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Dissertação

Produção de biocombustíveis a partir de resíduos e efluentes da indústria arrozeira:
Biodiesel e metano

Vitor Alves Lourenço

Pelotas, 2020

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Orientador: Prof. Dr. Willian Cézar Nadaleti

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Vitor Alves Lourenço

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RESUMO

LOURENÇO, Vitor Alves. **Produção de biocombustíveis a partir de resíduos e efluentes da indústria arrozeira:** Biodiesel e metano. 2019. 146f. Dissertação (Mestrado em Ciências Ambientais) – Programa de Pós-Graduação em Ciências Ambientais, Centro de Engenharias, Universidade Federal de Pelotas, Pelotas 2018.

O esgotamento dos combustíveis fósseis, o aumento do preço do petróleo cru e as altas emissões de gases do efeito estufa e poluentes tornam emergencial a busca e o aperfeiçoamento de técnicas de produção de energias limpas e renováveis. Nesse contexto, incluem-se os biocombustíveis. Suas fontes de produção apresentam na forma de biomassa de culturas e resíduos agrícolas, resíduos sólidos urbanos, efluentes, dentre outros. Tendo em vista o alto potencial de produção de energia a partir de efluentes e outros resíduos de indústrias de arroz no Brasil, torna-se fundamental o estudo e o desenvolvimento de biocombustíveis oriundos destes subprodutos. Assim, esse trabalho teve como objetivo a produção de dois biocombustíveis, o biodiesel e o metano, que tiveram como matéria-prima os resíduos e efluentes gerados em processos de beneficiamento de arroz. Para tanto, foram determinados: 1) as melhores condições para transesterificação básica metílica de óleo vegetal do farelo de arroz para produção de biodiesel; 2) o potencial de inibição e potencialização do glicerol do biodiesel à Atividade Metanogênica Especifica (AME) do lodo da parboilização de arroz, e em quais proporções tais efeitos estão presentes; 3) o potencial de produção de biodiesel e metano das indústrias de arroz do estado do Rio Grande do Sul, assim como o potencial de geração de energia térmica e elétrica oriundas de tais biocombustíveis. O estudo se complementa, portanto, em três frentes: experimental, de planejamento energético e de aplicação da energia gerada. Os resultados mostraram que além de estar dentro dos parâmetros exigidos pela ANP, ASTM e EN, o biodiesel produzido com uma razão molar de 6:1 de óleo para álcool, 1,0% de catalisador e 120 minutos apresentou o maior rendimento obtido nesse estudo, igual a 98,09%. Já com relação a produção de metano a adição de 1% de glicerol promoveu o período de fase estacionária mais longa para os microrganismos do lodo, resultando em 539,45% de geração, superior ao sistema sem glicerol, totalizando um volume de 945,23±5,34 mL de metano produzido em 168 horas de experimento. Considerando o potencial energético levantado nesse estudo o Rio Grande do Sul (RS) possui potencial de produção de 8.34E+02 $m^3.d^{-1}$ de biodiesel de óleo vegetal de farelo de arroz e um potencial médio de gerar 8.44E+04 $Nm^3.d^{-1}$ de metano através da digestão individual do efluente no Rio Grande do Sul. Com a adição de 1% glicerol bruto no processo de digestão anaeróbia do efluente da parboilização do arroz, o RS alcança um potencial de atingir uma produção média de 4.55E+05 $Nm^3.d^{-1}$. Assim, análise mostrou que podem ser gerados 2.93E+06 $kWh.d^{-1}$ de energia elétrica e 5.55E+06 $kWh.d^{-1}$ de energia térmica no estado através da produção e uso do biodiesel e do metano como fontes de energia.

Palavras-chave: óleo vegetal; farelo de arroz; transesterificação; glicerol; AME; efluente; codigestão

ABSTRACT

LOURENÇO, Vitor Alves. **Production of biofuels from rice industry residues and wastewater:** Biodiesel and methane. 2019. 146f. Dissertation (Master Degree in Environmental Sciences) - Post-graduation Program in Environmental Sciences, Engineering Center, Federal University of Pelotas, Pelotas 2018.

The unavoidable depletion of fossil fuels, the increase in the price of crude oil and the high emissions of greenhouse gases and pollutants make the search and improvement of techniques to produce clean and renewable energies an emergency. In this context, biofuels are included. Its sources of production present in the form of biomass from crops and agricultural waste, solid urban waste, effluents, among others. In view of the high potential for energy production from effluents and other waste from rice industries in Brazil, it is essential to study and develop biofuels from these by-products. Thus, this work aimed at the production of two biofuels, biodiesel and methane, which had as raw material the residues and effluents generated in rice processing processes. For this, were determined: 1) the best conditions for basic methyl transesterification of vegetable oil from rice bran for biodiesel production; 2) the potential for inhibition and enhancement of biodiesel glycerol to the Specific Methanogenic Activity (SMA) of the sludge from rice parboiling, and in what proportions such effects are present; 3) the potential for production of biodiesel and methane in the rice industries of the state of Rio Grande do Sul, as well as the potential for generating thermal and electrical energy from such biofuels. The study is complemented, therefore, on three fronts: experimental, energy planning and application of the generated energy. The results showed that in addition to being within the parameters required by ANP, ASTM and EN, the biodiesel produced with a 6:1 molar ratio of oil to alcohol, 1.0% catalyst and 120 minutes showed the highest yield obtained in this study, equal to 98.09%. Regarding methane production, the addition of 1% glycerol promoted the longest period of stationary phase for the sludge microorganisms, resulting in 539.45% of generation, superior to the system without glycerol, totalling a volume of 945.23±5.34 mL of methane produced in 168 hours of the experiment. Considering the energy potential raised in this study, Rio Grande do Sul (RS) has a production potential of 8.34E+02 $m^3.d^{-1}$ of rice bran vegetable oil biodiesel and an average potential to generate 8.44E+04 $Nm^3.d^{-1}$ of methane through the individual digestion of the effluent in the Rio Grande do Sul. With the addition of 1% crude glycerol in the process of anaerobic digestion of the rice parboiling effluent, RS had reached a potential to reach an average production of 4.55E+05 $Nm^3.d^{-1}$. Thus, analysis shows that 2.93E+06 $kWh.d^{-1}$ of electric energy and 5.55E+06 $kWh.d^{-1}$ of thermal energy can be generated in the state through the production and use of biodiesel and methane as energy sources.

Keywords: rice bran; vegetable oil; transesterification; glycerol; SMA; wastewater; co-digestion

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1. INTRODUÇÃO

De acordo com Nadaleti e Przybyla (2018) e Nadaleti (2019), o potencial de produção de energia a partir de efluentes e resíduos de indústrias de parboilização de arroz no Brasil, se corretamente equacionado, é capaz de promover a autossuficiência energética do setor. O grão representa um importante componente da economia nacional (QUEIROZ *et al*., 2007), o país fechou a safra de 2018/19 com cerca de 10,45 milhões de toneladas de arroz produzidos (CONAB, 2020), sendo o estado do Rio Grande do Sul (RS) o maior produtor nacional (IBGE, 2018). Nesse contexto, torna-se pertinente explorar a produção de biocombustíveis oriundos de resíduos e efluentes da indústria arrozeira, estudando o potencial de produção destes no estado do Rio Grande do Sul, assim como seu potencial de geração de bioenergia.

Desde o final do século XIX o petróleo vem sendo utilizado como principal matriz energética, correspondendo à 33,3% do consumo global de energia (VARÃO, *et al*., 2016; BP JIANG *et al*., 2017; GLOBAL, 2018). O esgotamento dos combustíveis fósseis e o aumento do preço do petróleo bruto torna emergencial a busca por novas fontes de energia, desse modo o desenvolvimento de energias limpas e renováveis representa, ainda, a possibilidade de redução da emissão de Gases do Efeito Estufa (GEE) (JIANG *et al*., 2017).

O crescente uso de energia renovável no Brasil se dá primordialmente por meio das usinas hidrelétricas, que atendem 66,6% da produção do país, entretanto, apesar da alta eficiência na geração de energia, a construção deste tipo de usina ocasiona diversos impactos ambientais negativos (EPE, 2019; ZIEMBOWICZ *et al*., 2018). Nesse contexto, surge o desenvolvimento e emprego de biocombustíveis para a geração de bioenergia, que se caracteriza como energia derivada da biomassa gerada a partir de combustível sólido, líquido e gasoso para diferentes usos, permitindo a redução de GEE quando substitutos de energias fósseis (SANTOS; TURNES; CONCEIÇÃO, 2012; CREUTZIG *et al*., 2015; GONZÁLEZ-GONZÁLEZ *et al*., 2018).

O emprego de bioenergia proporciona um melhor equilíbrio para o ciclo biogeoquímico do carbono, pois permite a reciclagem das fontes de origem biológica através da produção de energia e o consumo do carbono resultante da fotossíntese (BESCHKOV, 2017). Suas fontes se apresentam na forma de biomassa de culturas e resíduos agrícolas, resíduos sólidos urbanos e efluentes com alto teor de matéria orgânica. A conversão da biomassa em biocombustível se dá, por exemplo, na digestão anaeróbia destes compostos para geração de biogás, ou na

transesterificação de lipídios para produção de biodiesel (SANTOS; TURNES; CONCEIÇÃO, 2012; MATHIOUDAKIS *et al*., 2017; SRINUANPAN; CHEIRSILP; PRASERTSAN, 2018).

No que diz respeito aos biocombustíveis líquidos, a produção vem ocorrendo por meio do uso de diferentes matérias-primas agrícolas de culturas oleaginosas e leguminosas para obtenção de bioetanol e biodiesel (RAMOS *et al*., 2017; GONZÁLEZ-GONZÁLEZ *et al*., 2018). Dentre as técnicas utilizadas para a produção do biodiesel a mais comum é a transesterificação dos óleos extraídos das biomassas para obtenção de Ácidos Graxos (AG), tal processo garante a redução da viscosidade e eleva a volatilidade, características presentes no óleo diesel (LIMA FILHO *et al*., 2017). Na transesterificação, um triglicerídeo reage com um álcool de cadeia curta na presença de uma base ou ácido forte (catalisador), produzindo uma mistura de ésteres de ácidos graxos (biodiesel) e glicerol (subproduto) (SINGH; SINGH, 2010; VISENTAINER, 2013).

O glicerol bruto contém aproximadamente 95% de glicerol em sua composição, sendo que para cada 10 Kg de biodiesel produzido é gerado cerca de 1 Kg de glicerol (FONTINELE *et al*., 2017; SILVA; SOUZA; ANTERO, 2017), ou seja, o aumento significativo na produção de biodiesel na última década resultou no acúmulo de grandes quantidades do subproduto, fazendo com que sejam necessárias novas alternativas para sua utilização (D'AUREA *et al*., 2017; SILVA; SOUZA; ANTERO, 2017).

Nessa conjuntura, a digestão anaeróbia surge como uma alternativa favorável para a aplicação de glicerol, através da codigestão deste subproduto com outros substratos orgânicos para a obtenção de biogás. O processo ocorre através da complexa interação de microrganismos capazes de degradar a matéria orgânica presente no sistema e convertê-la, principalmente, em metano e dióxido de carbono (SCHIWINGEL *et al*., 2016). O incremento do glicerol pode favorecer a digestão anaeróbia ao ser utilizado pelos microrganismos para obtenção de energia, melhorando a razão entre carbono e nitrogênio (C/N) e elevando a produção de biogás e metano (CH_4) (MEIER *et al*., 2016; KURAHASHI *et al*., 2017).

Dessa forma, o objetivo geral desse estudo foi produzir biocombustíveis que tenham como matéria-prima os subprodutos, resíduos e efluentes gerados em processos do beneficiamento de arroz, assim como determinar o potencial de geração de bioenergia do setor arrozeiro no RS.

