cai, J., Wu, W., Liu, R., Huber, G.W., 2013. A distributed activation energy model for the pyrolysis of lignocellulosic biomass. Green Chem. 15(5), 1331-1340.

Cantero, D.A., Bermejo, M.D., Cocero, M.J., 2015. Reaction engineering for process intesification of supercritical water biomass refining. J. Supercrit. Fluids 96, 21-35.

Cardenas-toro, F.P., Foster-Carneiro, T., Rostagno, M.A., Petenate, A.J., Filho, F.M., Meireles, M.A.A., 2014. Integrated supercritical extraction and subcritical water hydrolysis for the recovery of bioactive compounds from pressed palm fiber. J. Supercrit. Fluids 93, 42-48.

Cebreiros, F., Guigou, M.D., Cabrera, M.N., 2017. Integrated forest biorefineries: Recovery of acetic acid as a by-product from eucalyptus wood hemicellulosic hydrolysates by solvent extraction. Ind. Crop. Prod. 109, 101-108.

Ciftci, D., Saldaña, M.D.A., 2015. Hydrolysis of sweet blue lupin hull using subcritical water technology. Bioresour. Technol. 194, 75-82.

Cocero, M.J., Cabeza, A., Abad, N., Adamovic, T., Vaquerizo, L., Martínez, C.M., Pazo-Cepeda, M.V., 2018. Understanding biomass fractionation in subcritical & supercritical water. J. Supercrit. Fluids 133, 550-565.

CONAB. 2018. Monitoring of the Brazilian crop. National Supply Company 5, 1-142.

Dagnino, E.P., Chamorroa, E.R., Romano, S.D., Felissia, F.E., Area, M.C., 2013. Optimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol production. Ind. Crop. Prod. 42, 363-368.

Danon, B., Marcotullio, G., Jong, W., 2014. Mechanistic and kinetic aspects of pentose dehydration towards furfural in aqueous media employing homogeneous catalysis. Green Chem. 16(1), 38-54.

Díaz, A.B., Marzo, C., Caro, I., I Ory, Blandino, A., 2017. Valorization of exhausted sugar beet cossettes by successive hydrolysis and two fermentations for the production of bio-products. Bioresour. Technol. 225, 225-233.

Faba, L., Diaz, E., Ordóñez, S., 2015. Recent developments on the catalytic technologies for the transformation of biomass into biofuels: A patent survey. Renewable Sustainable Energy Rev. 51, 273-287.

FAO. 2016. Rice market monitor. Food and Agriculture Organization of the United Nations 19(2), 1-35.

Fleig, O.P., Lopes, E.S., Rivera, E.C., Filho, R.M., Tovar, L.P., 2018. Concept of rice husk biorefining for levulinic acid production integrating three steps: Multi-response optimization, new perceptions and limitations. Process. Biochem. 65, 146-156.

Germec, M., Ilgın, M., İlhan, E., Turhan, I., 2016. Optimization of acidic hydrolysis conditions of rice husk for fermentable sugar production. Energy Sources Part A 38, 3103-3108.

Gullón, P., Salazar, N., Muñoz, M.J.G., Gueimonde, M., Madiedo, P.R., Gavilán, C.G.R., Parajó, J.C., 2011. Assessment the fermentability of xylooligosaccaharides from rice husks. Bioesour. Technol. 6(3), 3096-3114.

Kumar, V., Binod, P., Sindhu, R., Gnansounou, E., Ahluwalia, V., 2018. Bioconversion of pentose sugars to value added chemicals and fuels: recent trends, challenges and possibilities. Bioresour. Technol. 269, 443-451.

Lachos-Perez, D., Martinez-Jimenez, F., Rezende, C.A., Tompsett, G., Timko, M., Foster-Carneiro, T., 2016. Subcritical water hydrolysis of sugarcane bagasse: An approach on solid residues characterization. J. Supercrit. Fluids 108, 69-78.

Lachos-Perez, D., Tompsett, G.A., Guerra, P., Timko, M.T., Rostagno, M.A., Martínez, J., Foster-Carneiro, T., 2017. Sugars and char formation on subcritical water hydrolysis of sugarcane straw. Bioresour. Technol. 243, 1069-1077.

Lau, B.B.Y., Luis, E.T., Hossain, M.M., Hart, W.E.S., Cencia-Lay, B., Black, J.J., To, T.Q., Aldous, L., 2015. Facile, room-temperature pre-treatment of rice husks with tetrabutylphosphonium hydroxide: Enhanced enzymatic and acid hydrolysis yields. Bioresour. Technol. 197, 252-259.

Lin, R., Cheng, J., Ding, L., Song, W., Qi, F., Zhou, J., Cen, K., 2015. Subcritical water hydrolysis of rice straw for reducing sugar production with focus on degradation by-products and kinetic analysis. Bioresour. Technol. 186, 8-14.

Martín, J.R., Bernal, C.M., Cobas, Y.P., Sosa, F.M.R., García, B.D., 2017. Additives enhancing enzymatic hydrolysis of lignocellulosic biomass. Bioresour. Technol. 244, 48-56.

Mayanga-Torres, P.C., Lachos-Perez, D., Rezende, C.A., Prado, J.M., Ma, Z., Tompsett, G.T., Timko, M.T., Foster-Carneiro, T., 2017. Valorization of coffee industry residues by subcritical water hydrolysis: recovery of sugars and phenolic compounds. J. Supercrit. Fluids 120(1), 75-85.

Megawati, Sediawan, W.B., Sulistyo, H., Hidayat, M., 2011. Kinetics of sequential reaction of hydrolysis and sugar degradation of rice husk in ethanol production: Effect of catalyst concentration. Bioresour. Technol. 102, 2062-2067.

Mohan, D., Banerjee, T., Goud, V.V., 2015. Hydrolysis of bamboo biomass by subcritical water treatment Bioresour. Technol. 191, 244-252.

Möller, M., Harnisch, F., Schröder, U., 2013. Hydrothermal liquefaction of cellulose in subcritical water—the role of crystallinity on the cellulose reactivity. Research Advances 27(3), 11035-11044.

Moscon, J.M., Priamo, W.L., Bilibio, D., Silva, J.R.F., Souza, M., Lunelli, F., Kuhn, R.C., Cancelier, A., Mazutti, M.A., 2014. Comparison of conventional and alternative technologies for the enzymatic hydrolysis of rice hulls to obtain fermentable sugars. Biocatalys. Agricult. Biotech. 3, 149-154.

NREL. 2018. Biomass Compositional Analysis Laboratory Procedures, Laboratory N.R.E.L. USA.

Ozbek, H.N., Fockink, D.H., Yanik, D.K., Gogus, F., Lukasik, R.M., 2018. The green biorefinery concept for the valorisation of pistachio shell by high-pressure CO_2/H_2O system. J. Clean. Prod. 196, 842-851.

Pedras, B., Salema-Oom, M., Sá-Nogueira, I., Simões, P., Paiva, A., Barreiros, S., 2017. Valorization of white wine grape pomace through application of subcritical water: analysis of extraction, hydrolysis, and biological activity of the extracts obtained. J. Supercrit. Fluids 127, 68-74.

Peng, Y., Wu, S., 2010. The structural and thermal characteristics of wheat straw hemicellulose. J. Anal. Appl. Pyrol. 88, 134-139.

Peterson, A.A., Vogel, F., Lachance, R.P., Fröling, M., Antal, M.J., Tester, J.W., 2008. Thermochemical biofuel production in hydrothermal media: a review of sub-and supercritical water technologies. Energ. Environm. Sci. 1, 32-65.

Phaiboonsilpa, N., Ogura, M., Yamauchi, K., Raemanolontsoa, H., Saka, S., 2013. Two-step hydrolysis of rice (*Oryza sativa*) husk as treated by semi-flow hot-compressed water. Ind. Crop. Prod. 49, 484-491.

Pinto, A.R.R., Antas, F., Santos, R.C.D., Bowra, S., Simões, P., Barreiros, S., Paiva, A., 2017. Effect of reactor configuration on the subcritical water hydrolysis of recycled paper mill sludge. J. Anal. Appl. Pyrol. 127, 68-74.

Potumarthi, R., Baandlhe, R.R., Nayak, P., Jetty, A., 2013. Simultaneous pretreatment and sacchariffication of rice husk by *Phanerochete chrysosporium* for improved production of reducing sugars. Bioresour. Technol. 128, 113-117.

Prado, J.M., Follegati-Romero, L.A., Foster-Carneiro, T., Rostagno, M.A., Maugeri-Filho, F., Meireles, M.A.A., 2014a. Hydrolysis of sugarcane bagasse in subcritical water. J. Supercrit. Fluids 86, 15-22.

Prado, J.M., Foster-Carneiro, T., Rostagno, M.A., Folegatti-Romero, L.A., Maugeri-Filho, F., Meireles, M.A.A., 2014b. Obtaining sugars from coconut husk, defatted grape seed, and pressed palm fiber by hydrolysis with subcritical water. J. Supercrit. Fluids 89, 89-98.

Prado, J.M., Lachos-Perez, D., Foster-Carneiro, T., Rostagno, M.A. 2016., Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugar: A review. Food. Bioprod. Process. 98, 95-123.

Rastogi, M., Shrivastava, S., 2017. Recent advances in second generation bioethanol production: an insight to pretreatment, saccharification and fermentation processes. Renewable Sustainable Energy Rev. 80, 330-340.

Sen, S.M., Gürbüz, E.I., Wettstein, S.G., Alonso, D.M., Dumesic, J.A., Maravelias, C.T., 2012. Production of butene oligomers as transportation fuels using butene for esterification of levulinic acid from lignocellulosic biomass: process synthesis and technoeconomic evaluation. Green Chem. 14(12), 3289-3294.

Shen, Z., Zhang, K., Si, M., Liu, M., Zhuo, S., Liu, D., Ren, L., Yan, X., Shi, Y., 2018. Synergy of lignocelluloses pretreatment by sodium carbonate and bacterium to enhance enzymatic hydrolysis of rice straw. Bioresour. Technol. 249, 154-160.

Wang, S., Sun, X., Yuan, Q., 2018. Strategies for enhancing microbial tolerance to inhibitors for biofuel production: a review. Bioresour. Technol. 258, 302-309.

Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, M., Jeelani, A., 2015. Extraction and characterization of lignin from different biomass resources. J. Mat. Res. Tech. 4(1), 26-32.

Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D., 2013. Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: a mini-review. Appl. Energy 104, 801-809.

Yu, Y., Wu, H., 2011. Effect of ball milling on the hydrolysis of microcrystalline cellulose in hot-compressed water. Environ. Energy Eng. 57, 793-800.

Zhang, H., Fan, M., Zhang, A., Xie, J., 2018. Enhancing enzymatic hydrolysis of sugarcane bagasse by ferric chloride catalyzed organosolv pretreatment and Tween 80. Bioresour. Technol. 258, 295-301.

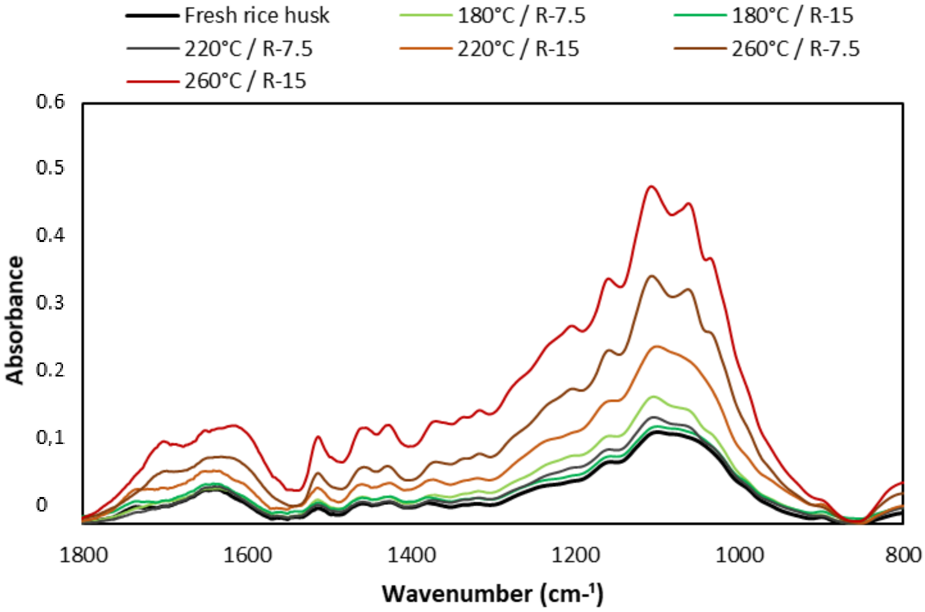
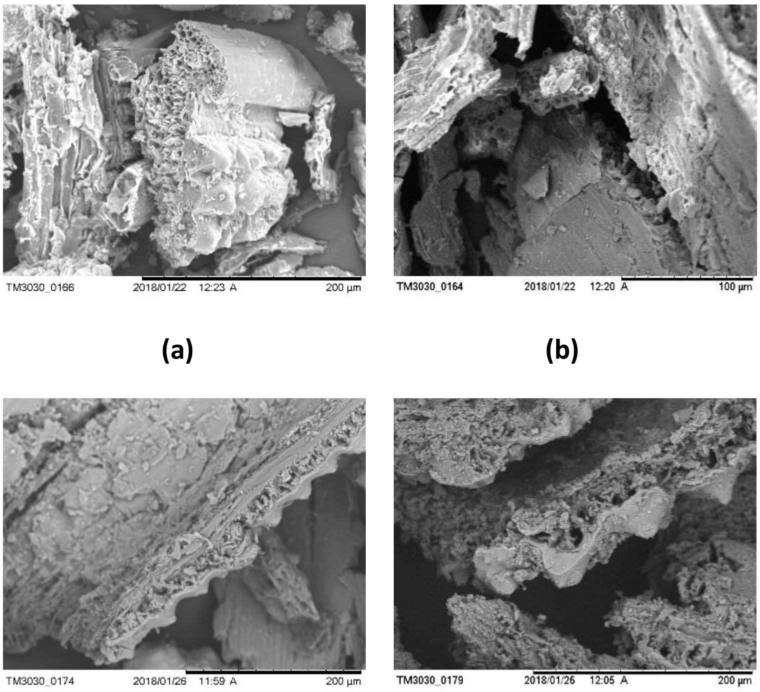


Figure S.1 - FT-IR spectroscopy analysis of fresh rice husks and solid coproducts after SWH process



(a) **(b)**

(c) **(d)**

Figure S.2 - SEM micrograph (magnification: 500×) of the surface of fresh rice husks (a) and solid coproducts after SWH process at 180°C (b), 220°C (c) and 260°C (d)

- CAPÍTULO 5 -

UTILIZAÇÃO DOS COPRODUTOS RESTANTES DA HIDRÓLISE COMO MATERIAL ADSORVENTE

Adsorption of 2-nitrophenol using rice straw and rice husks hydrolysed by subcritical water

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Abstract

The potential of rice straw and rice husks as adsorbents after being processed by subcritical water hydrolysis (SWH) was investigated as an alternative to enjoy the coproducts of cellulosic bioethanol. The influences of SWH temperature (453, 493 and 533 K) and liquid/solid ratio (7.5 and 15 g water/g biomass) on the rice straw and rice husks characteristics and also on the adsorption capacity of 2–nitrophenol were evaluated at pH 4 and 7. Adsorption kinetics, equilibrium and thermodynamic parameters were also studied under different experimental conditions. The adsorption capacity favored at pH 7. Pseudo–first order model was suitable to predict the kinetic curves for 2–nitrophenol concentrations of 25, 50, 75 and 100 mg/L, and for both adsorbents tested. The isotherm data were fitted by the Freundlich model for the adsorbents evaluated. In general, the thermodynamic results revealed a spontaneous and exothermic process. The best adsorption capacity for fresh rice straw (55.35 ± 1.45 mg/g) and fresh rice husk (69.94 ± 2.63) were observed at pH 7. The maximum adsorption capacity were obtained for rice straw (92.97 ± 1.31 mg/g) and rice husk (91.23 ± 2.86 mg/g) that has undergone an SWH at 453 K and 7.5 g water/g biomass. It was demonstrated that the solid products of SWH, rice straw and rice husks showed an increase in the adsorption capacity of, respectively, 67.9 and 30.4%. These coproducts can be used as alternative adsorbents to remove 2–nitrophenol in a wide range of concentrations. This is one way to become the production of cellulosic bioethanol more feasible.

Keywords: Rice coproducts, Hydrolyzed solids, Subcritical technology, Adsorption, Toxic compound.

5.1 INTRODUCTION

Bioethanol produced from lignocellulosic sources still faces problems related to this complex recalcitrant structure. The presence of lignin and the cellulosic complex determine the high resistance of plant material to various biological, physical, and chemical agents (Amiri & Karimi, 2018). Several processes are being developed to dissociate cellulose and hemicelluloses from lignocellulosic biomass. The processes commonly used are diluted acid or enzymatic hydrolysis (Martín et al., 2017). One of the main problems of diluted acid hydrolysis is the high level of inhibitors produced during the reaction, which affects the subsequent fermentation (Zhang et al., 2018). Within the biorefinery concept and as clean technology, subcritical water hydrolysis (SWH) is being used as an efficient technology for dissociating lignocellulosic biomass. SWH is a promising technology because it has a potential for breaking down biopolymers of cellulose and hemicelluloses into monomeric sugars like xylose and glucose for biofuels production by fermentation or gasification (Li et al., 2016). SWH is not widespread yet at industrial scale, but there are some industrial plants that are currently using this technology in some countries. In Japan, for example, the Rematec Corp. Sakai SC factory processes approximately 70 tons of lignocellulosic biomass per day using subcritical water technology to obtain products of interest. In the Denmark, the SCF technologies A/S Danish Company has a pilot plant that processes 30 L/h of sludge, algae, manure, and residues from the food industry (Abaide et al., 2019b).

To become SWH a more feasible process, the solid co–products can be used for other applications. An alternative application of the co–products is to utilize them as an adsorbent material for removing organic contaminants from water (Rehman et al., 2012). One group of organic contaminants comprises phenols, nitrophenols, and nitrobenzenes, which compose part of many products such as pesticides, insecticides, and drugs (Luo et al., 2014).

Nitrophenols are listed as the main cause of cancer due to the high toxicity and ability to be accumulated in the human body. The high chemical toxicity and low biodegradation of nitro compounds can cause serious problems of pollution in the environment (Liu et al., 2011). The 2–nitrophenol is more toxic than other isomeric forms of nitrophenol and is of intense concern due to its high stability and solubility in water (Alam et al., 2017). Some treatments by chlorination generate chlorinated by–products that are poisonous and stable due to the aromatic ring in 2–nitrophenol structure (Kupeta et al., 2018). The allowable limit of 2–nitrophenol in natural waters is in the range of 0.01 – 2.0 μg/L (Huong et al., 2016).

Several methods are being used to remove nitrophenols from wastewater, including biodegradation process, photocatalytic degradation, Fenton process, and adsorption (Chen et al., 2017a; Kristanti et al., 2012; Rodrigues et al., 2018). Among these techniques, adsorption is widely used because it has an easy operation and simple design requirements. However, due to high costs of commercially activated carbon, researchers are studying various low–cost adsorbents derived from natural materials, industrial solid wastes, and/or agricultural co–products (Nguyen et al., 2013). Rice straw and rice husks are abundant and inexpensive co–products. In one of the last estimates, annual global quantities of 283 and 149 million tons per year are produced of rice straw and rice husks, respectively (FAO, 2016). Rice straw and rice husks are being studied for the recovery of fermentable sugars for producing bioethanol or biogas (Abaide et al., 2019c; Lin et al., 2015), and also with respect to the use of solid biomass as adsorbent (Franco et al., 2016; Li et al., 2019). However, to the best of our knowledge, none study could be found in the main database (Scopus and ISI Web of Science, for instance) that reported the evaluation of adsorption capacity of hydrolyzed rice straw (HRS) and hydrolyzed rice husks (HRH) obtained by SWH. Therefore, the objective of this work was to study the adsorption capacity of HRS and HRH submitted to different conditions of hydrolysis for 2–nitrophenol removal in a model solution. The potential of fresh rice straw, fresh rice husks, HRS, and HRH to adsorb 2–nitrophenol was evaluated in batch systems and compared each other based on adsorption kinetics and equilibrium and thermodynamic parameters.

5.2 MATERIALS AND METHODS

5.2.1 Materials

Rice straw was obtained from farms in the central region of state of Rio Grande do Sul/Brazil, from 2016/2017 harvest. Rice husks were kindly donated by a rice manufacturing company located in the same region. Immediately after the reception, both rice straw and rice husks were oven dried for 24 h at 333 K. The dry biomass was ground in a Willey Knife Mills equipment (SL 30, Solab, Brazil) with a 20 mesh separation grid. The milled rice straw and rice husks were frozen at 268 K until the further experimental assays. The reagent 2-nitrophenol (purity of 98%) was purchased from Sigma Aldrich (Brazil) and it was used without further purification.

5.2.2 SWH of rice straw and rice husks

The fresh rice straw (fresh RS) and fresh rice husks (fresh RH) were submitted to SWH according to procedure described in previous works (Abaide et al., 2019a; Abaide et al., 2019c). Briefly, 20 g of fresh RS was loaded in the reactor vessel, for each assay, and distilled water was pumped with a constant mass flow rate (flow rate defined according to the experimental assays). Immediately after the system was pressurized with water (pipes and reactor vessel), the pump was turned off and the micrometering valve was closed. The band heater was turned on for increasing the temperature to the desired value (according to each assay). The pressure was fixed at 25 MPa. For rice husks, 30 g were weighed and the same experimental procedure was performed. Three levels of temperature were selected (453 K; 493 K and 533 K) for the subsequent assays.

For rice straw, the flow rate was set as 10 and 20 mL/min to satisfy the liquid / solid ratios (R) of 7.5 g water/g straw and 15 g water/g straw, respectively, for a total reaction time of 15 min. For fresh RH, the flow rates were set as 15 and 30 mL/min to satisfy the values of R of 7.5 g water/g husks and 15 g water/g husks, respectively, for a total reaction time of 15 min. All assays were completely randomized and were performed in duplicate.

5.2.3 Characterization

The moisture, contents of ash, and total extractives were determined directly in the samples according to the methodologies of Association of Official Analytical Chemists and National Renewable Energy Laboratory (AOAC, 1997; Rehman et al., 2012). The analyses were performed in triplicate and the responses are expressed as a mean ± standard deviation.

After SWH, the solid coproducts contained into the reactor vessel were transferred to a Petri dish, taking care to prevent loss. The samples were dried at 378 K and the amount of coproduct was determined by difference between the initial amount of dried biomass and the final dried mass remaining in the reactor at the end of the process, using a digital analytical balance (AY-220, Marte, Brazil). The yields (Y, wt.%) of the solid coproducts were calculated according to Eq. 1.

$$Y = \left(m_{SWH} / m_{fresh} \right) \cdot 100 \tag{1}$$

Where: m_{SWH} is the dry mass (g) remaining inside the reactor after SWH and m_{fresh} is the initial dry mass (g).

The specific surface area (m^2/g) for fresh RS, fresh RH, HRS, and HRH were determined by N_2 adsorption isotherms, which were performed in an adsorption analyzer

(Micromeritics, ASAP 2020, USA) using BET (Brunauer, Emmett and Teller) method. Fourier Transform Infrared (FT-IR) spectroscopy (IR Prestige 21, Shimadzu, Japan) was used to record the FT-IR spectra of the samples. The spectra were obtained with nominal resolution of 4 cm^{-1} and within the spectral range between 4000 and 400 cm^{-1}. The analysis allows comparing the samples of fresh RS and fresh RH with the samples submitted to SWH process in order to evaluate the modification in functional group in the surface.

The morphology of the particles was determined by scanning electron microscopy (SEM) in the samples of fresh RS,fresh RH, HRS, and HRH. The samples were placed in stubs and covered with gold. Afterward, the samples were analyzed at 15 kV acceleration voltage in a scanning electron microscope (TM3030, HITACHI, Japan).

5.2.4 Batch adsorption study

Firstly, 0.05 g of the adsorbents for each category (fresh RS, fresh RH, HRS and HRH submitted to different SWH conditions (temperature and R) were investigated on the 2-nitrophenol adsorption at 298 K for 24 h. The adsorption effect of the pH was analyzed by adjusting at pH 4 and 7 of the 2-nitrophenol solutions using 0.1 M of HCl and 0.1 M of NaOH solutions. The experimental assays were carried out in a thermostated agitator (Marconi, MA 093, Brazil), stirred at 150 rpm in Erlenmeyer flasks (250 mL) containing 50 mL of 2-nitrophenol solutions, with 100 mg/L initial concentration (C_0).

Secondly, using fresh RS, fresh RH, HRS 493 K / R-7.5 and HRH 493 K / R-7.5 at pH 7, the effects of concentration (25, 50, 75 and 100 mg/L) and time (aliquots collected at regular intervals until equilibrium) were evaluated. The concentration of 2-nitrophenol in aqueous solutions was analyzed by spectrophotometry (UV-2700, Shimadzu, Japan) at 400 nm. The assays were performed in duplicate. The adsorption capacity at time (q_t, mg/g) and equilibrium adsorption capacity (q_e, mg/g) were determined according to Eq. 2 and Eq. 3, respectively.

$$q_t = \left(V\left(C_0 - C_t\right)/m\right)\cdot 100 \tag{2}$$

$$q_e = \left(V\left(C_0 - C_e\right)/m\right)\cdot 100 \tag{3}$$

Where: C_0 is the initial 2–nitrophenol concentration in the liquid phase (mg/L), C_e is the equilibrium 2–nitrophenol concentration in liquid phase (mg/L), C_t is the concentration of 2–nitrophenol (mg/L) for solution collected in the regular time interval *t*, *t* is the time interval (h), *m* is the amount of adsorbent (g) and *V* is the volume of solution (L).

5.2.5 Kinetics, equilibrium and thermodynamics evaluation

A pseudo–first–order (PFO) model (Eq. 4) (Lagergren, 1898) and pseudo–second–order (PSO) model (Eq. 5) (Ho & Mackay, 1998) were tested to represent the 2–nitrophenol adsorption on fresh RS, fresh RH, HRS 493 K / R–7.5, and HRH 493 K / R–7.5.

$$q_t = q_1\left(1 - \exp\left(-k_1 \cdot t\right)\right) \tag{4}$$

$$q_t = t \Big/ \left(1/\left(k_2 \cdot {q_2}^2\right) + t/q_2\right) \tag{5}$$

Where: k_1 (1/h) and k_2 (g/mg h) are the constant rates of PFO and PSO models, q_1 and q_2 (mg/g) are the theoretical values for the adsorption capacity.

The adsorption isotherm models of Henry (Foo & Hameed, 2010) and Freundlich (Freundlich, 1906) were used to investigate the adsorption of 2–nitrophenol by fresh RS, fresh RH, HRS 493 K / R–7.5, and HRH 493 K / R–7.5.

$$q_e = k_F \cdot C_e^{1/n} \tag{6}$$

$$q_e = k_H \cdot C_e \tag{7}$$

Where: q_e (mg/g) adsorption capacity in equilibrium, k_F is the Freundlich constant ((mg/g)/(mg/L)$^{1/n}$), 1/n is the heterogeneity factor, q_m is the maximum adsorption capacity (mg/g) and k_L is the Langmuir constant (L/mg).

The adsorption thermodynamic estimation was performed by the standard values of Gibbs free energy change (ΔG^0, kJ/mol), enthalpy change (ΔH^0, kJ/mol), and entropy change (ΔS^0, kJ/mol.K)(Fröhlich et al., 2018; Lima et al., 2019). These values were estimated by Eq. 8, Eq. 9 and Eq.10.

$$k_e = \left(C_0 - C_e\right) / C_e \tag{8}$$

$$\Delta G^0 = -R \cdot T \cdot \ln\left(k_e\right) \tag{9}$$

$$\ln\left(k_e\right) = \Delta S^0 / R - \Delta H^0 / \left(R \cdot T\right) \tag{10}$$

Where: T is the temperature (K), R is the universal gas constant (8.314 J/mol.K) and k_e is the dimensionless thermodynamic equilibrium constant.

The adsorption kinetic and isotherm data were evaluated by using general non-linear fitting method (Levenberg-Marquardt). The quality of fit was estimated by the coefficient of determination (R^2) and by the residual root-mean squared error (RMSE). Thermodynamic parameters were estimated by linear regression and R^2 was used as a fit quality indicator. All the required parameters for kinetic, isotherm and thermodynamic studies were estimated using the Matlab® software (Mathworks, USA).

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization

5.3.1.1 Raw material characterization

The moisture, ash and extractives content in fresh RS (mass wet basis) were 9.0 ± 0.1%, 12.2 ± 0.6% and 17.5 ± 1.1%, respectively. For fresh RH, the moisture, ash and extractives content were 9.1 ± 0.5%, 16.6 ± 0.7%, 11.4 ± 1.1%, respectively. The extractives value can affect the adsorption capacity when fresh materials are used as adsorbents. Extractives are composed of organic compounds of low molecular weight, such as phenolic compounds, terpenes, saturated and unsaturated fatty acids, proteins and flavonoids. Although the composition may vary depending on climatic conditions of cultivation, the extractive content for fresh RH is closer to that one (11.0%) reported by Fleig et al. (2018). For fresh RS, the extractive content is closer to that one (17.8%) reported by He et al. (2009).

5.3.1.2 Yield

Yield, ash content, and BET surface area (m^2/g) of fresh RS, fresh RH, and HRS and HRH submitted to various hydrolysis conditions are presented in Table 12. The yields of HRS were found in the range of 40.20 ± 0.86 to 83.79 ± 0.88 wt.%. The lowest value is very close to the values obtained using rice straw hydrochars prepared by microwave assisted hydrothermal treatment (42.53%) at 453 K for 50 min (Li et al., 2019) and to rice straw treated with H_2SO_4 / $FeCl_3$ in a reactor temperature of 433 K for 20 min (45.2%) (Kim et al., 2014). When water is used in the subcritical state, higher temperatures (493–533 K) are required to dissociate lignocellulosic biomass. At the same temperature, a higher dissociation of rice straw is found as the R increases from 7.5 to 15 g water/g biomass. The reduction of yield as the temperature increases may be attributed to the increase of ionization constant of water at high temperature. The concentrations of H^+ and OH^- increased, thus facilitating the hydrolysis of cellulose and hemicelluloses into monosaccharides, which dissolve in water, thereby reducing the mass (Cocero et al., 2018).

Table 12 - Main characterization of the fresh rice straw and husks and hydrolyzed by Subcritical water Rice straw and husks

Samples	**Temperature (K)**	**Liquid / solid ratio (g water /g biomass)**	**Yield (%)**	**Ash (%)**	**BET surface area (m^2/g)**
Fresh RS	-	-	-	12.20 ± 0.62	1.85
HRS 453 K / R-7.5	453	7.5	81.33 ± 0.88	11.06 ± 1.13	1.83
HRS 453 K / R-15	453	15	83.79 ± 1.61	12.47 ± 1.37	1.73
HRS 493 K / R-7.5	493	7.5	53.70 ± 1.16	14.53 ± 0.19	7.04
HRS 493 K / R-15	493	15	57.36 ± 2.71	14.78 ± 2.36	4.82
HRS 533 K / R-7.5	533	7.5	40.20 ± 0.86	16.29 ± 1.63	10.61
HRS 533 K / R-15	533	15	45.67 ± 2.93	15.92 ± 1.41	8.17
Fresh RH	-	-	-	16.60 ± 0.70	1.17
HRH 453 K / R-7.5	453	7.5	89.26 ± 1.44	17.26 ± 0.16	1.95
HRH 453 K / R-15	453	15	91.02 ± 1.07	15.70 ± 0.37	1.43
HRH 493 K / R-7.5	493	7.5	77.30 ± 2.39	18.68 ± 1.32	12.17
HRH 493 K / R-15	493	15	53.60 ± 3.27	19.51 ± 2.96	13.95
HRH 533 K / R-7.5	533	7.5	55.42 ± 1.53	20.87 ± 1.63	24.24
HRH 533 K / R-15	533	15	56.20 ± 2.17	24.05 ± 1.28	21.00

RS: rice straw; RH: rice husks; HRS: hydrolyzed rice straw; HRH: hydrolyzed rice husks; R: liquid/solid ratio

The yields obtained for HRH samples that were submitted to subcritical water were in the range of 53.60 ± 3.27 to 91.02 ± 1.07 wt.%. Similar behavior to that which occurred for rice straw was observed. However, when evaluating the temperature rise from 493 to 533 K, small differences in the yields are identified. This behavior may be attributed to the high content of silica present in rice husks, which has a recalcitrant structure (Bijay-Singh et al., 2013). Therefore, for higher temperatures (533 K), there is no reaction with this fraction (silica) and, consequently, there is no substantial reduction of mass of rice husks.