1.1 Objetivos

1.1.1 Objetivo Geral

O objetivo do presente estudo foi a produção de biocombustíveis que tenham como matéria-prima os subprodutos, resíduos e efluentes gerados em processos do beneficiamento de arroz, a fim de estimar o potencial de geração de bioenergia do setor arrozeiro no Rio Grande do Sul.

1.1.2 Objetivos Específicos

- Realizar a transesterificação básica metílica de óleo vegetal de farelo de arroz e determinar as melhores condições para a produção do biodiesel;
- Determinar o potencial de inibição e potencialização do glicerol metílico oriundo da produção do biodiesel à Atividade Metanogênica Específica do lodo da parboilização de arroz;
- Determinar o potencial de produção de biodiesel e de metano das indústrias arrozeiras do Rio Grande do Sul, assim como de produção de energia térmica e elétrica derivada dos biocombustíveis.

1.2 Hipóteses

- É possível obter biodiesel de boa qualidade utilizando óleo vegetal do farelo de arroz via transesterificação básica metílica;
- O glicerol é capaz de elevar o potencial de produção de metano do lodo da parboilização de arroz em digestão anaeróbia;
- As indústrias arrozeiras podem se tornar energeticamente autossuficientes ao utilizar resíduos e efluentes gerados em suas etapas de produção para produzir biodiesel e metano.

2. REFERENCIAL TEÓRICO

2.1 Indústrias de arroz

De acordo com a *Food and Agriculture Organization of the United Nations* (2018), o Brasil é o nono maior produtor de arroz no mundo. O país fechou a safra de 2018/19 com cerca de 10,45 milhões de toneladas de arroz produzidos e possui estimativas de uma produção para 2019/20 de aproximadamente 10,52 milhões de toneladas (CONAB, 2020).

O consumo per capita do grão no cenário nacional gira em torno de 25 kg/ano, consolidando o arroz como um grande setor da economia do país (QUEIROZ *et al*., 2007; SPINOSA *et al*., 2016). O estado provedor de grande parte da produção de arroz no Brasil é o Rio Grande do Sul, o mesmo foi responsável pela produção de 70,1% da safra nacional de 2017/2018, totalizando uma oferta de mais de 8 milhões de toneladas do grão (CONAB, 2019).

De todo o arroz consumido no país, cerca de 25% do arroz é do tipo parboilizado (PARAGINSKI *et al*., 2014). O beneficiamento do arroz parboilizado não envolve apenas a retirada da casca e do farelo como no caso do arroz branco. A parboilização envolve ainda uma unidade específica onde o grão sofre encharcamento em tanques com água a 60 °C, por cerca de quatro horas, seguida das etapas de vaporização e secagem (AGEITEC, 2016).

2.1.1 Efluente da parboilização de arroz

O ponto crítico da geração de efluentes em uma indústria de arroz parboilizado ocorre na etapa de encharcamento, por utilizar um grande volume de água que por sua vez retém propriedades do grão durante o banho (AMATO; BITTENCOURT; GUINDANI, 1989), sendo que para cada quilo de arroz parboilizado são gerados de 2 a 4 L de efluente (BASTOS *et al*., 2010; SANTOS; TURNES; CONCEIÇÃO, 2012).

O efluente gerado se caracteriza com altas cargas de substâncias orgânicas e nutrientes, como Nitrogênio (N) e Fósforo (P) (FARIA *et al*., 2006; QUEIROZ *et al*., 2007), que quando dispostos em corpos hídricos sem tratamento adequado, podem acarretar no processo de eutrofização (OKUNUKI *et al*., 2004; FARIA *et al*., 2006). Bastos *et al*. (2010) relatam que a variabilidade na caracterização do efluente da parboilização de arroz decorre de aspectos sazonais relacionados à produção do grão, de modo que diferentes estudos apresentam efluentes do mesmo setor industrial com alta variação em sua caracterização (Tabela 1):

Tabela 1 – Caracterização do efluente bruto da parboilização de arroz em diferentes estudos

Parâmetro	Gerber *et al*. (2018)	Isoldi *et al*. (2003)	Bastos *et al*. (2010)	Queiroz; Koetz (1997)	Queiroz *et al*. (2007)	Nadaleti *et al*. (2018)
DQO ($mgOL^{-1}$)	398,70	2539,60	4206,8	1019,19	4206,80	6447,50
P ($mgPL^{-1}$)	7,90	-	-	-	-	-
NTK* ($mgNL^{-1}$)	23,10	120,90	78,10	-	32,44	-
pH	6,30	-	4,64	4,59	4,60	3,47
SST** (mgL^{-1})	153,40	-	-	89,01	-	-
C/N	-	21,00	53,68	37,90	72,73	-

*Nitrogênio Total Kjeldahl
**Sólidos Suspensos Totais

Tal variação pode influir no rendimento da produção de biogás e metano durante a digestão anaeróbia do efluente, uma vez que os microrganismos que atuam no processo requerem condições físico-química de acordo com suas especificidades. De acordo com Khalid et al. (2011) o pH ideal para o desenvolvimento de bactérias metanogênicas se encontra na neutralidade. Já para a relação C/N, Pereira (2013) indica que os digestores anaeróbios devem ser operados com uma razão C/N entre 20 e 30.

2.1.2 Óleo Vegetal de Arroz

Durante o beneficiamento do arroz (*Oryza sativa*) é gerado o farelo de arroz, um resíduo agrícola oriundo das etapas de descasque e polimento do grão que, em geral, é destinado para a produção de ração animal (EVANGELISTA, 2011; PEREIRA, 2013). Tal farelo contém de 15 a 23% de óleo (ZULLAIKAH *et al*., 2005; SINHA; AGARWAL; GARG, 2008) constituído de cerca de 68 a 71% de triacilgliceróis, 2 a 3% de diglicerói, 5 a 6% de monogliceróis e 2 a 3% de ácidos graxos livres (PESTANA; MENDONÇA; ZAMBIAZI, 2008).

O óleo do farelo de arroz é um dos óleos vegetais mais nutritivos (LAI *et al*., 2005; SILVA, 2008; LIN *et al*., 2009), sendo consumido em larga escala nos países asiáticos, especialmente no leste do continente, por seus benefícios à saúde humana (GOFFMAN; PINSON; BERGMAN, 2003; PESTANA, 2007; WALTER, 2009). Apresenta aproximadamente 80% de AG insaturados, o que tornaria o óleo propenso à oxidação, se não fosse a presença de antioxidantes naturais em sua composição (XU; GODBER, 1999; KRISHNA, 2002; CHOI; JEONG; LEE, 2007; CHOTIMARKORN; SILALAI, 2008). A principal diferença entre o óleo bruto de farelo de arroz e a maioria dos óleos vegetais é que, devido à presença de lipase ativa, o

óleo de arroz possui alto teor de Ácidos Graxos Livres (AGL) (PEREIRA *et al*., 2015) (Tabela 2):

Tabela 2 - Ácidos graxos constituintes do farelo e óleo de arroz

AG	(%)
C14:0 Mirístico	0,1 a 2,4
C16:0 Palmítico	12,3 a 20,5
C16:1 Palmitoléico	0,1 a 0,2
C18:0 Esteárico	1,1 a 3,0
C18:1 Oléico	37,1 a 52,8
C18:2 Linoléico	27,0 a 40,7
C18:3 Linolênico	0,5 a 2,3
C20:0 Aráquico	0,3 a 0,7
C22:0 Behênico	0,5 a 1,0
C24:0 Lignocérico	0,4 a 0,9

Fonte: TORTOSA; BARBER (1979).

Em decorrência de sistemas enzimáticos presentes no farelo, os triglicerídeos são rapidamente hidrolisados em AGL, elevando o teor de acidez, desse modo, a viabilidade de extração de óleo para refino para consumo humano se dá apenas quando o teor de acidez se apresenta reduzido (EVANGELISTA, 2011), uma vez que, segundo a ANVISA (1999), o percentual de AGL em óleos vegetais utilizados na alimentação humana deve ser de no máximo 0,3g/100g. Em estudo realizado por Zullaikah *et al*. (2005), já no tempo zero de armazenamento o percentual de AGL do farelo de arroz se encontrava acima do pré-estabelecido pela ANVISA (1999).

Desse modo o beneficiamento de arroz oferece uma fonte de triglicerídeos de baixo custo capaz de promover a produção de biodiesel (LAI *et al*., 2005; SINHA; AGARWAL; GARG, 2008; OLIVEIRA, 2012; PEREIRA, 2013). Sinha, Agarwal e Garg (2008) relatam que o óleo vegetal de farelo de arroz produz um biodiesel com excelentes propriedades físico-químicas, devido aos seus antioxidantes naturais (SINHA; AGARWAL; GARG, 2008). Desse modo, a alta qualidade do biodiesel

propicia seu uso em misturas com outras oleaginosas ou com diesel mineral (EVANGELISTA, 2011).

2.2 Matriz Energética

Energias fósseis representam 65,9% de toda a energia elétrica gerada no mundo, enquanto a energia eólica, solar, geotérmica, maremotriz e de resíduos sólidos ou efluentes somam apenas 5,0% (VARÃO, *et al*., 2016; JIANG *et al*., 2017; BP GLOBAL, 2018;). No Brasil, o petróleo é responsável por prover 43,7% produção de energia primária, enquanto o diesel corresponde a 16,7% do consumo final por fonte (EPE, 2019).

Os combustíveis fósseis geram um conjunto de problemáticas, desde sua extração ao seu consumo. O Dióxido de Carbono (CO_2), Óxido de Nitrogênio (NO) e Dióxido de Enxofre (SO_2) originários já nas usinas dos combustíveis, derivam em diversos impactos ambientais negativos, como as emissões de GEE (DREIDY; MOKHLIS; MEKHILEF, 2017). Mudanças climáticas decorrentes dessas emissões antropogênicas despertaram a preocupação de diversos países, que passaram a direcionar suas políticas energéticas de modo a incentivar, ou até mesmo obrigar, o uso de energia renováveis por parte das concessionárias de energia elétrica, com a possibilidade de subsídios públicos para a instalação de usinas renováveis (ACEMOGLU; KAKHBOD; OZDAGLAR, 2017; WANGA *et al*., 2017).

Fontes que atendam a demanda energética atual ainda representam desafios, em principal, quando o tema é abordado com enfoque econômico e global (MARQUES; STUMBO; CANELA, *et al*., 2017). Segundo dados apresentados pela *IEA - International Energy Agency* (2018), até o ano de 2040, haverá um acréscimo de mais de 25% na demanda enérgica, evidenciando a necessidade de novas fontes energéticas para que seja possível suprir tal expansão de forma sustentável. A informação revela melhora no cenário energético global, já que a necessidade do crescimento poderá ocorrer mais lentamente do que previsto no passado, tal melhora se dá em decorrência das novas políticas empregadas ao redor do mundo, que priorizam o uso de energias renováveis (IEA, 2018).

A oferta energética brasileira oriunda de fontes renováveis se dá majoritariamente por meio de energia hidroelétrica, que responde por 65,2% da oferta interna e apresenta alta eficiência de geração (EPE, 2018; ZIEMBOWICZ *et al*., 2018). Entretanto, a construção deste tipo de usina ocasiona diversos impactos ambientais

negativos, representados pela perda de fragmentos florestais, matas ciliares, paisagens culturais e naturais causadas pela inundação decorrente dos desvios do curso d'água e represamento do corpo d'água (ZIEMBOWICZ *et al*., 2018). De acordo com Santos *et al*. (2017), hidrelétricas podem apresentar maiores emissões de GEE que usinas termoelétricas, em principal nos casos onde as hidrelétricas possuem baixa geração anual de energia e grandes reservatórios, responsáveis por armazenar os gases que posteriormente serão lançados para atmosfera ao se chocarem com as pás das turbinas. Assim, torna-se emergencial a diversificação da matriz energética nacional (RUFFATO-FERREIRA *et al*., 2017).