For HRS biomass had lower yields as the temperature increased. This is attributed to the increased degradation of hemicelluloses at temperatures above 473 K and cellulose at temperatures close to 533 K (Allen et al., 1996; Cantero et al., 2015). This may also be explained by observing the spectrum in FT–IR (Supplementary information). For rice straw, the 1100 cm^{-1} band also increases as the temperature increases. This behavior is due to the dissociation of the hemicelluloses and exposure of the cellulose structure. Bands close to 913 cm^{-1} indicate the C–O, C–C and C–OH stretches of the sugar units of cellulose (Xu et al., 2013). For higher temperatures, from 493 to 533 K, SWH induced coke formation in rice straw and rice husks, since the 1600 cm^{-1} (C=C bond) band increases its intensity due to the higher dissociation of hemicelluloses and cellulose (Möller et al., 2013).

5.3.1.3 Ash content

The HRS and HRH that remaining in the reactor had high ash contents in the range of 11.06 ± 1.13 to 16.29 ± 1.63 wt.% (Table 12). The increase in ash content may be attributed to the removal of hemicelluloses (453 K) and cellulose (533 K) from both biomass submitted to SWH (Allen et al., 1996; Cantero et al., 2015). These results are very different from those found in works that used hydrothermal treatment to obtain hydrochars. For example, a hydrothermal process was applied in watermelon peel to carbonization this biomass (Chen et al., 2017b). In that work, approximately 600 mL slurry of watermelon peel was placed in stainless steel and then heated to either 463 or 533 K and maintained for 1 h, 6 h, or 12 h. When the temperature increased from 463 to 533 K in the same time interval, there was no difference in the ash contents. However, when evaluating the hydrothermal process at the same temperature, but at different time intervals, the ash content of watermelon peel decreased for longer time intervals. This fact is attributed to the longer residence time, which may lead to higher dissociation of inorganic minerals in water (Li et al., 2019). A study that used microwave–assisted hydrothermal with dilute H_2SO_4 to process red seaweed (*Gracilaria lemaneiformis*) was reported (Cao et al., 2019). The increase in temperature from 433 to 473 K decreased the ash content from 14.3 to 10.9 wt.%. This may have occurred due to the dissolution of the inorganic compounds in the acid (Kambo & Dutta, 2015).

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5.3.1.4 BET surface area and morphology

The fresh RS and HRS have BET specific surface areas ranging from 1.85 to 10.61 m^2/g (Table 12). Fresh RH and HRH have BET surface areas ranging from 1.17 to 24.24 m^2/g. The BET surface areas for the HRS 453 K / R-7.5 and HRS 533 K / R-7.5 were 1.83 m^2/g and 10.61 m^2/g, respectively, showed an increase of approximately 5 times in the BET surface area. This may be attributed to the increase of the ionic product of the subcritical water. As the temperature increases (453 to 533 K), the value of the dielectric constant for water decreases. Higher ionic product could make water act as a weak acid/base catalyst and accelerate the hydrolysis of biomass (Reza et al., 2014). The highest value for BET surface areas for the subcritical is slightly higher than that found by Li et al. (2019). The authors (Li et al.,2019) used a microwaves system, for 40 min to assist hydrothermal treatment of rice straw, obtaining a value of 8.21 m^2/g for the temperature of 453 K, with R of 10 g water/g straw. This may have occurred for longer exposure time to the process, increasing the dissolution.

The BET surface areas for the fresh RH and the HRH at a temperature of 453 K also have values in the range of 1.17 - 1.95 m^2/g, and rice husks biomass that have been subjected to high temperatures (HRH 493 K / R-7.5, 12.17 m^2/g, and HRH 533 K / R-7.5, 24.24 m^2/g) showed an increase of approximately 7 to 20 times in the BET surface areas. These values are close to those found when rice husks bio-char produced by liquefaction was studied (Leng et al., 2015). In this study, the authors performed the thermochemical liquefaction of the rice husks for 20 min in three different arrangements: with water, water and ethanol mixture, and ethanol, both under subcritical conditions (533-613 K). The best result found (21.7 m^2/g) was for thermochemical liquefaction using water and ethanol (5:5) mixture at 533 K. This result is close to found by this research, which also used 533 K (only water) and 15 min.

It is important to highlight the effect of R on the surface area when the same temperature is maintained, since with the ratio increase from 7.5 to 15 g water/g biomass, smaller values of BET surface area were obtained. When temperature is set at 493 K and 533 K, there was an increase in the reducing sugars obtained from the SWH in rice straw and husks under conditions in which the R was 7.5 g water/g biomass (Abaide et al., 2019a; Abaide et al., 2019c). These results are due to increased residence time (consequence of the reduction of the R) in the SWH assay. This behavior is because there is an increase in the depolymerization with low flow rates due to the longer residence time (Prado et al., 2016). Thus, there is an increase in the surface area of the particles.

Overall, there are no changes in the morphology (SEM images) of rice straw and rice husks when the solids hydrolyzed by subcritical water are evaluated at 453 K for both biomass (Supplementary information). However, for the conditions which the SWH temperatures were 493 and 533 K, a rupture in the cellular structure may be observed, which also justifies the increase in the BET surface area. Channels of different shapes, which were originated from disruption of hemicelluloses and cellulose fibers and high rough surface, may be attributed to the lignin that was exposed due SWH (Brienzo et al., 2017). These characteristics might provide adsorption sites for different adsorbates.

5.3.2 Adsorption capacity

The Figures 26 shows adsorption capacities for 2-nitrophenol removal in solutions with initial pH 4 and 7 for fresh RS, fresh RH, HRS, and HRH. The time was 24 h, and the initial concentration of 2-nitrophenol was set at 100 mg/L, the dosage of adsorbent was 0.5 g/L and the temperature was 298 K.

The higher adsorption capacities for almost all the samples evaluated were observed in solutions with an initial pH 7, with the exception of the sample HRH 533 K / R-15. The best adsorption capacities were reached for the samples HRS 453 K / R-7.5 and HRH 453 K / R-7.5, with values of 92.97 ± 1.31 and 91.23 ± 0.81 mg/g, respectively. These adsorption capacities are slightly higher than that one (78.05 mg/g) found in a work that used polyurethane crosslinked pine cone biomass to adsorb 2-nitrophenol (Kupeta et al., 2018). The authors modified the surface of pine cone biomass with polyurethane crooslinked in order to evaluate the adsorption capacity of 2-nitrophenol and obtained the best value of 78.05 mg/g (at equilibrium condition).

The effect of the initial pH of the aqueous solution in the adsorption process may be attributed to the dependency of phenol ionization at different pH values. At pH 4 (acid) we observed a strong H-bonding interaction between 2-nitrophenol and the surface charged with oxygen atoms of the sample (C–O stretches of the sugar units of cellulose).

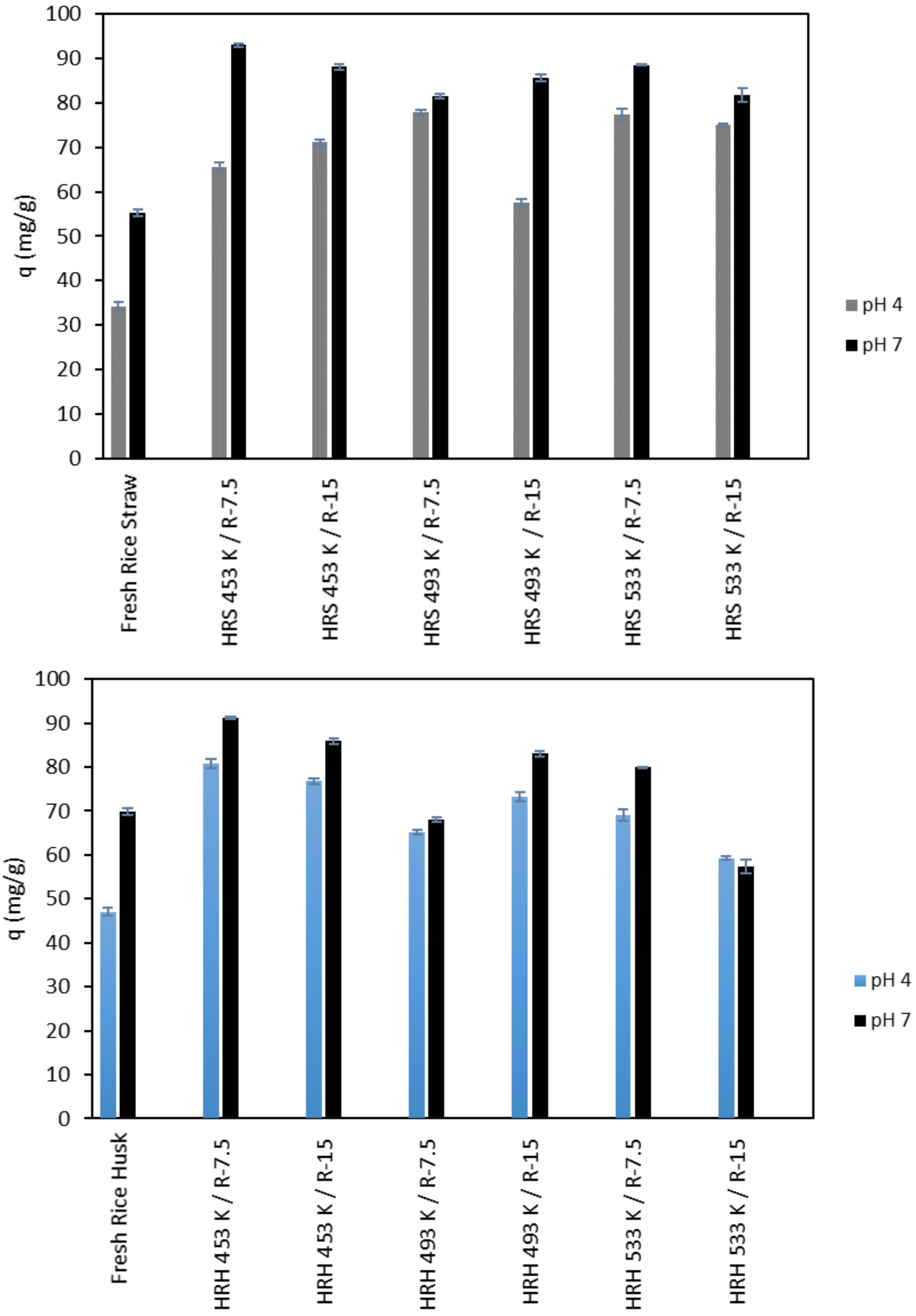

Figure 26- Adsorption capacity on 100 mg/L of 2-nitrophenol solution at pH 4 and 7 for (a) fresh HRS and RS 493 K / R-7.5 and (b) fresh RH and HRH 493 K / R-7 as adsorbents

At pH 7, phenolate anions are formed by the dissociation of 2-nitrophenol, reducing the amount of H atoms in the molecule. Thus there is a stronger interaction between the O atoms of 2-nitrophenol and the H atoms on the surface of the samples (C–OH and C–H stretches of the sugar units of cellulose) (Yaacoubi et al., 2015). The adsorption capacity values for HRS 493 K / R-7.5 and HRH 493 K / R-7.5, may shows a decrease (compared to HRS 453 K / R-7.5 and HRH 453 K / R-7.5). This may have occurred due to the small removal of cellulose that occurred at this temperature (493 K) with the consequent reduction of functional groups, which could interact with 2-nitrophenol

The high adsorption capacities found for SWH generated coproducts from the removal of 2-nitrophenol demonstrate the great importance of using this type of material from the bioethanol industry. This is because, the coproducts obtained in all SWH conditions presented potential as an adsorbent, aiming at the removal of 2-nitrophenol. It should be noted that fresh RS and fresh RH also had an acceptable adsorption capacity. This demonstrates the potential of these biomasses, since an integrated use of these can be achieved, obtaining sugars and still materials with capacity of adsorption. In order to study the adsorption kinetics and isothermal equilibrium models, the initial pH 7 was selected for study and two solid coproducts hydrolyzed by subcritical water were selected, one for rice straw and one for rice husks. The samples RS 493 K / R-7.5 and RH 493 K / R-7.5 were selected. The criterion for this selection was based on a possible application of these two biomass at large-scale industrial processes. Based on previous studies, SWH at 493 K and R of 7.5 g water/g biomass was the condition that most yielded fermentable sugars (Abaide et al., 2019a; Abaide et al., 2019c). Thus, because it is important to carry out an integrated assessment in an industrial scale process, the condition with the highest sugar yield would be the one that the industry would use in its production line, and the coproducts that would result from this line would be the potential adsorbent materials.

5.3.3 Adsorption kinetics of 2-nitrophenol

The kinetic curves for the adsorption of 2–nitrophenol were established with contact time from 0 to 24 h, with an adsorbent dosage of 0.5 g/L at 298 K, pH 7, and initial 2–nitrophenol concentrations of 25, 50, 75 and 100 mg/L. The results of the kinetic curves for 2–nitrophenol adsorption on fresh RS and HRS 493 K / R–7.5 are presented in Figure 27, while the results of the kinetic curves for 2–nitrophenol adsorption on fresh RH and HRH 493 K / R–7.5 are presented in Figure 28. The adsorption capacity curves presented in Figures 27 and 28 show a typical adsorption behavior, which the adsorption capacity of the 2–nitrophenol increases tending to q_e. A similar kinetic adsorption profile is observed for both co–products.

When the adsorption kinetics are compared at different temperatures in the same concentration, for fresh RS and HRS 493 K/ R-7.5, the adsorption process is faster for higher temperatures, finding equilibrium in approximately 20 h (except for the 298 K assay with HRS 493 K / R-7.5, with initial concentration of 100 mg/L) (Fig. 27a). For the tests performed at 308 and 318 K, the equilibrium is reached with smaller removals than those achieved at 298 K. This type of behavior was also verified in a study that used pretreated oat husks for adsorpting ciprofloxacin from water (Movasaghi et al., 2019). The kinetic data were obtained by Movasaghi et al. (2019) at 288, 299 and 318 K for an initial concentration solution of 60 mg/L at pH 7.

For fresh RH and HRH 493 K / R-7.5, the equilibrium occurs faster (10 h) for the assay at 318 K. The assays at 308 K reach the equilibrium close to 24 h, and for assay at 298 K the process did not have enough time to find the equilibrium (Fig. 28). The adsorption kinetic curves of 2-nitrophenol on fresh RS, fresh RH, HRS 493 K / R-7.5, and HRH 493 K / R-7.5 were fitted to the PFO model.

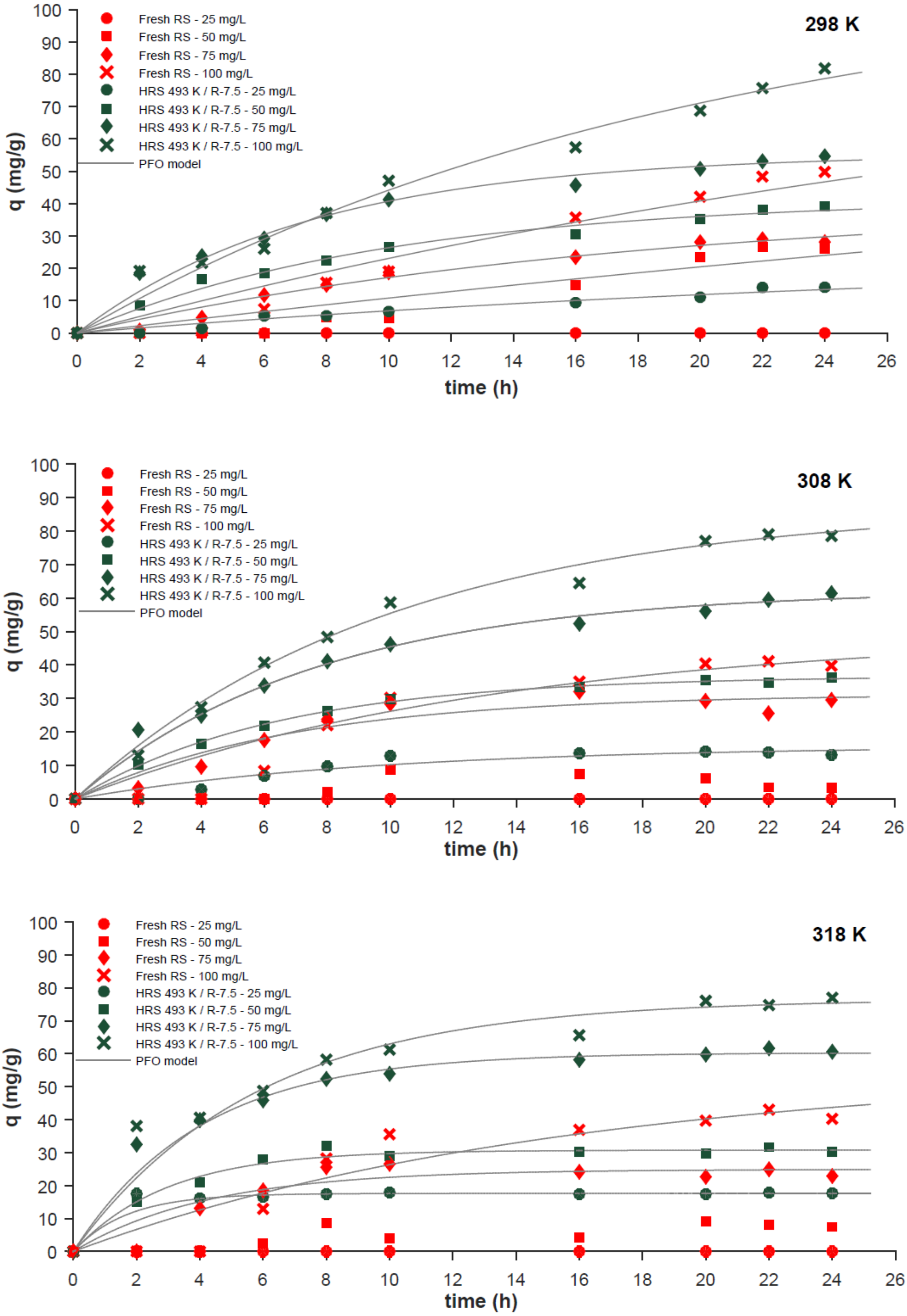

Figure 27 - Kinetic curves for 2-nitrophenol adsorption on fresh RS and HRS 493 K / R-7.5 at (a) 298 K, (b) 308 K and (c) 318 K (both at pH 7 and adsorbent dosage of 0.5 g/L)

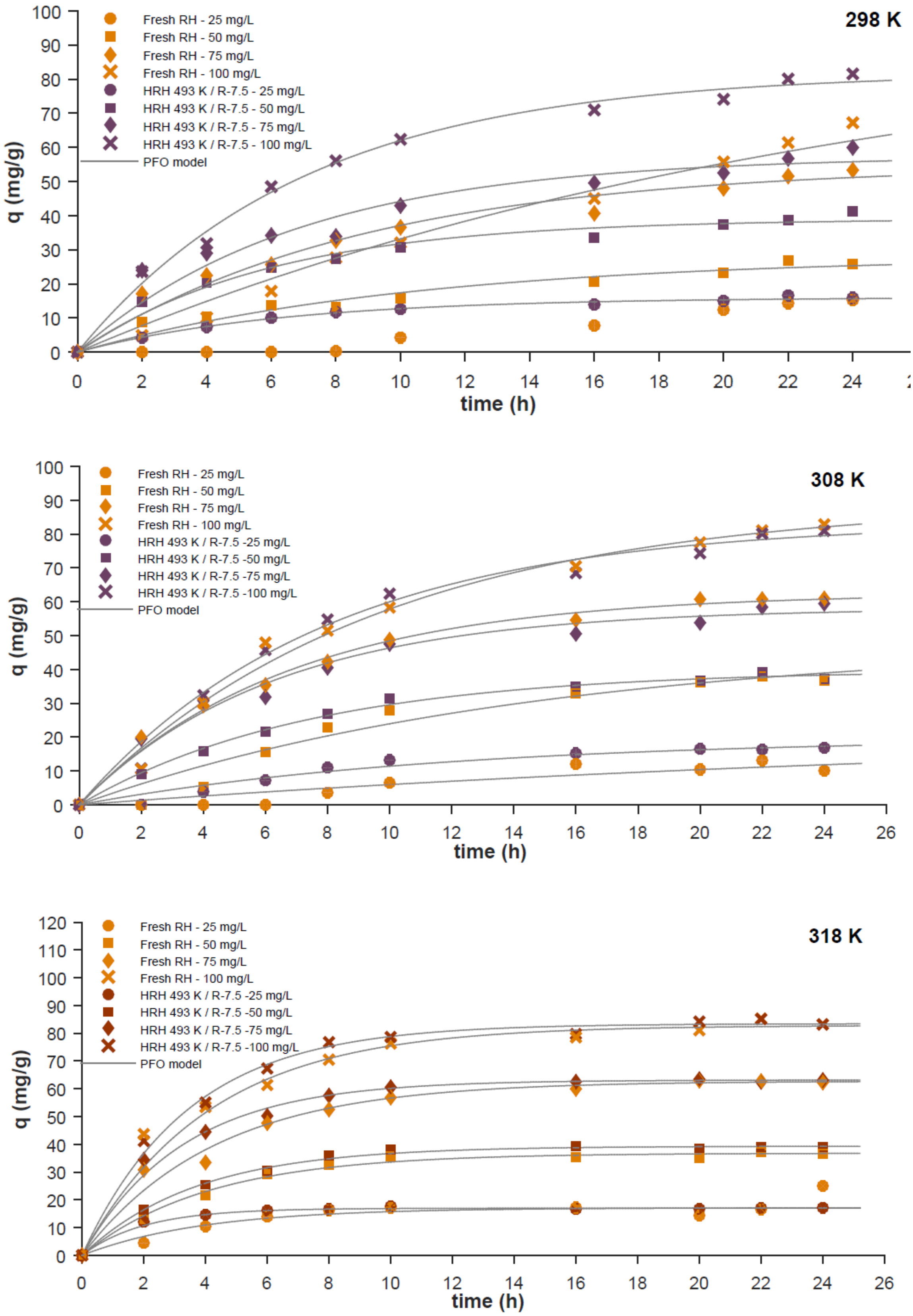

Figure 28 - Kinetic curves for 2-nitrophenol adsorption on fresh RH and HRH 493 K / R-7.5 at (a) 298 K, (b) 308 K and (c) 318 K (both at pH 7 and adsorbent dosage of 0.5 g/L)

Based on R^2 and RMSE presented in Tables 13 and 14, the adsorption kinetics of 2-nitrophenol on fresh RS, fresh RH, HRS 493 K / R-7.5, and HRH 493 K / R-7.5 were better illustrated by the PFO kinetic model. The pseudo-second-order rate constant decreased with increasing 2-nitrophenol concentration, suggesting that the adsorption rate depends on the available biomass adsorption sites (Njoku et al., 2015). Therefore, at low concentration, the equilibrium is reached faster than at higher concentration.

5.3.4 Isotherms and thermodynamic parameters

The adsorption equilibrium isotherms were obtained at three different temperatures (298, 308 and 318 K) and were determined based on adsorption kinetic studies. The isotherms were performed at pH 7, with adsorbent dosage of 0.5 g/L and an initial 2-nitrophenol concentration of 25, 50, 75 and 100 mg/L. The Freundlich was the best isotherm equilibrium model and the quality of fit was identified by the R^2 value and by nonlinear error functions RMSE (Table 15). The Freundlich model was fitted for all samples at 298, 308 and 318 K (Fig. 29). From Table 15, it is possible to observe that the R^2 and *RMSE* values for Henry are, respectively, slightly lower (R^2) and larger (*RMSE*) than those obtained by Freundich.

Fresh RS, fresh RH, HRS 493 K / R-7.5, and HRH 493 K / R-7.5 followed the Freundlich isotherm model, which involved multilayer adsorption. The stronger binding sites on the surface are occupied first and the binding strength decreased with the increasing degree of site occupancy, which reduced the adsorption during the time (Freundlich, 1906).

From thermodynamic viewpoint, 2-nitrophenol on fresh RS, HRS 493 K / R-7.5, fresh RH, and HRH 493 K / R-7.5 were evaluated according to the values of ΔG^0, ΔH^0 and ΔS^0 (Table 16). For both adsorbents, a spontaneous and favorable adsorption process was confirmed by the negative ΔG^0 values (Sarin et al., 2006).

Table 13 - Kinetic parameters for the 2-nitrophenol adsorption on fresh RS and HRS 493 K / R-7.5

Assay at 298 K	**C_0* (mg/L)**							
	Fresh RS				HRS 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	**	100	40.60	100	25	41.61	55.44	113.1
k_1 (1/h) $\times 10^{-3}$	**	11.44	56.90	26.2	32.15	100.6	132.8	55.57
R^2	**	0.84	0.97	0.93	0.95	0.98	0.99	0.98
RMSE	**	4.62	1.99	5.44	1.32	1.70	2.08	4.07
PSO model								
q_2 (mg/g)	**	28.62	31.85	45.56	24.74	50	63.4	98.10
k_2 (g.mg/h) $.10^{-3}$	**	2.40	4.50	1.50	1.80	2.20	2.70	0.98
R^2	**	0.59	0.83	0.94	0.90	0.98	0.98	0.92
RMSE	**	7.39	4.58	2.66	1.66	1.73	2.39	7.70
Assay at 308 K	**C_0* (mg/L)**							
	Fresh RS				HRS 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	**	**	31.26	50.0	15.79	36.75	62.51	87.79
k_1 (1/h) $\times 10^{-3}$	**	**	144.9	74.1	103.8	155.7	129.8	99.86
R^2	**	**	0.91	0.90	0.87	0.99	0.99	0.99
RMSE	**	**	3.73	5.61	2.20	0.61	1.94	2.79
PSO model								
q_2 (mg/g)	**	**	41.59	60.0	18.0	40.06	79.64	105.0
k_2 (g.mg/h) $\times 10^{-3}$	**	**	2.90	1.20	7.30	5.80	1.62	1.00
R^2	**	**	0.88	0.83	0.84	0.96	0.99	0.97
RMSE	**	**	4.22	7.27	2.33	2.24	2.00	4.22
Assay at 318 K	**C_0* (mg/L)**							
	Fresh RS				HRS 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	**	**	24.9	55.72	17.61	30.74	60.30	76.55
k_1 (1/h) $\times 10^{-3}$	**	**	233.2	63.90	595.8	337.3	249.6	172.8
R^2	**	**	0.87	0.86	0.99	0.98	0.99	0.98
RMSE	**	**	3.81	7.14	0.41	1.44	1.91	3.80
PSO model								
q_2 (mg/g)	**	**	29.42	91.16	18.11	34.52	67.41	93.44
k_2 (g.mg/h) $\times 10^{-3}$	**	**	9.22	0.4	119.5	13.7	5.9	2.0
R^2	**	**	0.82	0.85	0.99	0.95	0.99	0.98
RMSE	**	**	4.49	7.50	0.41	2.28	1.40	2.78

* Initial 2-nitrophenol concentration; ** The model does not fit the data

Table 14 - Kinetic parameters for the 2-nitrophenol adsorption on fresh RH and HRH 493 K / R-7.5

Assay at 298 K	**C_0* (mg/L)**							
	Fresh RH				HRH 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	**	28.08	54.79	100	16.35	39.03	57.50	81.93
k_1 (1/h) $\times 10^{-3}$	**	96.6	113.2	40.3	147.5	168.1	146.2	141.4
R^2	**	0.94	0.96	0.98	0.98	0.96	0.94	0.99
RMSE	**	2.21	3.35	3.36	0.81	2.34	4.83	2.83
PSO model								
q_2 (mg/g)	**	37.92	71.52	82.64	20.83	47.93	72.1	103.6
k_2 (g.mg/h) $\times 10^{-}$	**	2.20	1.40	1.00	6.94	3.76	2.09	1.40
R^2	**	0.94	0.97	0.87	0.98	0.98	0.96	0.99
RMSE	**	2.03	2.71	8.68	0.80	1.52	3.72	2.08
Assay at 308 K	**C_0* (mg/L)**							
	Fresh RH				HRH 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	23	48.28	62.52	89.48	19.87	39.86	58.13	83.54
k_1 (1/h) $\times 10^{-3}$	30.1	68.5	149.91	104.0	8.54	135.6	159.6	126.6
R^2	0.92	0.94	0.99	0.99	0.95	0.99	0.97	0.99
RMSE	2.32	3.81	1.92	2.07	1.67	1.14	3.14	3.49
PSO model								
q_2 (mg/g)	28.39	77.05	78.98	121.7	29.84	52.59	72.46	111.4
k_2 (g.mg/h) $\times 10^{-}$	1.00	0.56	1.88	0.73	2.0	2.2	2.2	0.98
R^2	0.78	0.93	0.99	0.99	0.93	0.98	0.98	0.98
RMSE	7.57	3.98	1.46	2.25	1.86	1.53	2.49	3.72
Assay at 318 K	**C_0* (mg/L)**							
	Fresh RH				HRH 493 K / R-7.5			
PFO model	25	50	75	100	25	50	75	100
q_1(mg/g)	17.09	36.8	62.74	82.82	16.96	39.32	63.16	83.45
k_1 (1/h) $\times 10^{-3}$	253.0	244.7	233.1	242.5	498.7	270.0	305.1	289.7
R^2	0.90	0.99	0.99	0.99	0.99	0.99	0.99	0.99
RMSE	2.27	1.34	1.81	2.88	0.34	0.96	1.17	2.48
PSO model								
q_2 (mg/g)	22.49	43.17	70.07	92.81	17.94	45.25	69.95	94.58
k_2 (g.mg/h) $\times 10^{-}$	10.5	6.76	5.46	4.11	63.6	7.63	6.82	4.22
R^2	0.83	0.97	0.99	0.99	0.99	0.98	0.99	0.99
RMSE	3.07	2.34	1.69	2.55	0.57	2.05	11.71	2.72

* Initial 2-nitrophenol concentration; ** The model does not fit the data

Table 15 - Equilibrium parameters for the 2-nitrophenol adsorption on fresh RS, fresh RH, HRS 493 K / R-7.5, and RRH 493 K / R-7.5

	Fresh RS			HRS 493 K / R-7.5		
Temperature (K)	298	398	318	298	308	318
Freundlich						
k_F (mg/g)(mg/L)$^{-1/n_F}$ $\times 10^{-3}$	56.3	0.7	1.1	343.2	379.3	379.7
$1/n_F$	1.47	2.37	2.27	1.19	1.16	1.15
R^2	0.91	0.89	0.99	0.99	0.99	0.98
RMSE	7.27	7.38	1.71	3.11	3.23	4.50
Henry						
k_H (g.L)-^{1}	0.45	0.33	0.32	0.77	0.78	0.77
R^2	0.87	0.68	0.80	0.98	0.98	0.98
RMSE	7.53	10.90	7.72	4.09	4.03	3.52
	Fresh RH			HRH 493 K / R-7.5		
Temperature (K)	298	398	318	298	308	318
Freundlich						
k_F (mg/g)(mg/L)$^{-1/n_F}$ $\times 10^{-3}$	312.2	242.3	577.8	569.7	465.3	466.4
$1/n_F$	1.17	1.27	1.08	1.09	1.12	1.12
R^2	0.98	0.99	0.99	0.99	0.99	0.99
RMSE	4.25	3.55	2.44	2.18	0.47	0.47
Henry (g.L)-^{1}						
k_H (L/mg) $\times 10^{-5}$	0.67	0.80	0.83	0.81	0.79	0.81
R^2	0.97	0.97	0.99	0.99	0.99	0.99
RMSE	3.68	5.53	1.02	1.28	2.17	2.47

The adsorption was favored at 318 K because more negative ΔG^0 values were found at this temperature for all adsorbents. This result was also obtained in another study that applied hydrochars from bamboo sawdust for removal of 2-naphthol and Congo red (Li et al., 2018). The authors evaluated the adsorption capacity of bamboo sawdust samples prepared by acid assisted hydrothermal carbonization. The adsorption tests occurred at temperatures of 298, 308 and 318 K and the results showed that the process spontaneity also increased with increasing the temperature.