Sobre a matriz energética do estado do Rio Grande do Sul, há grande atividade de termoelétricas, uma vez que o estado tem localização geográfica que propicia a exploração de carvão mineral e seu aproveitamento energético (GOMES; CRUZ; BORGES, 2003). De acordo com o último Balanço Energético do Rio Grande do Sul divulgado, dos 10.139.167 kW de potência instalada em 2014, mais de 22% correspondiam à operação de 114 usinas termelétricas (BERS, 2015). Já no ano de 2017, de acordo com o último Balanço Energético Nacional (2018), cerca de 26% da capacidade instalada de energia elétrica do estado era proveniente de termelétricas.

Diante desse cenário surge a necessidade da produção de bicombustíveis e do emprego de bioenergia geradas através dos biocombustíveis sólidos, líquidos e gasosos capazes de substituir combustíveis fósseis em diferentes usos e reduzir assim emissões de GEE, propiciando diversificação da matriz energética (SANTOS; TURNES; CONCEIÇÃO, 2012; CREUTZIG *et al*., 2015; GONZÁLEZ-GONZÁLEZ *et al*., 2018).

2.2.1 Cenário Energético Industrial do Rio Grande do Sul

O estado do Rio Grande do Sul possui um setor industrial desenvolvido, ocupando a 3ª posição nacional e representando 27,5% da economia do estado, sendo que seus principais ramos são a agroindústria, a indústria química, a metalomecânica e a de couro/calçados (RIO GRANDE DO SUL, 2011). Totalizando em 2014, 22,44% do consumo final energético do estado sendo ultrapassado apenas pelo setor de transportes (BERS, 2015).

Em 2017 o setor foi responsável pelo maior consumo de energia elétrica no estado, 33%, sendo que no mesmo ano o consumo de eletricidade apresentou acréscimo de 3,9% em relação ao ano anterior (EPE, 2018). Em geral, as indústrias

vêm sofrendo elevação em seus custos de produção em decorrência do uso de energia elétrica (CNI, 2016). Ao passo que o setor possui grande dependência da energia elétrica, a gestão energética empresarial apresenta grande foco em estratégias para a otimização da contratação e do consumo (ZHAO, 2011).

Zhao (2011) destaca a importância de fortalecer a autonomia produtiva da indústria de modo a promover retornos financeiros oportunizando que passivos ambientais suscetíveis de reaproveitamento ou reajustes energéticos sejam a solução da problemática. De acordo com Salazar (2012) e com dados divulgados pela Empresa de Pesquisa Energética (EPE, 2018), tal possibilidade não vem sendo explorada pelo setor industrial em todo o Brasil, uma vez que ao que diz respeito ao consumo de energia do setor, praticamente não houve alteração da matriz quanto à participação de fontes renováveis e não renováveis.

De acordo com a classificação da EPE, as indústrias de beneficiamento de arroz são enquadradas como Indústrias de Alimentos e Bebidas, tal categoria é responsável por 9% do consumo final de energia do setor industrial nacional (EPE, 2018), sendo que na região Sul, assim como no RS, o consumo é ainda maior, onde a fabricação de produtos alimentícios é responsável pelo maior consumo de energia elétrica, 23,4% (BERS, 2015; EPE, 2018).

O beneficiamento do arroz envolve diversos processos, variando de acordo com os métodos adotados pelas indústrias. Os principais processos são: recebimento, armazenamento do grão, encharcamento e gelatinização (nas indústrias de parboilização), estufa, o secador, descascamento, brunição, armazenamento final e expedição (ABIAP, 2013). Em geral, o principal custo produtivo das indústrias arrozeiras é o consumo de energia elétrica, podendo superar 40% da totalidade, de modo que possui grande influência na lucratividade das indústrias que desenvolvem tal atividade (VELASQUEZ; SANTOS; BORGES, 2012). Dentre os processos do beneficiamento industrial do grão, os que possuem maior influência na demanda de energia elétrica são os de descascamento, que representa 52% da demanda, seguido pela etapa de parboilização, com 28% do consumo geral (ROCHA, 2010).

Nadaleti (2019) realizou um estudo de caso em uma dessas indústrias, onde foi discutido o potencial energético proveniente de sistemas que operam com um grupo gerador de CHP (*Combined Heat and Power*), utilizando gás de síntese de hidrogênio proveniente das cascas de arroz e o biogás do tratamento anaeróbio dos

efluentes. O autor determinou um potencial de produzir mais de 2,17E+04 MWh de eletricidade considerando apenas o uso do biogás gerado.

2.3 Biodiesel

Emissões veiculares de motores a diesel estão associadas à maiores riscos de internações hospitalares ocasionadas por doenças cardiovasculares, pulmonares e respiratórias, além de agravar quadros alérgicos ou infecciosos (TAKANO; YANAGISAWA; INOUE, 2007; BELL *et al*., 2009; CONNELLAN, 2017). As emissões oriundas dos motores a diesel causam ainda danos a fauna e flora expostas à atmosfera contaminada (IJAZ *et al*., 2016). Devido aos malefícios causados pelo diesel e ao esgotamento dos combustíveis fósseis, o biodiesel passou a ser estudado como possível substituto (SINGH; SINGH, 2010; LEEVIJI *et al*., 2016).

O biodiesel é um biocombustível líquido que vem sendo largamente empregado, caracterizando-se como qualquer combustível alternativo renovável que ao substituir total ou parcialmente o diesel de petróleo em motores de ignição por compressão interna, oferece vantagens socioambientais (LIMA FILHO *et al*., 2017; RAMOS *et al*., 2017; GONZÁLEZ-GONZÁLEZ *et al*., 2018). Além de ser economicamente vantajoso, com alta disponibilidade e renovável, o biocombustível sintético possui produção simplificada, especialmente quando comparado a outros biocombustíveis (GOODMAN; KALEY; FINNEY, 2016).

Caracteriza-se ainda como um combustível biodegradável e atóxico, constituído de uma mistura de ésteres metílicos ou etílicos de ácidos graxos produzido a partir de óleos vegetais, gorduras animais e algas, comestíveis ou não (IJAZ *et al*., 2016; PANCHAL; PADUL; KACHOLE, 2016; URRUTIA *et al*., 2016; RIBEIRO; CALERA; FLU MIGNAN, 2017).

Vantagens socioeconômicas são ainda mais evidentes no Brasil em decorrência da alta produção de matérias-primas para o biodiesel, o que tornou o país um dos precursores na sua produção, garantindo uma posição de destaque no desenvolvimento e uso dessa fonte de energia (RIBEIRO; CALERA; FLU MIGNAN, 2017). De acordo com a EMBRAPA (2014), o aumento da produção de biodiesel impacta positivamente a economia dos municípios beneficiados e a geração de emprego formal na agricultura.

A inserção do biodiesel na matriz energética nacional ocorreu através do Programa Nacional de Produção e Uso do Biodiesel (PNPB), lançado em 2004, onde

foi promovido o estudo de misturas do biocombustível ao óleo diesel fóssil. Em janeiro de 2008, por meio da Lei n° 11.097/2005, passou a ser obrigatório a adição de 2% de biodiesel ao diesel, com previsão de acréscimo gradual. De acordo com o cronograma estabelecido pela Lei nº 13.263/2016, em março de 2019 o biodiesel passou a compor 10% da mistura. Em decorrência do acréscimo gradual, a produção de biodiesel cresce no país, em 2018 a produção no país cresceu 24,7% em relação ao ano anterior atingindo o montante de 5.350.036 m³ (EPE, 2019).

A Resolução da ANP nº 45/2014 determina as obrigações quanto ao controle da qualidade a serem atendidas pelos diversos agentes econômicos que comercializam o produto em todo o território brasileiro, de modo que a caracterização do biodiesel deve ser realizada através das especificações da Associação Brasileira de Normas Técnicas (ABNT), das normas internacionais da *American Society for Testing and Materials* (ASTM), da *International Organization for Standardization* (ISO) e do *Comité Européen de Normalisation* (EN).

Desde 1900, já se tem conhecimento do emprego de óleos vegetais como combustível, porém devido ao seu alto peso molecular e alta viscosidade cinética o seu uso direto em motores a diesel resultou em diversos problemas operacionais (GHESTI *et al*., 2012). Diante disto, o óleo vegetal passou a ser modificado quimicamente antes de ser utilizado como fonte de energia, através de técnicas como transesterificação, emulsificação, esterificação e o craqueamento, que garantem características semelhantes às do combustível fóssil (SILVA, 2008).

A técnica mais usual para produção de biodiesel é a reação de transesterificação, reação química entre a matéria-prima e um álcool na presença de um catalisador (SAJID; KHAN; ZHANG, 2016). A reação entre o triglicerídeo presente na matéria-prima e o álcool de cadeia curta empregado produz ésteres de ácidos graxos e glicerol (SINGH; SINGH, 2010; VISENTAINER, 2013).

2.3.1 Matérias-Primas

A produção de biodiesel ocorre a partir de oleaginosas, sebo animal, óleo residual de fritura, microalgas e resíduos de tratamento de esgotos (ALI *et al*., 2017; CARDOSO; SHIKIDA; FINCO, 2017). No Brasil, a soja tem grande destaque como matéria-prima do biocombustível, sendo responsável por 63% da produção, seguida pelo sebo bovino com 12% (EPE, 2019).

Segundo a EMBRAPA (2012), o Rio Grande do Sul é um dos líderes nacionais da produção de biodiesel a partir do óleo de soja e do sebo bovino, porém outras culturas são estudadas como potenciais fontes para produção do biocombustível. A Embrapa Clima Temperado, localizada no município de Pelotas-RS, realiza pesquisas acerca do sistema de produção de culturas de oleaginosas como a soja, pinhão-manso, mamona, tungue e crambe, estudando-as como matéria-prima para geração de biodiesel (EMBRAPA, 2012). Desse modo, outras oleaginosas que representam potenciais fontes de biodiesel são estudadas atualmente (MICUANSKI, 2014) e neste contexto, o Brasil apresenta grande potencial exploratório devido à grande diversidade de óleos vegetais e sua alta produtividade agrícola.

2.3.2 Transesterificação

As últimas três décadas foram marcadas por grandes avanços científicos acerca do biodiesel, porém sua produção industrial não passou por significativas mudanças no mecanismo de seus processos (EVANGELISTA, 2011). Apesar das descobertas de diversas tecnologias capazes de obter o produto, a geração do biocombustível permanece sendo realizada através da transesterificação de óleos vegetais com uso de catalisadores homogêneos, uma vez que várias inovações em relação ao processo de produção existem em nível tecnológico, porém ainda sem uso em escala industrial (EVANGELISTA, 2011; MARTÍNEZ *et al.*, 2019). Na transesterificação os triglicerídeos, ou triacilgliceróis, presentes majoritariamente na composição de óleos, reagem com um álcool gerando ésteres e glicerol, conforme consta na Figura 1 (EVANGELISTA, 2011; OLIVEIRA, 2012):

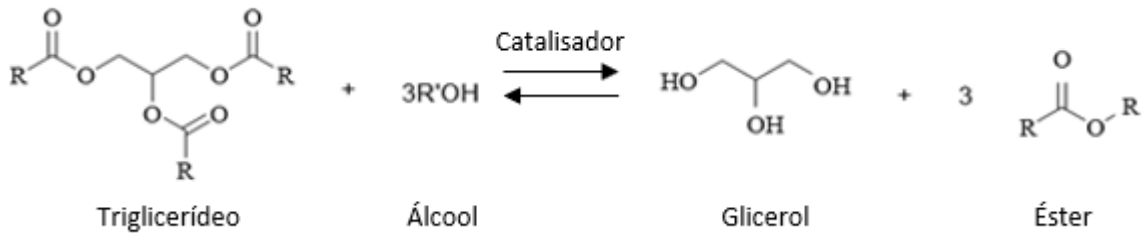

Figura 1 – Reação de transesterificação
Fonte: OLIVEIRA, 2012.

A reação envolve três etapas consecutivas e reversíveis (Figura 2), onde primeiramente ocorre a reação do triglicerídeo com um álcool gerando diacilglicerol,

seguida da reação do diacilglicerol com uma segunda molécula de álcool produzindo um moniacilglicerol. Por fim, ocorre a reação de outra molécula de álcool com o produto anterior gerando glicerol, liberando um mol de éster em cada etapa (OLIVEIRA, 2012; IJAZ *et al*., 2016):

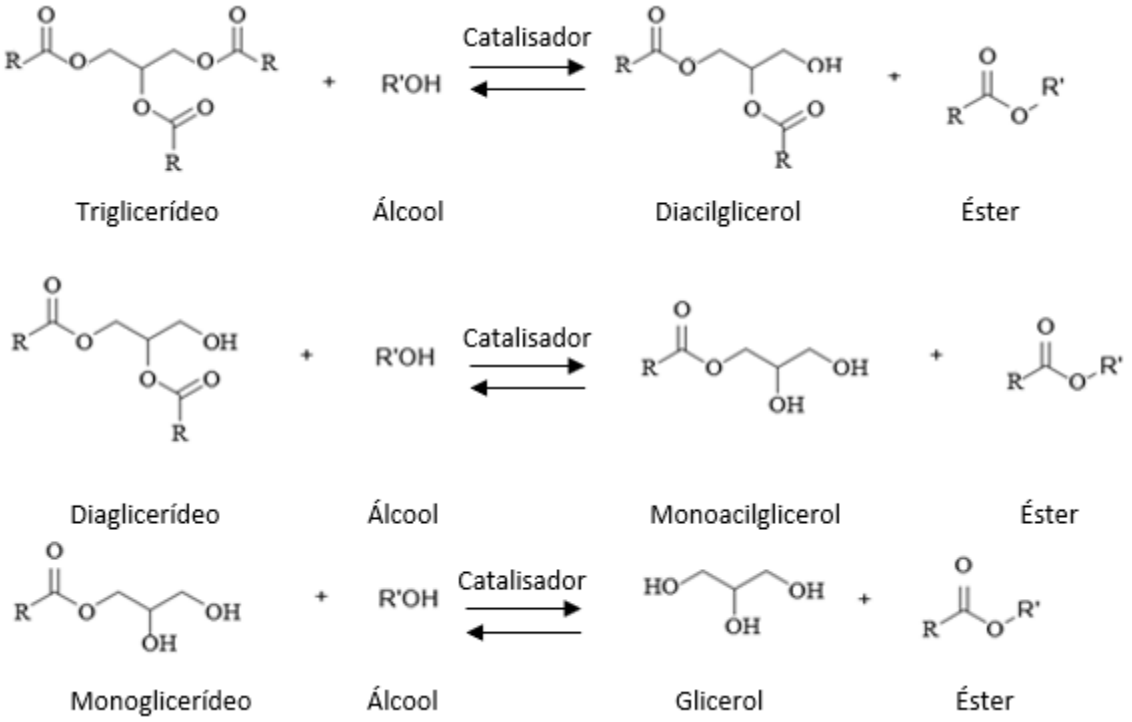

Figura 2 – Etapas da reação de transesterificação
Fonte: OLIVEIRA, 2012.

Devido à reversibilidade das reações promovidas na técnica de transesterificação, é necessário empregar um excesso de álcool no processo para que haja um deslocamento do balanço para o sentido da formação dos produtos, para maior produção de ésteres através da completa conversão dos ácidos graxos (D'AGOSTO, 2015). Sendo assim, ao invés da razão molar de 3:1 de álcool para óleo é comum a utilização de uma razão de no mínimo 6:1, variando até 12:1, de acordo com o tipo de álcool e de óleo utilizado (ENCINAR *et al*., 2002; RAMADHAS; JAYARAJ; MURALEEDHARAN, 2005; BALASUBRAMANIAN; SIRCAR; SIVAKUMAR, 2018; KHIARI *et al*., 2018).

Os álcoois mais utilizados são o metanol e o etanol, seguidos do propanol butanol e álcool amílico (NAVAS *et al*., 2018). Em condições semelhantes de transesterificação o metanol é capaz de alcançar maior rendimento (BOZ; KARA, 2009), ademais, o consumo de metanol é reduzido e a separação dos ésteres e da

glicerina ocorre com maior facilidade (SILVA, 2008). Já o etanol apresenta menor toxicidade e possui grande oferta no Brasil, porém sua cadeia mais longa tornam os ésteres etílicos mais solúveis na glicerina (D'AGOSTO, 2015). Sendo assim, ambos apresentam vantagens e desvantagens como constam na Tabela 3:

Tabela 3 – Vantagens e desvantagens ao comparar o uso de metanol fóssil etanol na produção do biodiesel

Álcool	**Vantagens**	**Desvantagens**
Metanol fóssil	- Consumo no processo é cerca de 45% menor; - Custo reduzido em quase 50%; - Maior Reatividade; - Tempo de reação reduzido em mais de 50%; - O consumo de eletricidade é menos da metade comparado ao etanol.	- É tradicionalmente um produto fóssil; - Alta toxicidade; - Maior volátividade e chama invisível.
Etanol	- Produção consolidada no Brasil; - Produz Biodiesel com maior índice de cetano e maior lubricidade, comparado ao metanol; - Produz combustível 100% renovável; - Gera maior ocupação e renda no meio rural; - Menor toxicidade; - Menor volatividade.	- Produz ésteres com maior afinidade à glicerina; - Os custos de produção pode ser 100% maiores que o metílico.

Fonte: Adaptado de SILVA, 2008.

Devido à alta polaridade do álcool, a velocidade da agitação na reação é de extrema importância, já que o triglicerídeo é apolar e viscoso (OLIVEIRA, 2012). Em geral, uma agitação de 600 rpm promove uma melhor conversão quando mantidas constantes todas as outras variáveis, como temperatura e tempo da reação (VYAS; SUBRAHMANYAM; PATEL, 2009).

De acordo com Nadaleti (2015), em decorrência da reversibilidade das reações, o tempo de reação se torna uma variável importante, uma vez que o equilíbrio reacional pode acontecer em tempos variáveis. O autor cita ser usual o emprego de 60 minutos de reação, entretanto, é possível encontrar autores que adotam mais ou menos tempo, de acordo com a necessidade da matéria-prima e do tipo de catalisador

empregado, sendo encontrado em literatura períodos de 30 à 180 minutos, por exemplo (DEMERBIAS, 2009; PUTRI; RELIGIA; ANGGRAINI, 2018; SARI *et al*. 2018; WIDIARTI *et al*., 2018).

Para que haja elevação da taxa da reação de transesterificação é adotado o emprego de catálises homogêneas, enzimáticas ou heterogêneas (BASKAR *et al*., 2017), sendo usual o emprego de catalisadores homogêneos básicos, como Hidróxido de Sódio (NaOH) e Hidróxido de Potássio (KOH), para a produção de biodiesel comercial (CHENDYNSKI *et al*., 2016; GUTIÉRRES-ZAPATA *et al*, 2017). De acordo com Nadaleti (2015), a catálise homogênea alcalina ocorre com maior velocidade e facilidade, além de requerer menor quantidade de álcool que a ácida. O autor afirma ainda que a quantidade de catalisador é de extrema importância, uma vez que pode desfavorecer a reação dependendo da sua origem e do estado de conservação do óleo.

Durante a transesterificação ocorre ainda a reação de saponificação entre o triacilglicerol com o catalisador básico, formando sabões responsáveis por dificultar a separação das fases e reduzir o catalisador disponível para a transesterificação em si, elevando o custo de produção (JITPUTTI, 2006; LOTERO *et al*., 2005).

2.3.3 Glicerol

A produção de 10 kg de biodiesel gera cerca de 1 kg de glicerol (PAPANIKOLAOU *et al*., 2017), assim, a oferta de glicerol cresce linearmente com o aumento da produção do biocombustível. Apenas no ano de 2017, o Brasil obteve uma produção acima de 4 milhões de metros cúbicos de biodiesel (ANP, 2018), ou seja, uma geração de mais de 400 mil toneladas de glicerol. É previsto que em 2021 a produção mundial de biodiesel acarrete a geração de 3 milhões toneladas de glicerol (KOUTINAS *et al*., 2014).

A alta produção do biocombustível propiciou a queda do preço deste subproduto, enfraquecendo seu mercado (OKOYE; HAMEED, 2016). Atualmente, o glicerol é submetido à processos de separação e purificação para se obter a glicerina a ser comercializada, com baixo valor agregado, para indústrias químicas de cosméticos e limpeza (ALMEIDA; ANDRADE; SANTOS, 2017). Tendo em vista que o setor industrial faz uso apenas da glicerina, o glicerol não refinado se caracteriza como um passivo ambiental (SILVA, 2016).

Sendo o glicerol um composto estável que consiste em três grupos funcionais hidroxila com propriedades hidrofílicas e higroscópicas, é capaz de elevar o potencial em inúmeras aplicações, ou seja, sua estrutura molecular e propriedades físico-químicas conferem multifuncionalidade ao composto (OKOYE; HAMEED, 2016). A composição química do glicerol varia de acordo com o catalisador e eficiência da transesterificação, porém a eficiência na recuperação do biodiesel e a presença de impurezas na matéria-prima também podem influir em sua composição da fração bruta de glicerol (YANG; HANNA; SUN, 2012). De acordo com Hansen *et al*. (2009), as composições químicas de gliceróis brutos oriundo de diferentes produtores apresentam variação entre 38% e 96% no teor de glicerina.

2.4 Biogás e metano

Produzido por microrganismos mesófilos e termofílicos na ausência de ar em diferentes ambientes, como estações de tratamento de efluentes, aterros e plantas de digestão para resíduos orgânicos agrícolas (RASI; VEIJANEN; RINTALAI, 2007; RYCKEBOSCH; DROUILLON; VERVAEREN, 2011), o biogás é uma fonte de energia que pode ser empregada para a substituição de combustíveis fósseis para carros, eletricidade e ainda como fonte de calor (TAHERZADEH *et al*., 2008; WEILAND, 2010).

O biocombustível é composto majoritariamente de CH_4, de 40 à 75%, e CO_2, de 15 à 60%, contendo ainda traços de outros componentes, como água (H_2O), de 5 à 10%, sulfeto de hidrogênio (H_2S), de 0,005 à 2%, siloxanos, de 0 à 0,02%, hidrocarbonetos halogenados, <0,6%, monóxido de carbono (CO), <0,6%, e nitrogênio (N_2), de 0 à 2%. Para a conversão do biogás em bioenergia, torna-se essencial o alto teor de CH_4 em sua composição, uma vez que possui elevado poder calorífico, enquanto um alto teor de CO_2 interfere negativamente por ser inerte em termos de combustão. (RYCKEBOSCH; DROUILLON; VERVAEREN, 2011). Para o uso do biogás para fins energéticos são realizados processos de purificação a fim de obter biometano, onde o combustível apresenta pelo menos 90% de CH_4 em sua composição (SRINUANPAN; CHEIRSILP; PRASERTSAN, 2018).

A produção de biogás via digestão anaeróbia de substratos orgânicos é relatada como uma das técnicas mais eficientes energeticamente e vantajosas ao meio ambiente para geração de biocombustíveis, reduzindo emissões de GEE quando substituto de combustíveis fósseis (WEILAND, 2010). O processo é realizado por um

consórcio de microrganismos dependente de diversos fatores, como pH, temperatura, relação C/N, entre outros (YADVIKA, *et al*., 2014).

2.4.1 Digestão anaeróbia

A digestão anaeróbia é uma técnica de tratamento de efluentes capaz de promover a remoção da matéria orgânica e produzir bioenergia por meio da interação da microbiota presente nos reatores e seus parâmetros com a matéria orgânica, transformando compostos orgânicos complexos em substâncias como o metano e o dióxido de carbono (GONZAGA; BARBOSA, 2016; NESHAT *et al*., 2017).