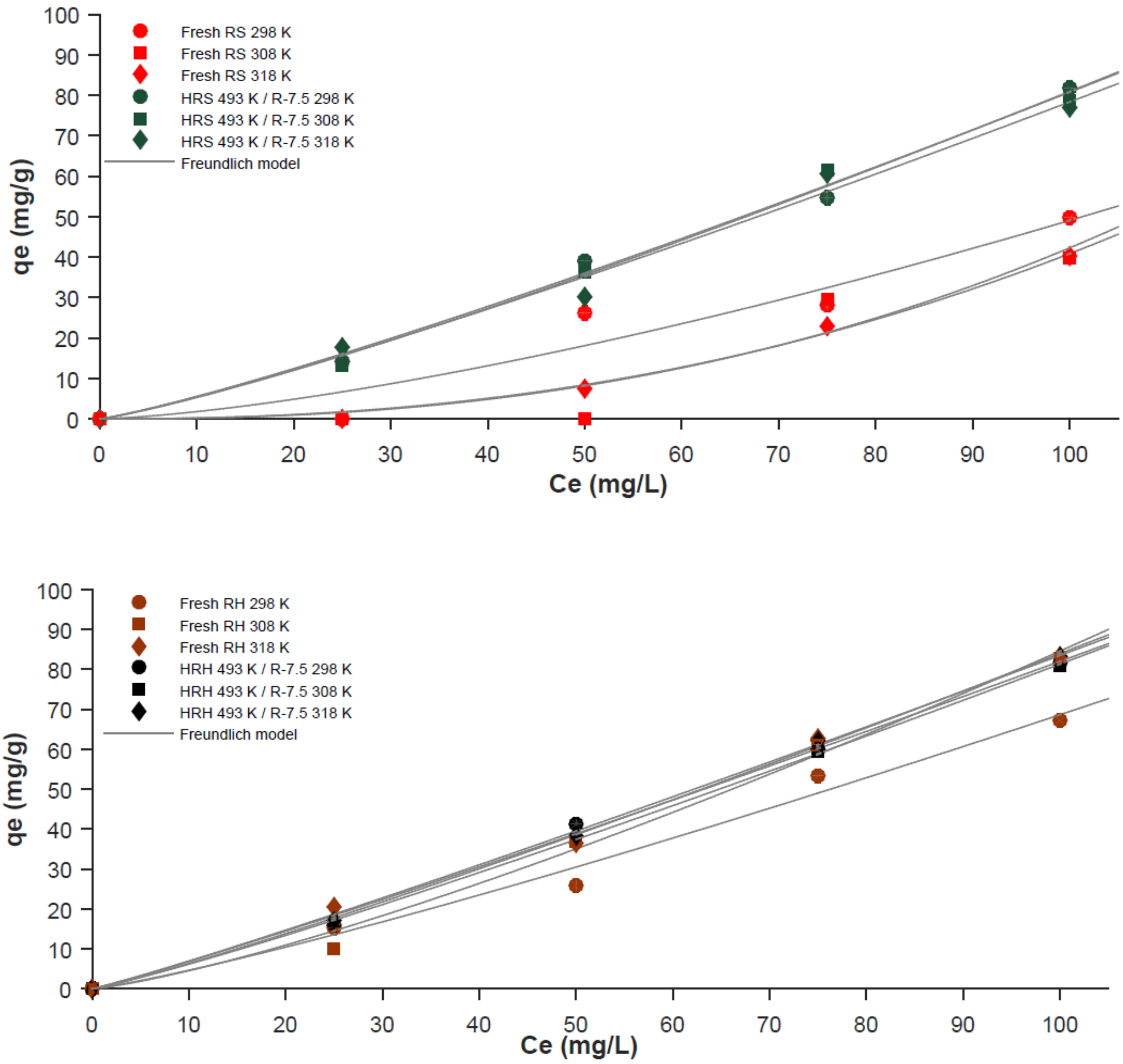

Figure 29 - Adsorption isotherms at 298, 308 and 318 K of 2-nitrophenol on (a) fresh RS and HRS 493 K / R-7.5 and (b) fresh RH and HRH 493 K / R-7.5

Comparing ΔH^0 with ΔS^0 for fresh RH, HRS 493 K / R-7.5, and HRH 493 K / R-7.5, ΔS^0 contributed much more than ΔH^0 to attain negative ΔG^0 values. Therefore, the positive ΔS^0 values indicated that some rearrangements occurred on the solid–liquid interface during the adsorption process (Chen et al., 2017a). The negative ΔH^0 value indicates that the adsorption was exothermic in nature. The adsorbent HRS 493 K / R-7.5 was an exception, with a higher contribution to enthalpy, being an endothermic process (positive ΔH^0).

Table 16 - Thermodynamic parameters for the 2-nitrophenol adsorption on fresh RS, fresh RH, HRS 493 K / R-7.5, and RRH 493 K / R-7.5

Adsorbent	T(K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol.K)
Fresh RS	298	- 0.02	-15.07	0.05
	308	- 1.06		
	318	- 1.40		
HRS 493 K / R-7.5	298	- 3.07	0.03	- 11.67
	308	- 3.33		
	318	- 3.18		
Fresh RH	298	- 1.77	-0.12	34.40
	308	- 4.03		
	318	- 4.22		
HRH 493 K / R-7.5	298	- 3.67	-0.03	4.67
	308	- 3.70		
	318	- 4.22		

ΔG^0: Gibbs free energy change; ΔH^0: enthalpy change; ΔS^0: entropy change.

5.4 CONCLUSION

Rice straw and rice husks were hydrolyzed by subcritical water at different conditions and were characterized and evaluated for 2–nitrophenol adsorption. High adsorption capacity (92.97 ± 1.31 mg/g) was obtained for rice straw hydrolyzed by subcritical water at 493 K for pH 7 and 2–nitrophenol initial concentration of 100 mg/L. PFO and Freundlich were the best fit for kinetic and isotherms models, respectively. Overall, the entropy effect was higher than enthalpy, and the adsorption process was spontaneous. This study confirmed that solid co–products from a lignocellulosic bioethanol facility are not waste but valuable resources for other applications.

Appendix A. Supplementary data

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

Conflict of interest

The authors inform that there are no conflicts of interest.

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REFERENCES

Abaide, E.R., Mortari, S.R., Ugalde, G., Valério, A., Amorim, S.M., Luccio, M.D., Moreira, R.F.P.M., Kuhn, R.C., Priamo, W.L., Três, M.V., Zabot, G.L., Mazutti, M.A. 2019a. Subcritical water hydrolysis of rice straw in a semi-continuous mode. *J. Clean. Prod*, **209**(1), 386-397.

Abaide, E.R., Três, M.V., Zabot, G.L., M, A.M. 2019b. Reasons for processing of rice coproducts: Reality and expectations. *Biomass Bioenergy*, **120**, 240-256.

Abaide, E.R., Ugalde, G., Luccio, M.D., Moreira, R.F.P.M., Tres, M.V., Zabot, G.L., Mazutti, M.A. 2019c. Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode. *Bioresour. Technol*, **272**, 510-520.

Alam, M.K., Rahaman, M.M., Abbas, M., Torati, S.R., Asiri, A.M., Kim, D., Kim, C. 2017. Ultra-sensitive 2-nitrophenol detection based on reduced graphene oxide/ZnO nanocomposites. *J. Electroanal. Chem.*, **788**, 1.

Allen, S.G., Kam, L.C., Zemann, A.J., Antal, M.J. 1996. Fractionation of sugar cane with hot, compressed liquid wate. *Ind. Eng. Chem. Researc*, **35**, 2709-2715.

Amiri, H., Karimi, K. 2018. Pretreatment and Hydrolysis of Lignocellulosic Wastes for Butanol Production: Challenges and Perspectives. *Bioresour. Technol*, **270**, 702-721.

AOAC. 1997. *Association of official analytical chemists – AOAC. 16th ed*. Of.Analys, Washington, USA.

Bijay-Singh, Shan, Y.H., Beebout, S.E.J., Yadvinder-Singh, Buresh, R.J. 2013. *Crop Residue Management for Lowland Rice-Based Cropping Systems in Asia*.

Brienzo, M., Fikizolo, S., Benjamin, Y., Tyhoda, L., Gorgens, J. 2017. Influence of pretreatment severity on structural changes, lignin content and enzymatic hydrolysis of sugarcane bagasse samples. *Renew. Energ*, **104**, 271-280.

Cantero, D.A., Bermejo, M.D., Cocero, M.J. 2015. Reaction engineering for process intesification of supercritical waterbiomass refining. *J. Supercrit. Fluids*, **96**, 21-35.

Cao, L., Yu, I.K.M., Cho, D., Wang, D., Tsang, D.C.W., Zhang, S., Ding, S., Wang, L., Ok, Y.S. 2019. Microwave-assisted low-temperature hydrothermal treatment of redseaweed (Gracilaria lemaneiformis) for production of levulinic acid and algaehydrochar. *Bioresour. Technol*, **273**, 251-258.

Chen, J., Sun, X., Lin, L., Dong, X., He, Y. 2017a. Adsorption removal of o-nitrophenol and p-nitrophenol from wastewater by metal–organic framework Cr-BDC. *Chinese J. Chem. Eng.*, **25**(25), 775-781.

Chen, X., Lin, Q., He, R., Zhao, X., Li, G. 2017b. Hydrochar production from watermelon peel by hydrothermalcarbonization. *Bioresour. Technol*, **241**, 236-243.

Cocero, M.J., Cabeza, A., Abad, N., Adamovic, T., Vaquerizo, L., Martínez, C.M., Pazo-Cepeda, M.V. 2018. Understanding biomass fractionation in subcritical & supercritical water. *J. Supercrit. Fluids*, **133**, 550-565.

FAO. 2016. Rice market monitor. *Food and Agriculture Organization of the United Nations*, **19**(2), 1-35.

Fleig, O.P., Lopes, E.S., Rivera, E.C., Filho, R.M., Tovar, L.P. 2018. Concept of rice husk biorefining for levulinic acid production integrating three steps: Multi-response optimization, new perceptions and limitations. *Process. Biochem*, **65**, 146-156.

Foo, K.Y., Hameed, B.H. 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.*, **156**, 2-10.

Franco, D.S.P., Tanabe, E.H., Bertuol, D.A., Reis, G., Dotto, G.L. 2016. Alternative Treatments to Improve the potential of Rice Husk as Adsorbent for methylene Blue. *Water Sci. Tech*, **75**(2), 296-305.

Freundlich, H. 1906. Over the adsorption in solution *Z. Phys. Chem. J. Phys. Chem.*, **57**, 358–471.

Fröhlich, A.C., Reis, G.S., Pavan, F.A., Lima, E.C., Foletto, E.L., Dotto, G.L. 2018. Improvement of activated carbon characteristics by sonication and its application for pharmaceutical contaminant adsorption. *Environ. Sci. Pollut. Researc*, **25**, 24713-24725.

He, Y., Pang, Y., Li, X., Liu, Y., Li, R., Zheng, M. 2009. Investigation on the Changes of Main Compositions and Extractives of Rice Straw Pretreated with Sodium Hydroxide for Biogas Production. *Energ. Fuels*, **23**(4), 2220-2224.

Ho, Y.S., Mackay, G. 1998. Kinetic models for the sorption of dye from aqueous solution by wood. *Process Safety Environ. Protect*, **76**, 183–191.

Huong, P., Lee, B., Kim, J., Lee, C. 2016. Nitrophenols removal from aqueous medium using Fe-nano mesoporous zeolite. *Mat. Design*, **101**, 210-217.

Kambo, H.S., Dutta, A. 2015. A comparative review of biochar and hydrochar in terms of production physico-chemical properties and application. *Renew. Sustain. Energy Rev.*, **45**, 359-378.

Kim, I., Rehman, M.S.U., Han, J. 2014. Fermentable sugar recovery and adsorption potential of enzymatically hydrolyzed rice straw. *J. Clean. Prod*, **66**, 555-561.

Kristanti, R.A., Kanbe, M., Toyama, T., Tanaka, Y., Tang, Y., Wu, X., Mori, K. 2012. Accelerated biodegradation of nitrophenols in the rhizosphere of Spirodela polyrrhiza. *J. Environ. Sci.*, **24**(5), 800-807.

Kupeta, A.J.K., Naidoo, E.B., Ofomaja, A.E. 2018. Kinetics and equilibrium study of 2-nitrophenol adsorption onto polyurethane cross-linked pine cone biomass. *J.Clean.Prod*, **179**(1), 191-209.

Lagergren, S. 1898. *About the theory of so–called adsorption of soluble substances*.

Leng, L., Yuan, X., Zeng, G., Shao, J., Chen, X., Wu, Z., Wang, H., Peng, X. 2015. Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. *Fuel*, **155**, 77-85.

Li, F., Liu, L., An, Y., He, W., Themelis, N.J. 2016. Hydrothermal liquefaction of three kinds of starches into reducing sugars. *J. Clean. Prod*, **112**, 1049-1054.

Li, Y., Meas, A., Shan, S., Yang, R., Gai, X., Wang, H., Tsend, N. 2018. Hydrochars from bamboo sawdust through acid assisted and two-stage hydrothermal carbonization for removal of thow organics from aqueous solution. *Bioresour. Technol*, **261**, 257-264.

Li, Y., Tsend, N., Li, T., Liu, H., Yang, R., Gai, X., Wang, H., Shan, S. 2019. Microwave assisted hydrothermal preparation of rice straw hydrochars for adsorption of organics and heavy metals. *Bioresour. Technol*, **273**, 136-143.

Lima, E.C., Hosseini-Bandegharaei, A., Moreno-Piraján, J.C., Anastopoulos, I. 2019. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption. *J. Molec. Liq.*, **273**, 425-434.

Lin, R., Cheng, J., Ding, L., Song, W., Qi, F., Zhou, J., Cen, K. 2015. Subcritical water hydrolysis of rice straw for reducing sugar production with focus on degradation by-products and kinetic analysis. *Bioresour.Technol*, **186**, 8-14.

Liu, C., Yong, D., Yu, D., Dong, S. 2011. Cell-Based biosensor for measurement of phenol and nitrophenol toxicity. *Talanta*, **84**, 766-770.

Luo, Y., Guo, W., Ngo, H.H., Nghiem, L.D., Hai, F.I., Zhang, J., Liang, S., Wang, X.C. 2014. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Sci. Total Environ.* , **473**, 619-641.

Martín, J.R., Bernal, C.M., Cobas, Y.P., Sosa, F.M.R., García, B.D. 2017. Additives enhancing enzymatic hydrolysis of lignocellulosic biomass. *Bioresour.Technol*, **244**, 48-56.

Möller, M., Harnisch, F., Schröder, U. 2013. Hydrothermal liquefaction of cellulose in subcritical water—the role of crystallinity on the cellulose reactivity. *Res. Adv.*, **27**(3), 11035-11044.

Movasaghi, Z., Yan, B., Niu, C. 2019. Adsorption of ciprofloxacin from water by pretreated oat hulls: Equilibrium, kinetic, and thermodynamic studies. *Ind. Crop. Prod*, **127**, 237-250.

Nguyen, T.A.H., Ngo, H.H., Guo, W.S., Zhang, J., Liang, S., Yue, Q.Y., Li, Q., Nguyen, T.V. 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresour. Technol*, **148**, 574-585.

Njoku, V.O., Islam, M.A., Asif, M., Hameed, B.H. 2015. Adsorption of 2,4-dichlorophenoxyacetic acid by mesoporous activated carbon prepared from H_3PO_4-activated langsat empty fruit bunch. *J. Environ. Manag.*, **154**, 138-144.

Prado, J.M., Lachos-Perez, D., Foster-Carneiro, T., Rostagno, M.A. 2016. Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugar: A review. *Food. Bioprod. Process*, **98**, 95-123.

Rehman, M.S.U., Kim, I., Han, J.I. 2012. Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass. *Carbohyd. Polym*, **90**, 1314-1322.