O processo (Figura 3) tem início com a hidrólise de materiais particulados complexos em compostos orgânicos simples, o segundo estágio é o da acidogenese, onde as bactérias fermentativas acidogênicas consomem os compostos orgânicos simples, transformando-os em ácidos orgânicos a serem consumidos por bactérias acetogênicas e arqueas metanogênicas. Na acetogenese, as bactérias acetogênicas fornecem substrato para os microrganismos metanogênicos, através da oxidação dos ácidos orgânicos. Por fim, ocorre a formação do biogás, onde os microrganismos metanogênicos atuam sobre os produtos gerados durante todo o processo (CHERNICHARO, 1997):

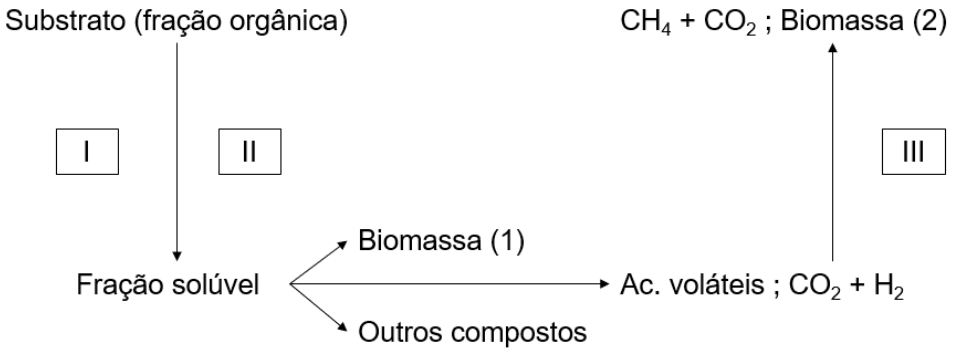

Figura 3 – Resumo esquemático do processo anaeróbio
I- hidrólise; II- acidogenese e acetogenese; III- metanogênese. Biomassa (1): crescimento consorciado de bactérias hidrolíticas e acidogênicas. Biomassa (2): microrganismos metanogênicos
FONTE: BUENO, 2010.

A digestão anaeróbia ocorre em três diferentes gamas de temperatura, a psicrofílica (<25 °C), mesofílica (25–40 °C) e termofílica (45–60 °C) (MAMUNA; TORIIA, 2017), sendo que a temperatura recomendada pela literatura para a produção de biogás fica em torno de 35°C (THAKUR *et al*., 2016). Outro parâmetro da digestão

anaeróbia é o potencial hidrogeniônico, de acordo com Khalid *et al*. (2011), é recomendada a neutralidade do meio para o desenvolvimento de bactérias metanogênicas, onde o pH abaixo de 6,0 ou acima de 8,5 leva a inibição do processo.

A relação entre o carbono e nitrogênio do substrato é um indicador importante para o controle de sistemas de tratamento biológico, onde o carbono fornece energia para os microrganismos e o nitrogênio favorece o crescimento (SILVEIRA, 2009). Biodigestores anaeróbios devem ser operados com uma relação de 20/1 a 30/1 de carbono para nitrogênio (PEREIRA, 2013), uma vez que substratos de relações C/N superiores são de baixo pH, baixa capacidade de tamponamento e possibilitam acúmulo de ácido graxo volátil no processo de digestão. Já relações C/N inferiores apresentam concentrações relativamente altas de amônia, inibindo a digestão anaeróbica pelo excesso necessário para o crescimento microbiano (WANG *et al*., 2012).

2.4.2 Codigestão anaeróbia com glicerol

A codigestão anaeróbia é uma técnica que promove a digestão simultânea de dois ou mais substratos que possuam características complementares, destacando-se como um processo promissor para produção de biogás, uma vez que eleva a estabilidade e eficiência do sistema, potencializando a produção de biogás e do rendimento de metano (CAPODAGLIO; RANIERI; TORRETTA, 2016; ANJUM *et al*. 2017; HAGOS *et al*., 2017; MARAGKAKI *et al*., 2017).

A técnica é capaz de aumentar de 25% a 400% a produção de biogás em relação à digestão anaeróbica de apenas um dos substratos (HAGOS *et al*, 2017), sendo assim, eleva o rendimento da digestão anaeróbia de resíduos sólidos e efluentes por meio de sinergismos estabelecidos através da mistura de diferentes substratos, como o suprimento de nutrientes, o balanço da relação C/N, a disponibilidade de matéria orgânica, a melhor capacidade de tamponamento e a diluição de compostos inibitórios (MAZARELI, 2015; AGDAG; SPONZA, 2007; XIE *et al*., 2011; CAPSON-TOJO *et al*., 2017; MARAGKAKI *et al*., 2017).

A falta de subsídios econômicos necessários para a purificação do subproduto da produção de biodiesel torna primordial a busca por novas aplicações para a glicerina excedente, como o seu incremento como cosubstrato na digestão anaeróbia de resíduos e/ou efluentes orgânicos para geração de biogás (KONRAD *et al*., 2014). A disposição incorreta do glicerol é capaz de promover impactos ambientais

negativos, já que a glicerina bruta em contato com a água se transforma em um tipo de sabão que dificulta a oxigenação do meio através de sua precipitação (BERTOZZO, 2013).

O uso de um cosubstrato como o glicerol na digestão anaeróbia pode facilitar o processo de produção de biogás e CH_4, já que alguns microrganismos podem utilizá-lo como fonte de carbono promovendo o equilíbrio necessário da razão C/N do meio (JONES; WOODS, 1986; MATA-ALVAREZ; MACÉ, S.; LLABRÉS, 2000; YEN; BRUNE, 2007; MEIER *et al*., 2016; KURAHASHI *et al*., 2017).

A aplicação do subproduto do biodiesel como cosubstrato da digestão anaeróbia de efluente de fecularia, em estudo realizado por Lins *et al*. (2014), promoveu uma produção 94% maior quando comparado a digestão anaeróbia do mesmo efluente sem adição de glicerol. Os mesmos autores encontraram uma elevação de 46% da produção de metano com a adição de glicerol ao processo de digestão anaeróbia. Larsen (2009) constatou que, enquanto a adição de 2% de glicerina na digestão anaeróbia de manipueira (efluente da fecularia) promove crescimento da produção de biogás, enquanto a adição de 3% é capaz de gerar queda na produção.

A adição de glicerol também favorece a produção de biogás na sua codigestão com dejeto suíno. Aguilar-Aguilar *et al*. (2017) relatam máxima produção de biogás na digestão de 4 g/L de glicerol bruto e 5 g/L de dejeto suíno por 35 dias, totalizando 521,5 mL de biogás gerado por grama de Demanda Química de Oxigênio (DQO) inicial. Araújo (2012) afirma que a utilização de glicerina bruta como cosubstrato também é eficiente na produção de biogás via digestão anaeróbia de dejetos ovinos, promovendo maior aporte energético quando comparado com a digestão sem sua adição.

De acordo com Bertozzo (2013), o processo de codigestão anaeróbia de dejetos bovinos leiteiros e glicerina bruta proporciona maior produção de biogás que a digestão individual dos dejetos, quando adicionada em cargas diárias menores que 2,5%. Siqueira (2012), que também estudou a adição de diferentes concentrações de glicerina bruta nos dejetos bovinos leiteiros, concluiu que a adição de 4% de glicerol resultou na maior produção de biogás e que a adição de 6% causou instabilidade do processo devido ao provável acúmulo de ácidos graxos voláteis. Tal discrepância pode estar relacionada à composição química do glicerol e da glicerina bruta, uma vez que ela varia de acordo com o tipo do catalisador e álcool empregados na produção

do biodiesel, assim como na eficiência da transesterificação e da recuperação e purificação do biodiesel (YANG; HANNA; SUN, 2012).

2.5 Atividade Metanogênica Específica

A AME é um dos métodos mais utilizados para quantificar e avaliar a atividade dos microrganismos responsáveis pela produção de metano, sendo de elevada importância para compreensão do comportamento da cultura quanto ao seu potencial de produção do gás (POETSCH; KOETZ, 1998; FLORENTINO; BISCARO; PASSOS, 2010; LOVATEL, 2016).

Embora não haja um protocolo padronizado para a execução do teste em relação a metodologia que deve ser seguida, sua importância é reconhecida em diversas literaturas, já que além de quantificar a atividade metanogênica específica de lodos anaeróbios, também pode ser utilizada na avaliação de inóculos na partida de reatores com diferentes grupos fisiológicos presentes nos lodos, avaliação do efeito inibitório de elementos tóxicos na digestão anaeróbia, avaliação da atividade da biomassa em reatores anaeróbios e potencial de biodegradabilidade (LOUZADA *et al*., 2005; SANTOS; CAMMAROTA; FRANÇA, 2005; SILVA *et al*., 2005; SONG *et al*., 2006; ZHOU; QIU, 2006; ENRIGHT *et al*., 2009; CHELLAPANDI; PRABAHARAN; UMA, 2010; ALVAREZ; CERVANTES, 2012; OZ *et al*., 2012; SCHNEIDERS *et al*., 2013).

A AME deve ser realizada em condições controladas de laboratório de modo que garanta a atividade bioquímica máxima de conversão de substratos orgânicos em biogás, através da incubação de uma pequena quantidade de biomassa em meio contendo nutrientes, viabilizando a determinação da capacidade máxima de produção de metano por unidade de tempo e por unidade de massa bacteriana (POETSCH; KOETZ, 1998; AQUINO *et al*., 2007).

As atividades bioquímicas responsáveis pela geração de metano são extremamente dependentes de condições ambientais como a temperatura, pH, potencial redox e disponibilidade de nutrientes. Sendo assim, é comum a preparação e inserção de nutrientes, glicose e bicarbonato de sódio para a ocorrência da máxima atividade metabólica das bactérias e simulação das condições dos reatores anaeróbios empregados em maiores escalas. A determinação da AME, usualmente realizada em batelada, se dá através de cálculo baseado na medição direta da taxa de produção de metano ou consumo de substrato, por unidade de biomassa (Sólidos

Suspensos Voláteis - SSV) e unidade de tempo (MONTEGGIA, 1997; LOVATEL, 2016).

Além de auxiliar no controle de operação dos reatores, a AME também apresenta grande utilidade na determinação da degradabilidade de efluentes em condições anaeróbias devido ao fato de que a remoção de elétrons equivalentes, ou seja, compostos reduzidos causadores da DQO, do efluente a ser tratado apenas ocorrerá com a formação do metano. Assim, a AME permite estabelecer a capacidade máxima de remoção de DQO da fase líquida, possibilitando uma estimativa sobre a carga orgânica máxima que pode ser aplicada, minimizando o risco de desbalanceamento do processo anaeróbio (POETSCH; KOETZ, 1998; AQUINO *et al*., 2007).