Reza, M.T., Andert, J., Wirth, B., Busch, D., Pielert, J., Lynam, J.G., Mumme, J. 2014. Hydrothermal Carbonization of Biomass for Energy and Crop Production. *Appl. Bioenergy*, **1**, 11-29.

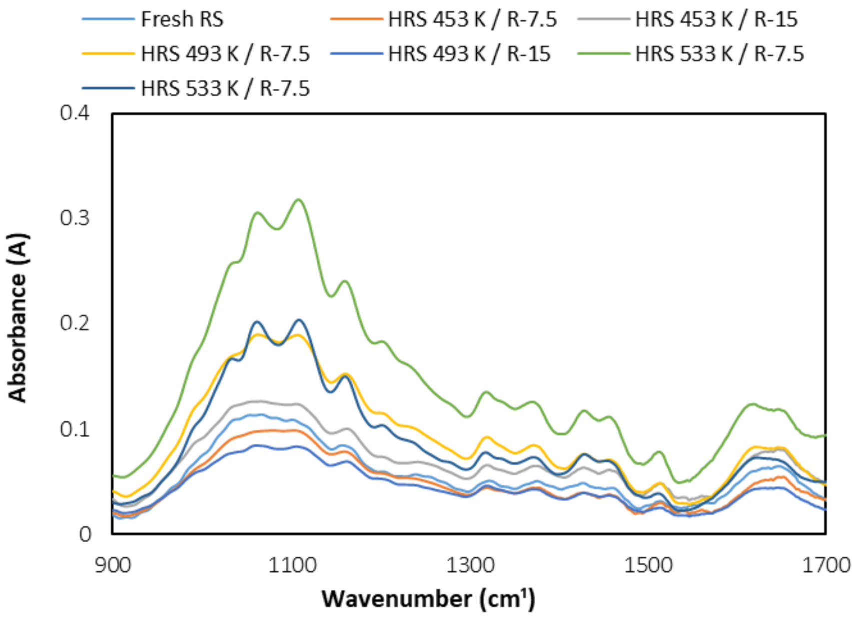
Rodrigues, C.S.D., Borges, R.A.C., Lima, V.N., Madeira, L.M. 2018. p-Nitrophenol degradation by Fenton's oxidation in a bubble column reactor. *J. Environ. Manag.*, **206**, 774-785.

Sarin, V., Singh, T.S., Pant, K.K. 2006. Thermodynamic and breakthrough collumn studies for the selective soorption of chromium from industrial effluent on activated eucalyptus bark. *Bioresour. Technol*, **97**, 1986-1993.

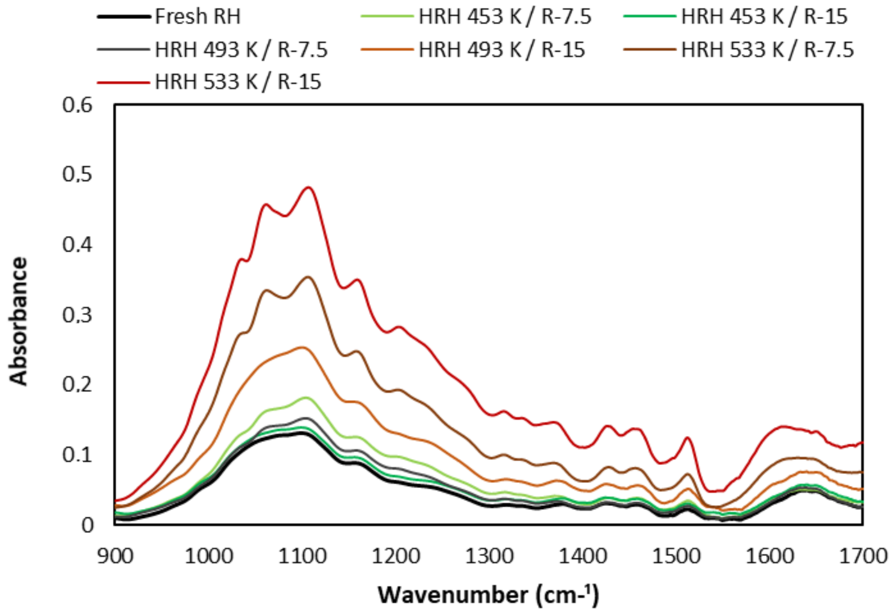
Xu, F., Yu, J., Tesso, T., Dowell, F., Wang, D. 2013. Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: a mini-review. *Appl. Energy*, **104**, 801-809.

Yaacoubi, H., Songlin, Z., Mouflih, M., Gourai, M., Sebti, S. 2015. Adsorption isotherm, kinetic and mechanism studies of 2-nitrophenol on sedimentary phosphate. *Mediterran J. Chem.*, **4**(4), 289-296.

Zhang, H., Fan, M., Zhang, A., Xie, J. 2018. Enhancing enzymatic hydrolysis of sugarcane bagasse by ferric chloride catalyzed organosolv pretreatment and Tween 80. *Bioresour. Technol*, **258**, 295-301.



(a)



(b)

Figure S.3 - FT-IR spectroscopy analysis (a) of fresh RS and subcritical HRS and (b) Fresh RH and HRS at different experimental conditions

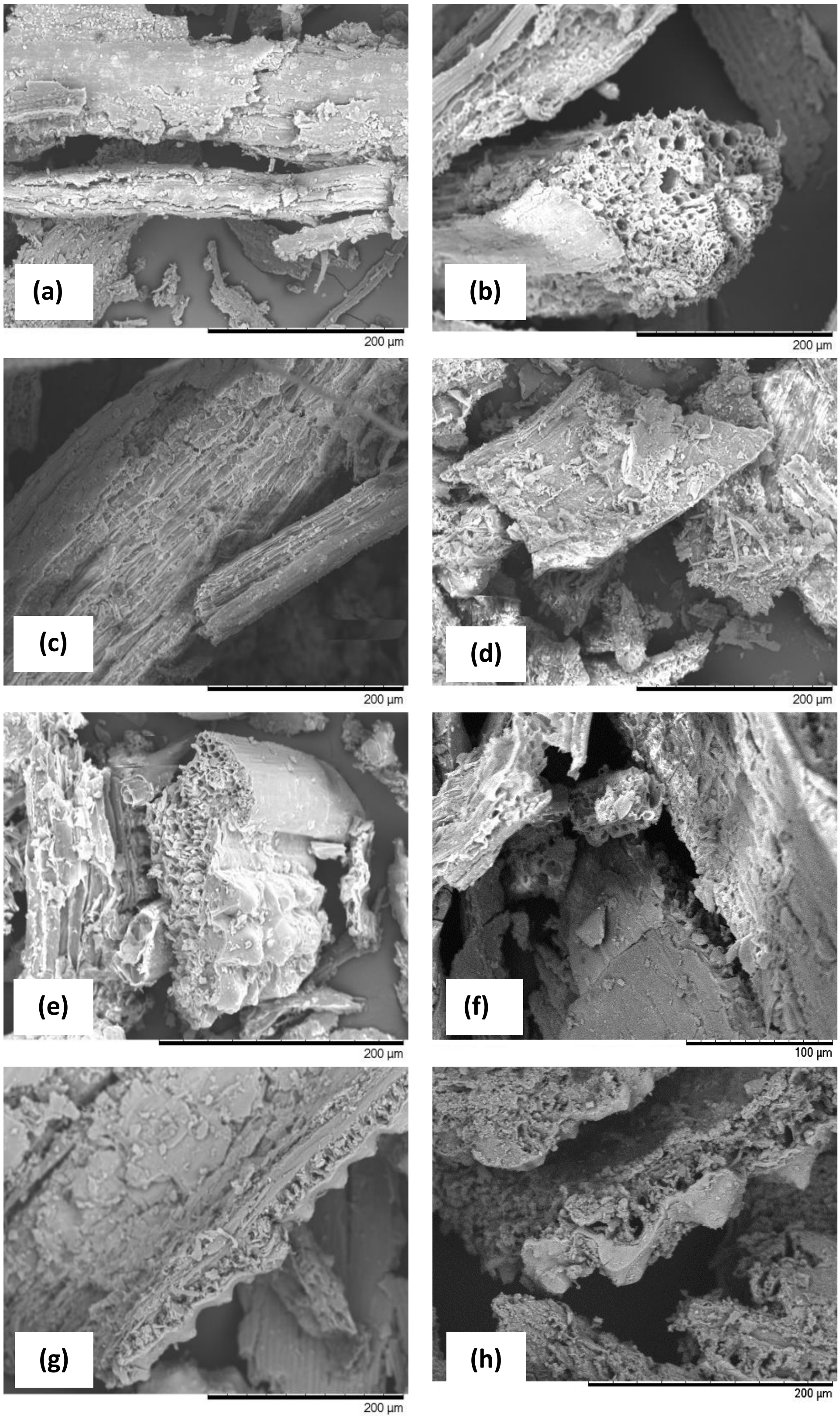


Figure S.4 - SEM micrographs (magnification: 500×). Surface of fresh rice straw (a) and solid remaining after SWH process at HRS 453 K (b), HRS 493 K (c) and HRS 533 K (d). Surface of fresh rice husks (e) and solid remaining after SWH process at HRH 453 K (f), HRH 493 K (g) and HRH 533 K (h)

- CAPÍTULO 6 -

DISCUSSÃO, CONCLUSÃO GERAL E SUGESTÕES PARA TRABALHOS FUTUROS

6.1 DISCUSSÃO

O presente trabalho envolveu a produção de quatro artigos que tiveram como enfoque o aproveitamento integrado da palha e das cascas de arroz, por meio da hidrólise com água subcrítica. Os principais produtos obtidos foram soluções contendo açúcares redutores, bioprodutos e coprodutos sólidos que têm potencial uso como adsorvente.

O primeiro artigo expõe uma revisão detalhada da literatura, explicitando as possíveis razões para se reaproveitar os coprodutos da indústria do arroz. No artigo "*review*" foram abordados os três coprodutos: a palha, a casca e o farelo de arroz. O farelo de arroz também foi destacado uma vez que ele também é um coproduto da indústria do arroz, sendo que para uma avaliação completa seria inapropriado não abordar possíveis processos que reaproveitem essa biomassa. A primeira abordagem da revisão foi acerca das principais características e propriedades da palha, casca e farelo de arroz. Com essa avaliação foi possível entender como é a composição das três biomassas e, assim, buscar tecnologias adequadas que pudessem realizar o adequado processamento, visando aumentar o valor agregado das mesmas.

Na sequência da revisão foram apontados estudos e aplicações atuais (globalmente) relacionados ao reaproveitamento dos coprodutos do arroz. As principais áreas destacadas foram a da construção civil, energia, alimentação animal e fertilizantes, adsorção e produção de óleo, extrativos e biodiesel. Os principais produtos e intermediários que podem ser obtidos de matrizes lignocelulósicas (coprodutos do arroz) foram apresentados juntamente com as tecnologias de seu processamento. Nesta abordagem, foram apresentadas as rotas tecnológicas de hidrólise que visam à obtenção de açúcares fermentescíveis e bioprodutos, sendo que dentre elas pode se destacar a hidrólise com água subcrítica. A grande importância desta revisão bibliográfica, que foi apresentada na forma de um "*review*", pode ser notada quando se analisam as tendências futuras de pesquisa envolvendo os coprodutos do arroz e as tecnologias utilizadas para seu processamento. Pela revisão, foi possível seguir uma direção no processamento dos coprodutos do arroz, focando a pesquisa no processamento da palha e das cascas de arroz com água subcrítica.

Os dois artigos da sequência avaliaram a hidrólise subcrítica da palha de arroz e das cascas de arroz, ambos em modo de operação semi-contínuo. É interessante observar que, para ambas as biomassas, a melhor condição de hidrólise subcrítica quando se avalia o rendimento em açúcares redutores (Y_{RS}) foi a que utilizou temperatura de 220°C e razão líquido / sólido de 7,5 g água/g biomassa. O Y_{RS} para a palha de arroz foi de 33,4 ± 4,3 g/100 g palha seca e para as cascas de arroz foi de 18,0 ± 2,9 g/100 g casca seca. Essa diferença no rendimento em açúcares redutores pode estar relacionada com a composição das duas biomassas. Como a palha de arroz tem maior teor de hemiceluloses (24,6%) do que as cascas de arroz (18,5%), a palha acaba tendo maior quantidade de açúcares hidrolisados provenientes dessa estrutura. A literatura aponta que na condição de 220°C, há maior dissociação das hemiceluloses, sendo que para a celulose ser hidrolisada a temperatura tem que ser superior à 250°C.

Entretanto, quando se compara o efeito da hidrólise subcrítica na eficiência de conversão (E) da celulose e hemiceluloses na mesma condição (220°C / R-7,5) para ambas biomassas, pode se notar que o valor de E foi maior para a palha de arroz (72,1 ± 4,6 g/100 g de carboidratos) do que para as cascas de arroz (39,5 ± 1,7 g açúcares/100 g carboidratos). Como as cascas de arroz têm maior teor de cinzas (16,6 ± 0,7%,) e de lignina (28%) do que a palha de arroz (teor de cinzas de 12,2 ± 0,6 % e teor de lignina de 9,4 %), a matriz recalcitrante da casca de arroz pode ter dificultado o acesso às hemiceluloses e celulose, o que provocou o menor valor de E para a mesma.

As eficiências de conversão da celulose em glicose tanto na palha (6,8 g/100g de celulose) quanto nas cascas de arroz (22,5 g/100 g de celulose) tiveram os maiores valores na condição 220°C / R-15. Com relação a eficiência de conversão das hemiceluloses em xilose para a palha de arroz, observou-se que a mesma condição de hidrólise (220°C / R-15) foi a que obteve maior eficiência (31,7 g/100 g de hemiceluloses). Já para os ensaios de hidrólise subcrítica das cascas de arroz, a maior conversão de hemiceluloses em xilose (71,5 g/100 g de hemiceluloses) foi obtida na condição 220°C / R-7,5. A eficiência de conversão das estruturas da celulose e hemiceluloses em função de cada tipo de monômero de açúcar pode indicar uma direção a ser seguida quando se visa obter um caldo hidrolisado para posterior fermentação. A seleção do microorganismo a ser utilizado no processo de fermentação depende do perfil e do teor de açúcares fermentescíveis obtido da etapa de hidrólise. Os valores observados para conversão de hemiceluloses e celulose em xilose e glicose, respectivamente, também demonstraram que as estruturas das hemiceluloses foram as mais dissociadas no processo de hidrólise com água subcrítica.

Por meio da caracterização termogravimétrica das amostras, realizando a derivada da curva da análise termogravimétrica (TGA) para ambas as biomassas, foi possível notar que ocorreu um comportamento diferente quando se avalia a dissociação da celulose e das hemiceluloses. Na hidrólise subcrítica a 260°C, a palha de arroz teve o teor de hemiceluloses reduzido de 24,4% a 9,4%, já a casca de arroz na mesma condição teve o teor de hemiceluloses reduzido de 18% para 6,5%. Isso demonstra que, para as cascas de arroz nessa condição de processamento (260°C), foi possível dissociar maior quantidade de hemiceluloses.

No artigo apresentado no capítulo 5, foi avaliada a capacidade de adsorção de 2-nitrofenol utilizando a palha e as cascas de arroz na forma *in natura* e a palha e as cascas de arroz que foram submetidas ao processo de hidrólise subcrítica. Foi realizada a análise da área superficial das partículas de palha e casca de arroz *in natura* e dos coprodutos de palha e casca de arroz que foram submetidos à hidrólise subcrítica. É interessante ressaltar que o maior aumento da área superficial ocorreu para ambas os coprodutos na condição em que a temperatura foi de 260°C e razão líquido/sólido foi de 7,5 g água/g biomassa seca. Nessa condição, a área superficial da palha de arroz aumentou de 1,85 m^2/g (palha de arroz *in natura*) para 10,61 m^2/g. Para as cascas de arroz, o aumento da área superficial foi mais acentuado, sendo que as cascas de arroz *in natura* possuíam um valor de 1,17 m^2/g e, após o processo de hidrólise subcrítica na condição exposta acima, a área alcançou o valor de 24,24 m/g.

A mudança maior na área das cascas de arroz frente à mesma condição de hidrólise subcrítica também pode ser visualizada por meio das imagens em microscopia eletrônica de varredura (MEV). Para a palha de arroz que foi submetida a 260°C, pode-se notar com aumento de 500× que ainda aparecem grandes estruturas vegetais que foram parcialmente quebradas. Para a casca de arroz, entretanto, a quebra das estruturas vegetais parece ser maior, com maior porosidade, o que explica o maior aumento da área superficial. Após caracterizadas as biomassas, foi possível avaliar por meio de ensaios de adsorção em longos intervalos de tempo (24 h), quais coprodutos do processo de hidrólise subcrítica da palha de arroz e das cascas de arroz possuiam maior capacidade de adsorver o 2-nitrofenol em valores de pH 4 e 7.

Os resultados obtidos mostraram que em pH 7, tanto as biomassas provenientes da hidrólise subcrítica da palha de arroz quanto as biomassas resultantes da hidrólise subcrítica das cascas de arroz tiveram elevada capacidade de adsorção frente ao 2-nitrofenol. As maiores capacidades de adsorção foram alcançadas para as biomassas que foram submetidas à condição de 180°C / R-7,5, tendo capacidade de adsorção, para ambas biomassas, ao redor de 92 mg/g. Isso pode ser atribuído à grande quantidade de celulose exposta presente nestas biomassas, que tiveram removidas, através da hidrólise subcrítica, as moléculas que se encontravam dissolvidas em suas estrutura (extrativos) e que poderiam dificultar o acesso das moléculas de 2-nitrofenol. Os grupos C-OH e C-H da celulose interagiram fortemente com os átomos de oxigênio do 2-nitrofenol que ficaram expostos devido à dissociação dos ânions fenolatos em pH 7.

Observando-se que o melhor resultado para obtenção de açúcares ocorreu na condição 220°C / R-7,5 para ambas as biomassas, foram selecionadas biomassas provenientes da hidrólise subcrítica destas condições para se avaliar o comportamento cinético do processo de adsorção, avaliando o equilíbrio e parâmetros termodinâmicos de adsorção. Esta seleção procedeu-se porque, em uma estratégia integrada de aplicação industrial, a ideia seria maximizar os produtos da hidrólise subcrítica, tanto com relação às soluções hidrolisadas quanto aos coprodutos sólidos obtidos.

As cinéticas de adsorção para palha de arroz, cascas de arroz e para essas biomassas submetidas à hidrólise subcrítica a 220°C / R-7,5 demonstraram que com o aumento da temperatura nos ensaios de adsorção a taxa de remoção do 2-nitrofenol no tempo era maior, sendo que em cerca de 10 h a 45°C a capacidade de adsorção da palha e das cascas de arroz submetidas à hidrólise subcrítica alcançaram os valores de 60 e 80 mg/g, respectivamente.

A avaliação termodinâmica demonstrou que, para ambas as biomassas restantes do processo de hidrólise subcrítica e para as biomassas na forma *in natura*, o efeito da entropia foi maior que o da entalpia, e que o processo de adsorção ocorreu espontaneamente. O estudo realizado no artigo 4 confirmou que os coprodutos sólidos provenientes do processamento de hidrólise subcrítica não são apenas resíduos e sim materiais de valor para aplicação de adsorção.

Com base no que foi realizado nesta pesquisa, também é possível apontar alguns desafios e realidades que foram observados no processamento da palha e cascas de arroz (biomassas lignocelulósicas) utilizando água subcrítica. Como realidades pode-se destacar:

- O efeito das variáveis temperatura e razão água/sólido na hidrólise subcrítica pode ser avaliado de maneira eficaz em escala de bancada utilizando reator semi-contínuo;
- O controle da pressão no interior do sistema torna-se difícil (para o sistema em escala de bancada) à medida que há o aumento da vazão de água que alimenta o reator;
- Dependendo da composição da biomassa, há maior ou menor cristalização de produtos na linha após a passagem no reator, o que dificulta o projeto do processo de maneira geral;

- O diâmetro médio das partículas de biomassas que formam o leito fixo dentro do reator é de enorme relevância. Para diâmetros muito inferiores há o entupimento dos filtros de saída do reator.

Os principais desafios que podem ser apontados são:

- O aumento de escala da unidade de hidrólise com água no estado subcrítico encontra dificuldades quando se deseja manter a temperatura no reator homogênea em toda a sua extensão;
- A operação em modo contínuo deve ser estudada, pois a manutenção de toda a linha em elevada pressão tendo alimentação de solvente e sólidos ao mesmo tempo é de difícil controle;
- No modo semi-contínuo, é importante estudar maneiras de se realizar a hidrólise subcrítica utilizando vários reatores em paralelo de modo a garantir a operação contínua do processo;
- É importante definir a configuração dos equipamentos em um processo em escala piloto, com o intuito de se obter frações de caldo hidrolisado com diferentes perfis de açúcares fermentescíveis.

6.2 CONCLUSÃO GERAL

A revisão bibliográfica relacionada aos coprodutos da manufatura do arroz, apresentada no capítulo 2, foi importante para se conhecer as características das biomassas de estudo e ainda as tecnologias de seu processamento. Além disso, serviu também para identificar as tendências futuras de pesquisas envolvendo a processamento integrado de palha e casca de arroz. Nos capítulos 3, 4 e 5 foi possível obter as principais respostas para as variáveis estudadas.

Para a caracterização lignocelulósica (análise DTG), dentre as biomassas utilizadas na forma *in natura*, a palha de arroz apresentou maior teor de hemiceluloses, que foi a estrutura mais dissociada em açúcares e bioprodutos.

As caracterizações da área superficial demonstraram que tanto a palha quanto as cascas de arroz apresentaram um valor baixo para esse parâmetro, entre 1 e 2 m²/g. O que pode ser confirmado pelas imagens obtidas em MEV, demonstrando grandes microestruturas vegetais em sua superfície.

Para as condições avaliadas na hidrólise com água subcrítica, a condição com temperatura de 220°C e razão líquido / sólido de 7,5 g água/g biomassa seca foi a que apresentou melhores resultados com relação ao rendimento de açúcares e a eficiência de conversão.

A partir da caracterização das soluções hidrolisadas da palha de arroz foi observado que a condição a temperatura de 220°C e razão líquido / sólido de 15 g água/g palha seca apresentou maiores teores de bioprodutos. O teor de ácido levulínico foi de 0,77 ± 0,33 g/100 g de palha de arroz, e para o ácido acético o valor encontrado foi de 3,85 ± 0,44 g/100 g de palha de arroz. Já para as soluções hidrolisadas das cascas de arroz a condição a temperatura de 260°C e razão líquido / sólido de 7,5 g água/g cascas secas foi a que apresentou os maiores teores de ácido levulínico (2,3 ± 0,3 g/L) e de ácido acético (21,9 ± 1,7 g/L).

A caracterização do material sólido obtido do processo de hidrólise subcrítica demonstrou uma mudança na morfologia das cascas e palha de arroz, sendo que na melhor condição (260°C / R-7,5) foi verificado o maior aumento na área superficial da palha de arroz (5,73 vezes), e das cascas de arroz (20,71 vezes). O que foi confirmado pelas imagens em MEV, que demonstraram a ruptura das microestruturas vegetais.

A partir da análise da capacidade de adsorção do composto 2-nitrofenol utilizando os coprodutos gerados no processamento pela hidrólise subcrítica foi possível verificar que em pH 7 foram obtidas as maiores remoções do composto orgânico. As biomassas de palha e cascas de arroz que foram submetidas a hidrólise subcrítica a 180°C e razão líquido / sólido de 7,5 g água/g biomassa seca apresentaram os maiores valores de capacidade de adsorção (ao redor de 90 mg/g). O modelo cinético de pseudo-primeira-ordem foi o que melhor se ajustou aos perfis cinéticos de adsorção e o modelo de Freundlich foi o que melhor se ajustou as isotermas de adsorção estudadas.

O desenvolvimento desta tese contribui com o avanço da fronteira do conhecimento por trazer informações sobre o efeito de variáveis do processo de hidrólise subcrítica para obtenção integrada de açúcares fermentescíveis, bioprodutos e coprodutos sólidos com elevada capacidade de adsorção.

6.3 SUGESTÕES PARA TRABALHOS FUTUROS

Da experiência adquirida na execução desta tese e com as informações obtidas, uma lista de sugestões é exposta abaixo com o objetivo de estimular pesquisas continuadas que busquem a aplicação industrial do processo estudado e o uso dos produtos obtidos:

i. Avaliar o aumento de escala do processo estudado para se verificar os efeitos da transferência de calor no interior do leito com biomassa;

ii. Estudar o efeito do gradiente de temperatura e das características da biomassa na cristalização de produtos da hidrólise subcrítica e que são fontes de entupimento de tubulações;

iii. Estudar o efeito da despressurização rápida da linha, explosão a vapor, antes de realizar a hidrólise subcrítica;

iv. Avaliar as soluções hidrolisadas obtidas em um processo de fermentação para obtenção de etanol;

v. Utilizando o mesmo equipamento, na etapa de finalização do processo, avaliar o efeito do aquecimento do sólido que está dentro do reator, sem que haja passagem de água, com intuito de produzir material carbonizado de elevada área superficial;

vi. Avaliar o efeito da remoção da lignina antes da etapa de hidrólise subcrítica;

vii. Aplicar a melhor condição de hidrólise subcrítica em uma mistura de palha e cascas de arroz;

viii. Avaliar a separação e purificação de ácido levulínico.

REFERÊNCIAS

AFZAL, A.; MOHIBULLAH, M.; SHARMA, V. K. Performance analysis of a rice husk power generating system: a case study. **International Journal of Sustainable Energy** v. 30, n. 1, p. 1-10, 2011.

BASU, P. **Combustion and Gasification in fluidized beds**. Nova Escócia: Taylor and Francis Group, LLC, 2006.

BRODT, S.; KENDALL, A.; MOHAMMADI, Y.; ARSLAN, A.; YUAN, J.; LEE, I. S.; LINQUIST, B. Life cycle greenhouse gas emissions in california rice production. **Field Crops Research,** v. 169, p. 89-98, 2014.

CASTRO, R. C. A.; FONSECA, B. G.; H.T.L; SANTOS; FERREIRA, I. S.; MUSSATO, S. I.; ROBERTO, I. C. Alkaline deacetylation as a strategy to improve sugars recovery and ethanol production from rice straw hemicellulose and cellulose. **Ind. Crops Prod. ,** v. 106, n. 1, p. 65-73, 2016.

CHUNGSANGUNSIT, T.; GHEWALA, S. H.; PATUMSAWAD, S. Environmental assessment of electricity production from rice husk: a case study in Thailand. **Electricity Supply Industry in Transition: Issues and Prospect for Asia**, n. 16, p. 20-51, 2005.

COCERO, M. J.; CABEZA, A.; ABAD, N.; ADAMOVIC, T.; VAQUERIZO, L.; MARTÍNEZ, C. M.; PAZO-CEPEDA, M. V. Understanding biomass fractionation in subcritical & supercritical water. **The Journal of Supercritical Fluids,** v. 133, p. 550-565, 2018.

CONAB. Follow-up of brazilian safra 2015/2016 - grains - eleventh survey. **National supply company,** v. 11, p. 1-176, 2016. ISSN 2318-6852.

EOM, I.; KIM, J.; LEE, S.; CHO, T.; YEO, H.; CHO, J. Comparison of pyrolytic products produced from inorganic-rich and memineralized rice straw (*Oryza sativa L.*) by fluidized bed pyrolyzer for future biorefinery approach. **Bioresour. Technol,** v. 128, p. 664-672, 2013.

FAO. Rice market monitor. **Food and Agriculture Organization of the United Nations,** v. 19, n. 2, p. 1-35, July 2016.

FRANCO, D. S. P. **Modificação na casca de arroz para a adsorção de azul de metileno em batelada e leito fixo**. 2016. Dissertação de Mestrado, Universidade Federal de Santa Maria, Santa Maria, Brasil.

IYE, E. L.; BILSBORROW, P. E. Assesment of the availability of agricultural residues on zonal basis for medium to large-scale bioenergy production in Nigeria. **Biomass Bioenergy** v. 48, p. 66-74, 2013.

HRNČIČ, M. K.; KRAVANJA, G.; KNEZ, Z. Hydrothermal treatment of biomass for energy and chemicals. **Energy,** v. 116, p. 1312-1322, 2016.

KIM, I.; REHMAN, M. S. U.; HAN, J. Fermentable sugar recovery and adsorption potential of enzymatically hydrolyzed rice straw. **Journal of Cleaner Production,** v. 66, p. 555-561, 2014.

KOOPMANS, A.; KOPPEJAN, J. Agricultural and forest residues generation, utilization and availability. **Regional consultation on modern applications of biomass energy,** v. 10, p. 1-23, 1997.

LACHOS-PEREZ, D.; MARTINEZ-JIMENEZ, F.; REZENDE, C. A.; TOMPSETT, G.; TIMKO, M.; FOSTER-CARNEIRO, T. Subcritical water hydrolysis of sugarcane bagasse: An approach on solid residues characterization. **J. Supercrit. Fluids,** v. 108, p. 69-78, 2016.

LAU, B. B. Y.; LUIS, E. T.; HOSSAIN, M. M.; HART, W. E. S.; CENCIA-LAY, B.; BLACK, J. J.; TO, T. Q.; ALDOUS, L. Facile, room-temperature pre-treatment of rice husks with tetrabutylphosphonium hydroxide: Enhanced enzymatic and acid hydrolysis yields. **Bioresour.Technol,** v. 197, p. 252-259, 2015.

LENG, L.; YUAN, X.; ZENG, G.; SHAO, J.; CHEN, X.; WU, Z.; WANG, H.; PENG, X. Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. **Fuel,** v. 155, p. 77-85, 2015.

LIMAYEM, A.; RICKE, S. C. Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects. **Prog. Energy Combust. Sci.,** v. 38, n. 4, p. 449-467, 2012.

LIN, R.; CHENG, J.; DING, J.; SONG, W.; QI, F.; ZHOU, J.; CEN, K. **Subcritical water hydrolysis of rice straw for reducing sugar production with focus on degradation by-products and kinetic analysis**. Bioresource Technol. 186**:** 8-14 p. 2015.

MARIN, D. C.; VECCHIO, A.; LUDUEÑA, L. N.; FASCE, D.; ALVAREZ, V. A.; STEFANI, P. M. Revalorization of rice husk waste as a source of cellulose and silica. **Fibers and Polymers,** v. 16, n. 2, p. 285-293, 2015.

MOLINER, C.; BOSIO, B.; ARATO, E.; RIBES, A. Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes. **Fuel,** v. 180, p. 71-79, 2016.

MONTANHER, S. F. **Utilização da biomassa de bagaço de laranja como material sorvente de íons metálicos presentes em soluções aquosas**. 2009. Tese de Doutorado, Universidade Estadual de Maringá, Maringá, Brasil.

MORESCHI, S. R. M.; PETENATE, A. J.; MEIRELES, M. A. A. Hydrolysis of Ginger Bagasse Starch in Subcritical Water and Carbon Dioxide. **Journal of Agricultural and Food Chemistry,** v. 52, p. 1753-1758, 2004.

OLIVEIRA, R. S.; PALÁCIO, S. M.; SILVA, E. A.; MARIANI, F. Q.; REINEHR, T. O. Briquettes production for use as power source for combustion using charcoal thin waste and sanitary sewage sludge. **Environmenta Science and Pollution Research**, 2017.

PRADO, J. M.; LACHOS-PEREZ, D.; FOSTER-CARNEIRO, T.; ROSTAGNO, M. A. Sub- and supercritical water hydrolysis of agricultural and food industry residues for the production of fermentable sugar: A review. **Food. Bioprod. Process,** v. 98, p. 95-123, 2016.

PRADO, J. M.; FOLLEGATI-ROMERO, L. A.; FOSTER-CARNEIRO, T.; ROSTAGNO, M. A.; MAUGERI-FILHO, F.; MEIRELES, M. A. A. Hydrolysis of sugarcane bagasse in subcritical water. **J. Supercrit. Fluids,** v. 86, p. 15-22, 2014.

REGULATORY, C. E. **Energy Regulatory Comission database SPP/VSPP**. Thailand 2015.

SHAFIE, S. M.; IMAHLIA, T. M.; MASJUKI, H. H. Life cycle assesment of rice straw co-firing with coal power generation in Malaysia. **Energy,** v. 57, p. 284-294, 2013.