3. MATERIAIS E MÉTODOS

A pesquisa experimental e a determinação do potencial teórico de produção dos biocombustíveis e bioenergia ocorreram de acordo com as etapas descritas no Fluxograma apresentado abaixo (Figura 4):

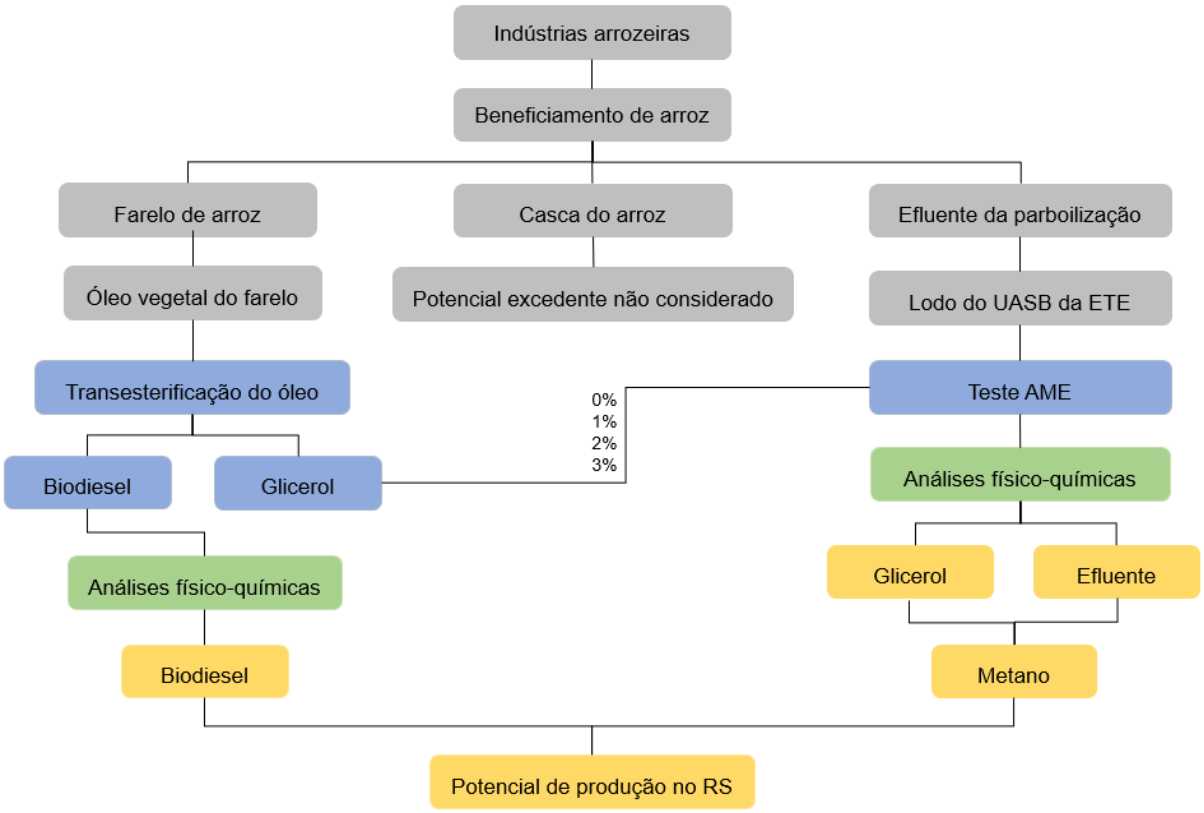

Figura 4 – Fluxograma da execução do projeto.

3.1 Produção de Biodiesel

3.1.1 Delineamento Experimental

A determinação das condições ideais para a produção do biodiesel de óleo vegetal de farelo de arroz refinado via transesterificação metílica, utilizando o KOH como catalisador (NADALETI, 2005), foi realizada por meio de delineamento experimental, através de arranjo fatorial 2^3 (Tabela 4):

Tabela 1 – Arranjo Fatorial 2^3

Razão molar	Catalisador	Tempo
-	-	-
+	-	-
-	+	-
+	+	-
-	-	+
+	-	+
-	+	+
+	+	+

O arranjo fatorial resultou em oito pontos com diferentes condições de produção de biodiesel oriundos de um ponto central com condições adaptadas de metodologia de Nadaleti (2015) e executado em triplicata. As variações das condições da metodologia aplicada ocorreram na razão molar entre o óleo vegetal e o álcool, a quantidade de catalisador, assim como o tempo no qual a reação foi aquecida e a agitada (Tabela 5):

Tabela 2 – Delineamento Experimental

Tratamento	Razão molar (álcool:óleo)	Catalisador (%)	Tempo (minutos)
P1	6,0:1	1,00	40
P2	9,0:1	1,00	40
P3	6,0:1	1,50	40
P4	9,0:1	1,50	40
P5	6,0:1	1,00	80
P6	9,0:1	1,00	80
P7	6,0:1	1,50	80
P8	9,0:1	1,50	80
PC	**7,5:1**	**1,25**	**60**

3.1.2 Transesterificação e purificação do biodiesel

A execução da reação de transesterificação se deu através de metodologia adaptada de Nadaleti (2015). Primeiramente o óleo foi aquecido em um agitador magnético até atingir 80° C, nesse momento foi inserida a barra magnética, responsável por fornecer a agitação do meio (600 rpm), e o álcool com o catalisador já diluído (Figura 5):

Figura 5 – a) Óleo vegetal refinado de farelo de arroz no agitador magnético sendo aquecido; b) catalisador Hidróxido de Potássio diluído; c) agitação e aquecimento promovendo a reação de transesterificação na mistura de óleo, catalisador e álcool.

Após o tempo de reação indicado pelo delineamento experimental, os produtos da reação foram transferidos para um balão de separação, onde permaneceram por um período de 3 horas, para em seguida ser realizada a retirada do glicerol. A fim de promover a purificação do biodiesel, foi adicionada água destilada aquecida à 80 °C no balão de separação, em uma proporção igual à um terço do volume de óleo utilizado na transesterificação. Após 24 horas foi realizada a separação do biodiesel e da água. A água residual foi descartada e o biodiesel alocado em estufa à 65 °C por um período de 12 horas, visando promover a remoção da umidade (Figura 6):

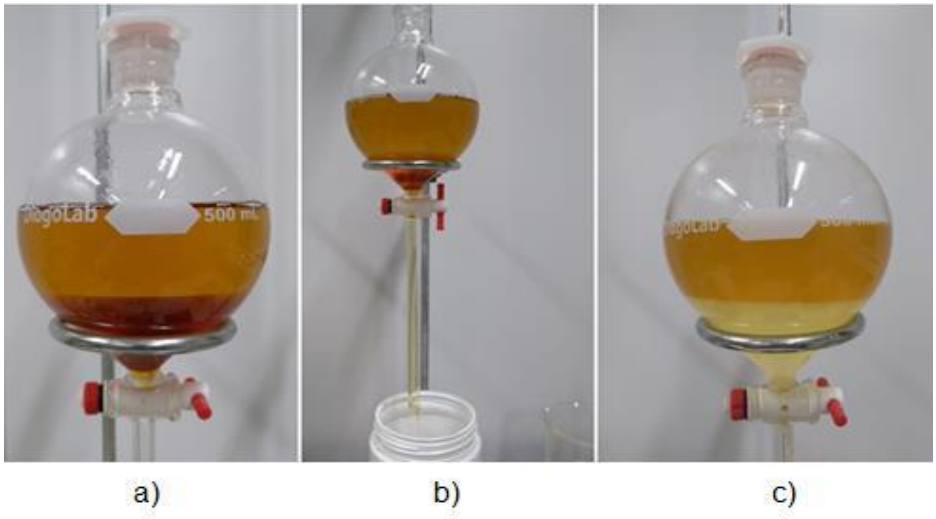

Figura 6 – a) Decantação do glicerol; b) remoção do glicerol; c) purificação do biodiesel.

3.1.3 Análises

O rendimento da reação de transesterificação foi determinado com base no volume de óleo vegetal empregado na reação e o volume de biodiesel produzido. A Viscosidade Cinemática (v), o Índice de Acidez (IA) e o Índice de Iodo (II) foram obtidos de acordo com os métodos padrão da ASTM, enquanto o Índice de Saponificação foi determinado de acordo com o método AOAC. Ademais, a umidade foi determinada pela perda de umidade por dessecação a 105 °C e o equipamento utilizado para determinar a Viscosidade Cinemática foi um Viscosímetro *Saybolt* modelo Q288SR. O método padrão de cada um dos parâmetros do biodiesel constam na Tabela 6:

Tabela 3 – Método padrão utilizado em cada parâmetro

Parâmetro	Método padrão
Viscosidade Cinemática	ASTM D445 (ASTM 2006)
Índice de Acidez	ASTM D664-67 (ASTM 2011)
Índice de Iodo	ASTM D459-97 (ASTM 1997)
Índice de Saponificação	AOCS CD3-25 (AOAC 1997)
Umidade	Perda por dessecação (INSTITUTO ADOLFO LUTZ, 1985)

Os Ésteres Metílicos de Ácidos Graxos (FAME) obtidos a partir da reação de transesterificação foram identificados em um cromatógrafo a gás equipado com detector de ionização de chama, *Shimadzu QP-2010*. A análise quantitativa foi realizada por normalização de área usando o software *GC Solution* em comparação com o *FAME Mix Padrão C4C24*, *Supelco*. Na Tabela 7 estão detalhadas as condições cromatográficas:

Tabela 4 – Condições da análise cromatográfica de ésteres metílicos de ácidos graxos do biodiesel

Parâmetro	Condições
Coluna	(100 m x 0,25 m x 0,25 µm)
Gás transportador	Nitrogênio
Volume injetado	1 µL
Razão de divisão	1:25
Pressão	44,695
Fluxo	1,2 mL/min
Temperatura da injeção	250 °C
Rampa de aquecimento	100 °C (5 min)– 7 °C min^{-1} to 200 °C (5 min)– °C min^{-1} to 230 °C (10 min)
Detector	Detector de ionização de chama
Temperatura do Detector	250 °C

Fonte: PACHECO *et al*. (2018).

A fim de determinar as melhores condições para a produção do biocombustível, foi realizada análise estatística dos resultados no *software IBM SPSS Statistics* através do Teste F e do Teste de Tukey, ambos a 5% de significância.

3.2 Atividade Metanogênica Específica

A determinação das concentrações às quais se apresentam o poder de potencialização e de inibição do glicerol ao lodo da parbolização do arroz proveniente de Reator UASB (*Upflow Anaerobic Sludge Blanket*) foi realizada a partir de adaptação da metodologia desenvolvida por Nadaleti em 2016, em fase de análise de concessão de patente, e análise estatística dos resultados.

Os biodigestores do teste de AME foram acondicionados à 35° C, em banho de aquecimento com termostato, e alimentados com 14 mL de lodo retirado do UASB da Estação de Tratamento de Efluentes (ETE) de uma indústria de parboilização de arroz (inóculo), 473 mL de água destilada, 13 mL de solução de glicose (80 g/L), 1 g de bicarbonato de sódio e diferentes proporções de glicerol (0%, 1%, 2% e 3%), sendo que para cada concentração de glicerol será realizada uma triplicata. Os biodigestores utilizados possuem um volume útil de 625 mL dos quais 20% é reservado para operar como *headspace:*

3.2.1 Quantificação da geração de metano

O sistema de quantificação desenvolvido por Nadaleti (2016), opera a partir do uso de um frasco de vidro, preenchido com solução de Hidróxido de Sódio (NaOH)

5% e indicador fenolftaleína, de modo que promove a dissolução do CO_2 no NaOH, promovendo a purificação do biogás e assim, permitindo a quantificação do metano gerado.

O biodigestor recebe uma conexão com o medidor, de modo que promova o transporte do biogás até a solução de NaOH presente no sistema de medição, as conexões são vedadas com silicone acético incolor, impedindo perdas de CH_4 para a atmosfera. A parte inferior do medidor recebe um tubo, onde é alocada uma agulha do tipo borboleta que permite o escape, por capilaridade, da solução de NaOH com fenoftaleína, que por fim é quantificada através da pesagem do frasco de coleta, utilizando-se fator de correção de acordo com o peso médio da solução de NaOH 5% e fenolftaleína. O sistema completo pode ser observado na Figura 7:

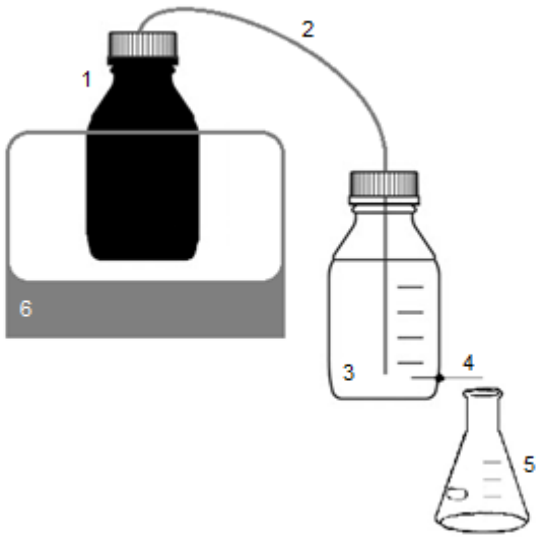

Figura 7 – Sistema utilizado para quantificar a produção de metano
1. Biodigestor; 2. Conexão; 3. NaOH com fenolftaleína; 4. Agulha; 5. Frasco de coleta; 6. Banho de Aquecimento

A quantificação do metano produzido foi realizada em intervalos de uma hora durante as primeiras doze horas de experimento e, posteriormente, a cada doze horas por um período de sete dias.

3.2.2 Determinação da AME

De acordo com metodologia de Aquino *et al*. (2007), o valor da AME, em $gDQOCH_4(gSSV.d)^{-1}$, foi calculado a partir da quantidade de lodo utilizada como

inóculo (gSSV) e a taxa máxima de produção de metano (gDQOCH$_4$.d^{-1}), fazendo uso da correção do volume do mol do gás em CNTP, uma vez que o experimento foi realizado a 35 °C.

3.2.3 Análises físico-químicas

Foram realizadas análises de DQO, Potencial Hidrogeniônico (pH) e Sólidos Totais (SST), Fixos (SSF) e Voláteis (SSV), de amostras de entrada e saída dos biodigestores. A DQO e o pH foram determinados com base na metodologia de *Standard Methods for the examination of water & wastewater* (2005), enquanto os sólidos totais, fixos e voláteis foram determinados pelos métodos A, B e C, respectivamente, da NBR 10664 (ABNT, 1989).

3.3 Potencial de produção de biocombustíveis e energia

Com base nos dados disponíveis nas licenças de operação das indústrias arrozeiras do Rio Grande do Sul concedidas pela Fundação Estadual de Proteção Ambiental (FEPAM, 2019), quanto a capacidade máxima de produção de arroz e vazão máxima de efluente de cada empreendimento do ramo no estado, dados da literatura e resultados obtidos nas etapas anteriores desse estudo, foi realizada a quantificação do potencial de produção dos biocombustíveis. Foram aplicadas três metodologias distintas para o cálculo do potencial de geração de metano para as indústrias de parboilização de arroz do Rio Grande do Sul a partir da codigestão anaeróbia:

- Speece (2001)

$$COD_{CH_4} = Q_{ww} * [(S_O - S) - ((Y_{obs} * K_{solid}) * (S_O - S))] \quad (1)$$

Onde:

COD_{CH_4}: DQO convertida em metano (kgDQO$_{CH4}$d^{-1});

Q_{ww}: vazão de efluente (m³/y);

S_O: concentração de DQO total no afluente (in kgDQOm^3);

S: concentração de DQO filtrada no efluente (kgDQOm^3);

Y_{obs}: coeficiente de produção de sólidos no sistema ($kgDQO_{lodo}kgDQO_{aplicada}^{-1}$), igual a 0,11;

K_{solid}: fator de conversão de sólidos voláteis totais (SVT) em DQO ($kgCODkgTVS^{-1}$), igual a 1,42.

Conversão da DQOCH4 de $kgDQO_{CH4}.d^{-1}$ para $m^3CH_4.d^{-1}$:

$$\mathrm{Q_{CH_4}} = \frac{\mathrm{COD_{CH_4}}}{\mathrm{K(t)}} \quad (2)$$

Onde:

$\mathrm{Q_{CH_4}}$: volume de metano produzido ($m^3.d^{-1}$);

$\mathrm{K(t)}$: fator de correção da temperatura de operação do reator ($kgCODm^3$).

Fator de correção de temperatura:

$$\mathrm{K(t)} = \frac{\mathrm{P\,K}}{\mathrm{R\,T}} \quad (3)$$

Onde:

P: pressão atmosférica (atm);

K: DQO correspondente a 1 mol de CH_4 ($DQOmol^{-1}$), igual a 64g;

R: constante universal dos gases ($atmL(mol.K)^{-1}$), igual a 0,08206;

T: temperatura de operação do reator (K).

- Metcalf & Eddy (2003)

$$\mathrm{X_m} = \mathrm{COD_{af}} - \mathrm{COD_{ef}} - \mathrm{COD_{SSV}} - \mathrm{COD_{CH_4}} \quad (4)$$

Onde:

$\mathrm{X_m}$: temperatura de operação do reator ($kgDQO.m^3$);

$\mathrm{COD_{af}}$: DQO afluente no reator ($kgDQO.m^3$);

$\mathrm{COD_{ef}}$: DQO efluente no reator ($kgDQO.m^3$);

$\mathrm{COD_{SSV}}$: DQO associada a matéria orgânica volátil em suspensão no reator (kgDQO.m^{-3});

$\mathrm{COD_{CH4}}$: quantidade de oxigênio necessária para oxidar completamente o metano para dióxido de carbono e água, igual a 0,35 (m^{3}CH$_4$(kgDQO^{-1})).

Volume ocupado por 1 mol de gás metano considerando temperatura do reator:

$$\mathrm{V_{CH_4}} = \frac{\mathrm{nRTz}}{\mathrm{P}} \quad (5)$$

Onde:

$\mathrm{V_{CH_4}}$: volume ocupado por 1 mol de gás metano (L);

n: número de mols do metano;

R: constante ideal dos gases (atmL(molK)$^{-1}$), igual a 0,082057;

T: temperatura (K);

Z: fator de compressibilidade do metano;

P: pressão (atm).

Desvio da idealidade de um gás real:

$$\mathrm{Z} = \frac{\mathrm{V_{Real}}}{\mathrm{V_{Ideal\,gas}}} \quad (6)$$

Onde:

$\mathrm{V_{Real}}$: volume molar real calculado a partir da equação de estado de Van der Waals;

$\mathrm{V_{Ideal\,gas}}$: volume molar ideal do metano.

Equivalente de DQO convertido em metano em condições anaeróbias:

$$CH_{4_{equivalente}} = \frac{\mathrm{V_{CH_4}}}{\mathrm{O_{CH_4}}} \quad (7)$$

Onde:

$CH_{4_{equivalente}}$: metano equivalente a DQO convertida (m^{3}CH$_4$(kg.COD)$^{-1}$);

O_{CH_4}: quantidade de oxigênio requerido para oxidar 1 mol de metano, igual a 64 ($gCODmol^{-1}$).

$$Q_{CH_4} = COD_{CH_4} * CH_{4_{equivalente}} \quad (8)$$

Onde:

Q_{CH_4}: produção de gás metano ($m^3.d^{-1}$).

- UNFCCC (2012)

$$Q_{CH_4} = Q_{ef} * COD_{ef} * Bo_{CH_4} * MCF * CFU * \eta * COD \quad (9)$$

Onde:

Q_{CH_4}: quantidade de metano ($kgCH_4h^{-1}$);

Q_{ef}: vazão efluente (m^3h^{-1});

COD_{ef}: DQO do efluente ($kgDQOm^{-3}$);

Bo_{CH_4}: capacidade máxima de produção de metano em massa ($kgCH_4(kgDQO)^{-1}$), igual a 0,25;

MCF: fator de correção de metano, referente a reatores anaeróbios, reatores UASB e reatores de leito fixo, igual a 0,8.

CFU: fator de correção devido à incerteza, igual a 0,9;

ηCOD: eficiência de remoção de DQO referente a reatores UASB, igual a 0,7;

O potencial de produção de energia elétrica e térmica a partir dos biocombustíveis serão cálculos com base na Equação 11 (NADALETI, 2017), sendo necessário determinar ainda o potencial de energia química, Equação 10 (NADALETI, 2017), em diferentes cenários a serem determinados de acordo com os resultados gerados nas etapas anteriores desse estudo.

$$CE = \overline{Q} * LCV \quad (10)$$

Onde:

CE: produção de energia química ($MJ.d^{-1}$);

$\bar{Q}$: volume de combustível ($m^3.d^{-1}$);
LCV: poder calorífico inferior do biocombustível ($MJ.m^{-3}$).

$$E = CE * \eta M * C \quad (11)$$

Onde:
E: produção de energia ($kW.d^{-1}$);
ηM: eficiência do motor (%), igual a 85 para geração de energia térmica e 45 para geração de energia elétrica para um sistema CHP alimentado com metano (SILVEIRA, 2019) e 80 para geração de energia térmica e 20 para geração de energia elétrica para o sistema CHP alimentado com biodiesel (KRISHNA *et al*., 2010);
C: conversão de MJ para kWh.

4. RESULTADOS E DISCUSSÃO

Os resultados dessa dissertação foram divididos em três artigos, conforme descrição a seguir:

Artigo 1: *South Brazilian potential of rice bran oil biodiesel production: production, physicochemical analysis and potential*, submetido em dezembro de 2019 na revista *Biofuels, Bioproducts and Biorefining*;

Artigo 2: *Optimization of methane production from rice parboiling anaerobic sludge by the addition of crude glycerol of rice bran oil biodiesel: Specific Methanogenic Activity*, submetido em fevereiro de 2020 na revista *Renewable Energy*;

Artigo 3: *Generation of biodiesel, biogas, thermal and electric energy from waste and effluent of rice parboiling industries in Brazil*, submetido em fevereiro de 2020 na revista *Environmental Science and Pollution Research*.

4.1 Artigo 1: South Brazilian potential of rice bran biodiesel production: physicochemical analysis and energetic study

ABSTRACT

Brazil has an obvious socioeconomic advantage to produce biofuel because of the availability of raw materials from the agro-industrial sector. Brazil is the ninth largest rice producer in the world, with the state of Rio Grande do Sul accounting for 70.1% of the production. Thus, rice cultivation is a low-cost source of triglycerides for biodiesel production to be explored in the Rio Grande do Sul. The rice processing generates a by-product, the rice bran, from which it is possible to extract vegetable oil. Thus, the objective of this study was the production of biodiesel from rice bran oil in order to determine the conditions in which its production occurs more efficiently, promoting characteristics in accordance with the norms, via methyl transesterification with homogeneous basic catalysis. The results determined the feasibility of producing biodiesel according to National Petroleum Agency (ANP), American Society for Testing and Materials (ASTM) and European Standardization Committee (EN) specifications for Kinematic Viscosity, Moisture, Acidity Index, Iodine Index, Saponification Index and yield. For the methodology applied, among the variations studied, the treatment using factorial arrangement that presented results within the norms and highest yield (98.90%) was that of 6:1 molar ratio of alcohol to oil, 1.0% of the catalyst and 120 minutes heating and stirring.
Keywords: Biofuel; potassium hydroxide; biodiesel; rice bran oil.

1. Introduction

In the global context, oil makes up around 33.3% of energy consumption,[1-3] but in Brazil, this number reaches 42.6% where 18.1% correspondent to diesel consumption, which stands out for being the most consumed energy source in the country.[4] Emissions from diesel engines may negatively influence or even cause respiratory diseases,[5] and its negative impacts affect not only the fauna, but also the flora.[6]

Studies show that biodiesel is the most promising alternative fuel for diesel replacement in diesel engines, as it is biodegradable, free of Sulphur, not toxic and renewable.[7] Its use as a substitute for diesel is capable to reduce emissions of greenhouse gases and smoke emissions.[8,9] Biodiesel is defined as a mixture of esters of fatty acids,[6] animal fats and algae, edible or not.[10] Among the techniques capable of promoting the production of biodiesel, the most employed at industrial scale is the transesterification of raw material that guarantees viscosity reduction and greater volatility, characteristics present in diesel oil.[11]

In the national context, the insertion of biodiesel into the energy matrix ocurred through the National Program for Biodiesel Production and Use (PNPB), it was published in 2004, where it was proposed the study of biofuel blends using fossil diesel

oil. In January 2008, through Law 11.097/2005, it became mandatory to add 2% biodiesel to diesel,[12] with a gradual increase over the years, according to the schedule established by Law 13.263/ 2016, and in 2018 biodiesel became 10% of the blend, followed by addition of 1% per year, reaching 15% in 2023.[13]

Brazil has an obvious socioeconomic advantage to produce biodiesel due to the availability of raw materials from the agro-industrial sector with high exploration potential that put the country in a relevant position in the development and consumption of biofuel.[14] Currently, soybean is the most exploited raw material for biodiesel production in Brazil, with 77.7% of the national production, followed by bovine tallow, 18.8%.[15]

According to Brazilian Agricultural Research Corporation (EMBRAPA), the state of Rio Grande do Sul is one of the national leaders in biodiesel production of soybean oil and bovine tallow, but other crops are being studied as potential sources for biofuel production.[16] A crop capable of providing a source of triglycerides at low cost in Rio Grande do Sul is the rice crop, since its processing generates as a byproduct the rice bran, considered to be an agricultural residue, from which it is possible to extract vegetable oil.[17-20] The use of vegetable oil for the production of biodiesel becomes attractive due to the high production of the grain in the state.