SHAH, S. A.; SOOMAR, M.; HUSSAIN, A. Comparative Emission Analysis Of Bituminous Coal, Sugarcane Bagasse and Rice Husk **Journal of Sindh University Research,** v. 48, n. 3, p. 685-688, 2016.

SINGH, R.; KRISHNA, B. B.; MISHRA, G.; KUMAR, J. Strategies for selection of thermo-chemical process for the valorisation of biomass. **Renewable energy,** v. 98, p. 1226-237, 2016.

USDA. **Food Price policy in an era of market instability**. Colorado, United States: 2015.

XU, H.; WANG, W.; LIU, X.; YUAN, F.; GAO, Y. Antioxidative phenolics obtained from spent coffee grounds (*Coffea arabica L.*) by subcritical water extraction. **Industrial Crops and Products,** v. 76, p. 946-954, 2015.

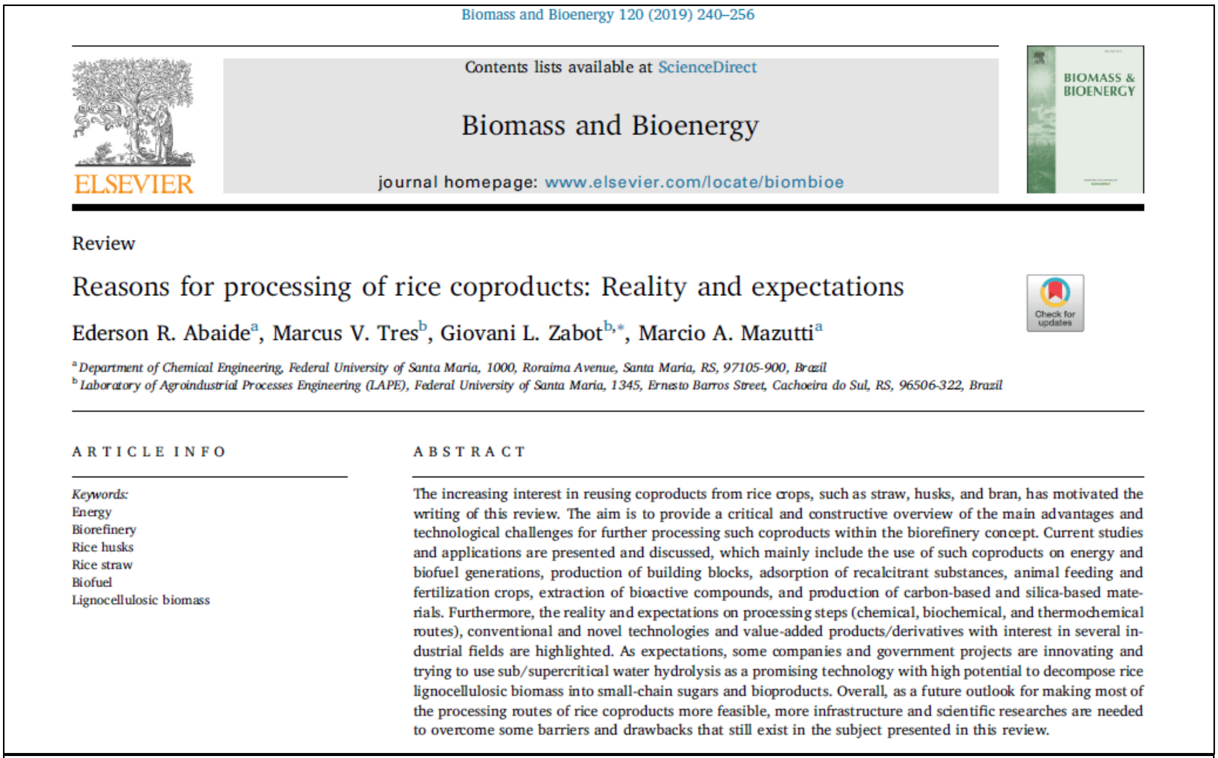
YANG, T.; WANG, J.; LI, B.; KAI, X.; LI, R. Effect of residence time on two-step liquefaction of rice straw in CO_2 atmosphere: differences between subcritical water and supercritical ethanol. **Bioresour. Technol,** v. 229, p. 143-151, 2017.

ZALENGERA, C.; BLANCHARD, R. E.; EAMES, P. C.; JUMA, A. M.; CHITAWO, M. L.; GONDWE, K. T. Overview of the Malawi energy situation and a pestle analysis for sustainable developement of renewable energy. **Renewable Sustainable Energy Rev,** v. 38, p. 335-347, 2014.

ZHAO, Y.; LU, W.; WANG, H.; LI, D. Combined Supercritical and Subcritical Process for Cellulose Hydrolysis to Fermentable Hexoses. **Environmental Science and technology,** v. 43, n. 5, p. 1565-1570, 2009.

ZHU, Z.; LIU, Z.; ZHANG, Y.; LI, B.; LU, H.; DUAN, N.; SI, B.; SHEN, R.; LU, J. Recovery of reducing sugars and volatile fatty acids from cornstalk at different hydrothermal treatment severity. **Bioresource Technology,** v. 199, p. 220-227, 2016.

APÊNDICE - PÁGINAS INICIAIS DOS ARTIGOS PÚBLICADOS



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Review

Reasons for processing of rice coproducts: Reality and expectations

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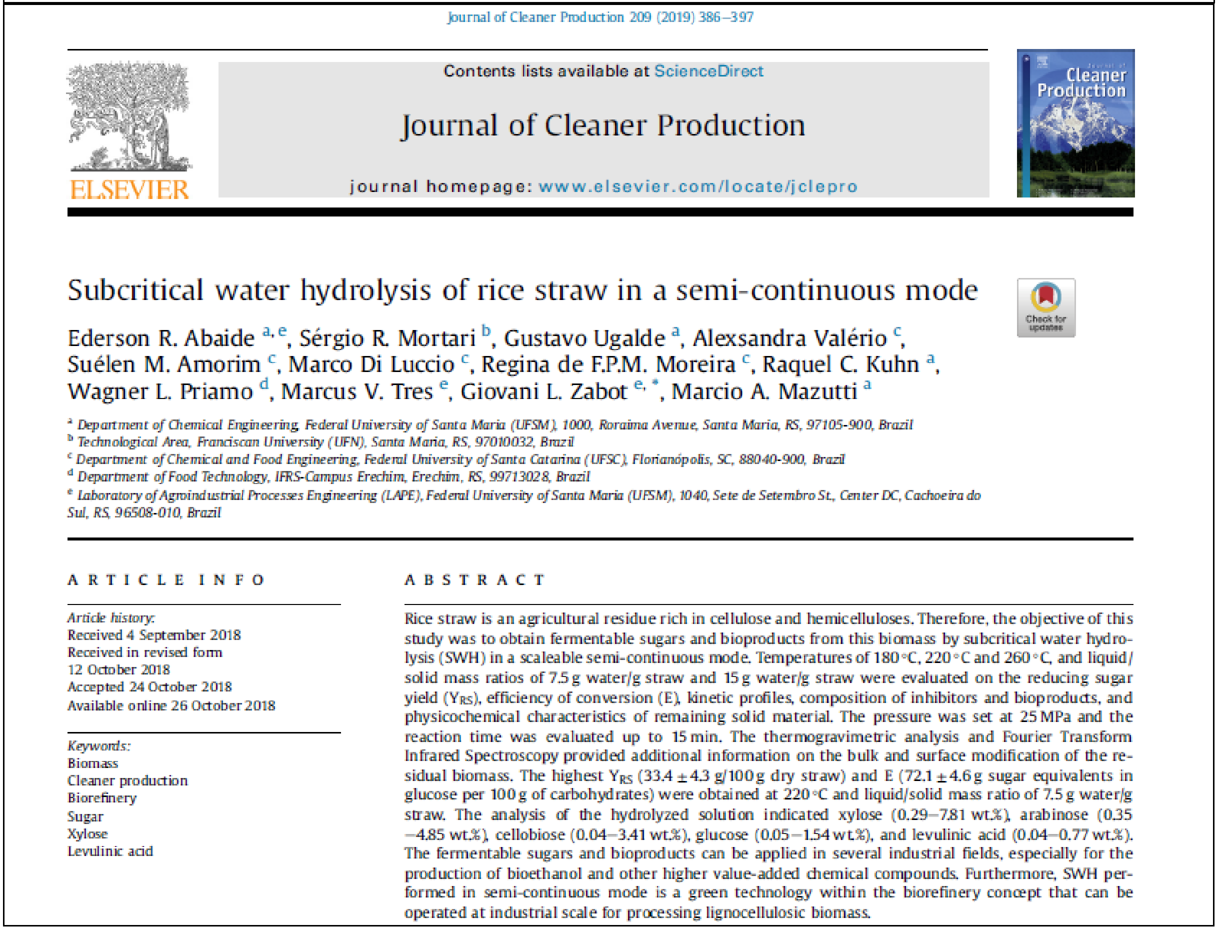
Lignocellulosic biomass

ABSTRACT

The increasing interest in reusing coproducts from rice crops, such as straw, husks, and bran, has motivated the writing of this review. The aim is to provide a critical and constructive overview of the main advantages and technological challenges for further processing such coproducts within the biorefinery concept. Current studies and applications are presented and discussed, which mainly include the use of such coproducts on energy and biofuel generations, production of building blocks, adsorption of recalcitrant substances, animal feeding and fertilization crops, extraction of bioactive compounds, and production of carbon-based and silica-based materials. Furthermore, the reality and expectations on processing steps (chemical, biochemical, and thermochemical routes), conventional and novel technologies and value-added products/derivatives with interest in several industrial fields are highlighted. As expectations, some companies and government projects are innovating and trying to use sub/supercritical water hydrolysis as a promising technology with high potential to decompose rice lignocellulosic biomass into small-chain sugars and bioproducts. Overall, as a future outlook for making most of the processing routes of rice coproducts more feasible, more infrastructure and scientific researches are needed to overcome some barriers and drawbacks that still exist in the subject presented in this review.



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Subcritical water hydrolysis of rice straw in a semi-continuous mode

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ABSTRACT

Rice straw is an agricultural residue rich in cellulose and hemicelluloses. Therefore, the objective of this study was to obtain fermentable sugars and bioproducts from this biomass by subcritical water hydrolysis (SWH) in a scaleable semi-continuous mode. Temperatures of 180 °C, 220 °C and 260 °C, and liquid/solid mass ratios of 7.5 g water/g straw and 15 g water/g straw were evaluated on the reducing sugar yield (Y_{RS}), efficiency of conversion (E), kinetic profiles, composition of inhibitors and bioproducts, and physicochemical characteristics of remaining solid material. The pressure was set at 25 MPa and the reaction time was evaluated up to 15 min. The thermogravimetric analysis and Fourier Transform Infrared Spectroscopy provided additional information on the bulk and surface modification of the residual biomass. The highest Y_{RS} (33.4 ± 4.3 g/100 g dry straw) and E (72.1 ± 4.6 g sugar equivalents in glucose per 100 g of carbohydrates) were obtained at 220 °C and liquid/solid mass ratio of 7.5 g water/g straw. The analysis of the hydrolyzed solution indicated xylose (0.29–7.81 wt.%), arabinose (0.35–4.85 wt.%), cellobiose (0.04–3.41 wt.%), glucose (0.05–1.54 wt.%), and levulinic acid (0.04–0.77 wt.%). The fermentable sugars and bioproducts can be applied in several industrial fields, especially for the production of bioethanol and other higher value-added chemical compounds. Furthermore, SWH performed in semi-continuous mode is a green technology within the biorefinery concept that can be operated at industrial scale for processing lignocellulosic biomass.

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Obtaining fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis in a semi-continuous mode

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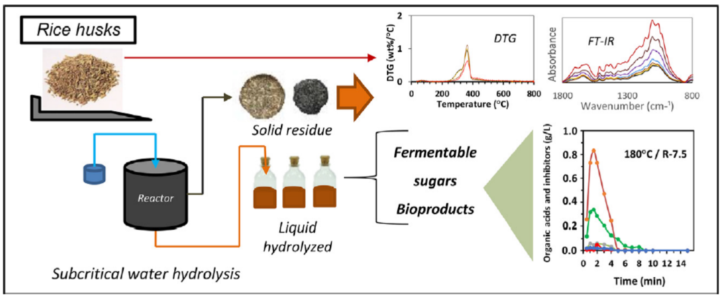
GRAPHICAL ABSTRACT



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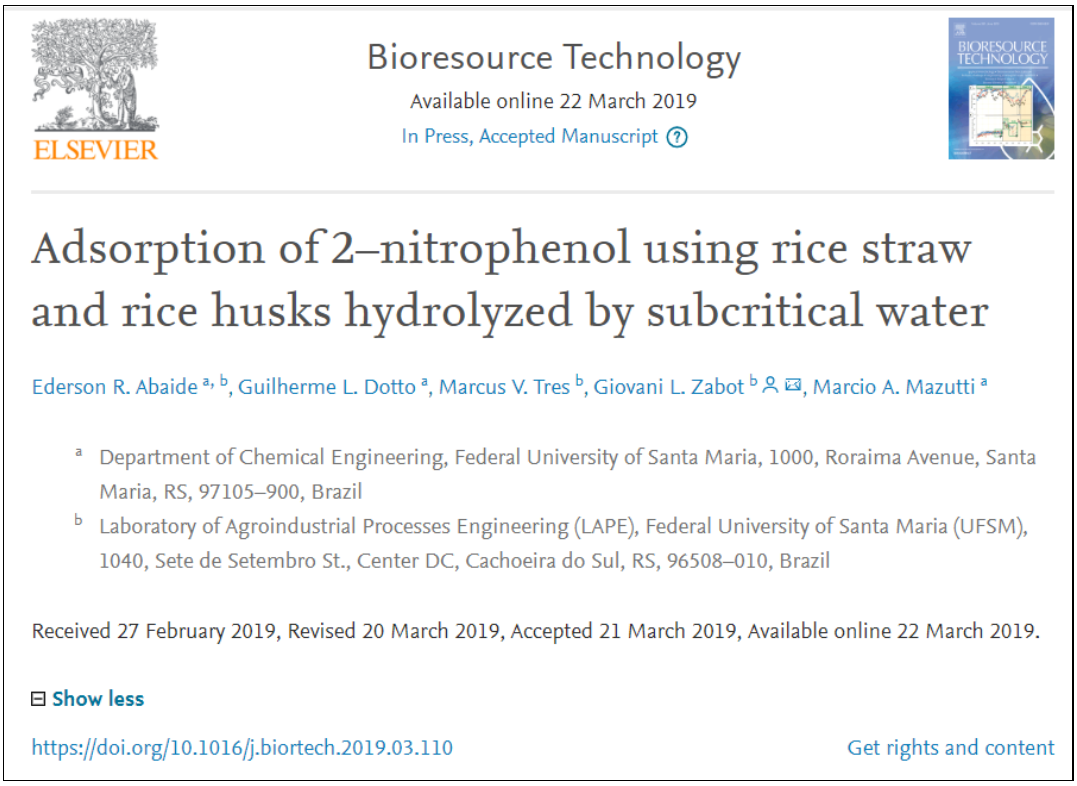
ABSTRACT

This work aimed at producing fermentable sugars and bioproducts from rice husks by subcritical water hydrolysis at 25 MPa in a semi-continuous mode. The influences of temperature (180 °C; 220 °C; 260 °C) and liquid/solid ratio (7.5 g water/g husks; 15 g water/g husks) on reducing sugar yield (Y_{RS}), efficiency (E), kinetic profiles (0–15 min), composition of sugars, inhibitors and organic acids, and physicochemical characteristics of the remaining solid material were evaluated and discussed in the work. The highest Y_{RS} (18.0 ± 2.9 g/100 g husks) and E (39.5 ± 1.7 g sugars/100 g carbohydrates) were obtained at 220 °C and 7.5 g water/g husks. In such condition, the hydrolyzed solutions presented cellobiose (18.0 g/L), xylose 17.7 g/L), arabinose (3.6 g/L), glucose (1.5 g/L), and levulinic acid (0.7 g/L). The fermentable sugars and bioproducts can be applied in several industrial fields, especially for the production of bioethanol and other higher value-added chemical compounds.



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Adsorption of 2–nitrophenol using rice straw and rice husks hydrolyzed by subcritical water

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