Nadaleti and Przybyla studied the use of synthesis gas and biogas produced from the rice husk and the rice parboiling effluent, respectively. The authors state that the potential of thermal and electric energy production of rice parboiling industries in Brazil is high and capable of promoting the energy self-sufficiency of this food sector, reducing the need to purchase electric energy from the concessionaire, in addition to the possibility of commercialization of surplus energy.[21]

Thus, it is necessary to study the production of biodiesel from rice bran oil in order to determine the conditions under which its production occurs more efficiently, promoting characteristics in accordance with the norms, via methyl transesterification with homogeneous basic catalysis. Considering that the technique presents great economic viability for industrial scale production in the current context, because despite the scientific growth regarding the production of biodiesel in the last decades, several innovations related to the production process exist only in a technological level, but still without use in industrial scale.[22,23]

Therefore, this study had the objective to produce biodiesel via basic transesterification of vegetable oil of rice bran through experimental delineation of 2^3

factorial arrangement, determining the best conditions for its production and presenting an alternative use of agricultural residue in order to encourage the use of biofuel.

2. Theoretical framework

2.1 Rice Sector in Brazil and Rio Grande do sul

According to the Food and Agriculture Organization of the United Nations, Brazil is the ninth largest rice producer in the world.[24] The country closed the 2017/18 harvest with around 12 million tons of rice produced and has estimated a production for 2018/19 of approximately 11.2 million tons.[25] The per capita consumption of the grain in the national scenario is around 25 kg/year, consolidating rice as a large sector of the country's economy.[26,27]

In the country, the largest producer of rice is the state of Rio Grande do Sul.[25] The state has a developed industrial sector, occupying the 3rd national position, responsible for 27.5% of the state's economy, and the main branches are agroindustry, chemical industry, metal-mechanics and leather/footwear.[28] In 2014, the sector amounted to 22.44% of the final energy consumption of the state being surpassed only by the transport sector.[29] In 2017, the sector was responsible for the highest consumption of electric power in the state, 33%, and in the same year the sector's electricity consumption had an increasement of 3.9% in relation to the previous year.[4]

In general, the industries have been experiencing a rise in their production costs due to costs related to the use of electric energy.[30] While the sector is heavily dependent on the use of electricity, corporate energy management has a strong focus on strategies for optimizing contracting and consumption.[31] Zhao emphasizes the importance of strengthening the productive autonomy of industry in order to promote financial returns, making environmental liabilities susceptible to be reused or readjusted to supply the energy demand, solving the problematic.[31]

The possibility of reusing is not explored by the industrial sector in all over Brazil, since the sector's energy consumption has practically no change in the matrix regarding the participation of renewable and non-renewable sources.[4,32] According to the classification of the Energy Research Company (EPE), the rice processing industries are classified as Food and Beverage Industries, this category accounts for 9% of the final energy consumption of national industrial sector,[4] and in the Southern region, as well as in the RS, the consumption is even higher, where food manufacturing accounts for the highest consumption of electricity, 23.4%.[4,29]

The processing of rice involves several processes, varying according to the methods adopted by the industries. The main processes are reception, grain storage, debarking, drenching and gelatinization (in the parboiling industries), greenhouse, dryer, debarking, bruning, final storage and shipping.[33] A common step in the processing of all types of rice produced in Brazil is the removal of the bark and grain meal.[34]

In general, the main productive cost of the rice industries is the consumption of electric energy, which can exceed 40% of the total. Then, it has a great influence on the profitability of industries that develop such activity.[35] Among the processes of the industrial processing of grain, the ones that have the greatest influence on the electric energy demand are those of debarking, which represents 52% of the demand, followed by the parboiling, with 28% of the general consumption.[36]

Nadaleti conducted a case study in one of these industries, which discussed the energy potential of systems that operate with a CHP generator (Combined Heat and Power) using hydrogen synthesis gas from rice bark and biogas from the anaerobic effluent treatment. The author has determined a potential to produce more than 2.17E+04 MWh of electricity considering only the use of biogas generated.[37]

2.2 Raw Materials

According to EMBRAPA, the state of Rio Grande do Sul is one of the national leaders in biodiesel production of soybean oil and bovine tallow.[16] Despite the prominence of the two raw materials in the state, *Embrapa Clima Temperado* located in the south of Rio Grande do Sul studies the application of other oleaginous crops to produce biodiesel, among them jatropha, castor bean, tungue and crambe.[16]

Another crop capable of providing a source of triglycerides to be explored in Rio Grande do Sul is the rice crop, since its processing generates a by-product, the rice bran, from which it is possible to carry out the extraction of vegetable oil, guaranteeing a low supply cost of raw material for biodiesel production.[19] Rice bran is considered to be an agricultural residue from the stages of husking and polishing of the grain which is generally intended for the production of animal feed.[17-20,22]

That possibility is promising because the high production of grain in the state, responsible for 70.1% of the national crop of 2017/2018, Rio Grande do Sul totaled an offer of more than 8 million tons of rice.[25] The rice grain contains from 5% to 14.8% of

bran with 15-23% of oil, consists of about 68 to 71% triglycerides, 2 to 3% diglycerols, 5 to 6% monoglycerols and 2 to 3% free fatty acids.[38-40]

As a result of enzymatic systems present in the bran, the triglycerides are rapidly hydrolyzed into Free Fatty Acids (FFA), raising the acidity content of the oil. Thus, the viability of extracting oil for refining for human consumption occurs only when the content of acidity is reduced.[22] According to brazilian National Health Surveillance Agency (ANVISA), the percentage of FFA in vegetable oils used in human food must be at most $0.3g.100g^{-1}$.[42] In a study conducted by Lai *et al*. at zero storage time, the percentage of rice bran FFA was above that established by ANVISA.[17,42] In this way, the processing of rice provides a low-cost source of triglycerides capable of promoting biodiesel production.[17-20]

Sinha, Agarwal and Garg report that rice bran vegetable oil produces a biodiesel with excellent physicochemical properties, due to its natural antioxidants.[18] The high quality of the biodiesel propitiates its use in mixtures with other oleaginous or mineral diesel.[22]

2.3 Transesterification

In the reactions involving transesterification a triglyceride reacts with a lower alcohol in the presence of a catalyst producing a mixture of esters of fatty acids and glycerol.[43-45] As a result of the reversibility of reactions involved in the technique, an excess of alcohol is necessary to occurs a displacement towards the formation of products.[46]

The most used alcohols are methanol and ethanol,[47] and under similar conditions methanol is able to achieve higher yield at a lower cost than other alcohols.[48] According to Nadaleti, due to the reversibility of the reactions, the reaction time becomes an important variable, since the reaction equilibrium can happen at variable times.[49] The author cites that the literature recommends the use of 60 minutes of reaction, however, it is possible to find authors who adopt more or less time, according to the need of the raw material and the type of catalyst employed.[50-53]

The speed of the agitation in reaction is extremely important,[19] in general, a 600 rpm agitation promotes better conversion results.[54] In order to increase the rate of the transesterification reaction, the use of catalysts is adopted, using basic homogeneous catalysts,[55] such as sodium hydroxide and potassium hydroxide, for the production of commercial biodiesel.[56,57] Nadaleti states that the homogeneous alkaline catalysis

occurs with greater speed and ease, besides reducing the amount of alcohol than the acid catalysis. Moreover, the amount of catalyst is very important, since it could disfavor the reaction depending on its origin and state of conservation of the oil.[49]

2.4 Quality Parameters

The ANP published in 2014 Resolution n° 45, determine the quality control obligations to be met by the various economic agents that commercialize the product throughout the Brazilian territory. Thus, the characterization of the biodiesel must be carried out through The Brazilian Association for Technical Standards (ABNT), the ASTM “American Society for Testing and Materials” international standards, the “International Organization for Standardization” (ISO) and the “European Committee for Standardization” (CEN).[58]

These parameters are required since the ANP Resolution n° 41 of 2014 defines biodiesel as a fuel for domestic combustion engines with compression ignition, renewable and biodegradable, derived from vegetable oils or animal fats, which can replace partial or totally diesel oil from fossil origin.[59] Thus, the characteristics of biodiesel are close to diesel since its use can be performed exactly in engines developed to be fed with diesel oil.

According to Paula *et al*., excessive amounts of glycerin, soap, water, mono, di- and triglycerides favor the formation of scale, soap deposits and corrosivity triggering engine failures. Being usual even the determination of the Saponification index (SI), that despite it does not have a parameter determined in the regulations referring to problems that the biofuel can cause for the engines when it is elevated, since according to the manufacturers of diesel injection system, the use of lower quality biodiesel may cause nozzle clogging, combustion chamber damage, or damage to other parts of the engines that have contact with the biofuel.[60]

3. Material and Methods

3.1 Transesterification and purification

The determination of the ideal conditions for the production of biodiesel from rice bran vegetable oil via basic methyl transesterification using potassium hydroxide as a catalyst was carried out by means of an experimental design arranged in a 2^3 factorial arrangement.

The methodology used to promote transesterification was based on the one presented by Nadaleti,[49] as well as the conditions adopted as central point of the factorial arrangement. The variations of conditions of the applied methodology occurred in the molar ratio between the vegetable oil and the methanol, the amount of catalyst and the time that reaction was heated and stirring.

The factorial arrangement resulted in eight points with different biodiesel production conditions starting from a central point, executed in triplicate (Table 1):

Biodiesel	Molar ratio (alcohol:oil)	Catalyst (%)	Time (minutes)
P1	6.0:1	1.00	40
P2	9.0:1	1.00	40
P3	6.0:1	1.50	40
P4	9.0:1	1.50	40
P5	6.0:1	1.00	120
P6	9.0:1	1.00	120
P7	6.0:1	1.50	120
P8	9.0:1	1.50	120
PC	7.5:1	1.25	60

Table 1 – Experimental Delineation.

Fig. 1 shows the stages of biodiesel production and purification. In order to promote the transesterification reaction, firstly the oil was heated in a heating plate of a magnetic stirrer until reaching 80 °C:

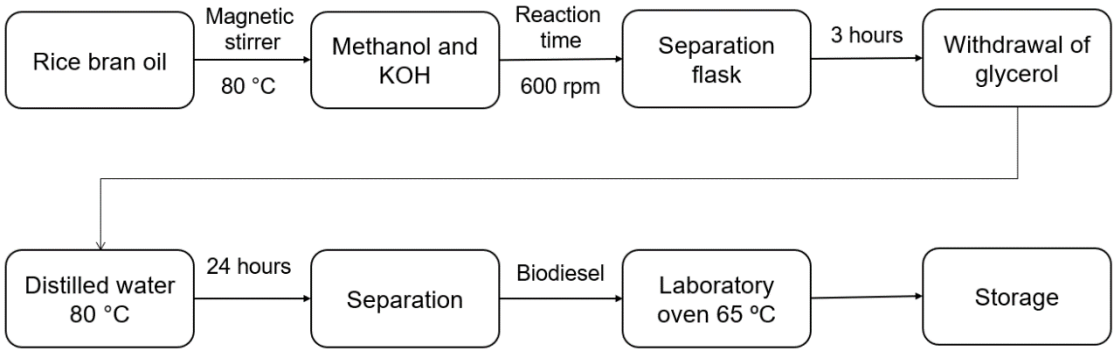

Fig. 1 – Stages of biodiesel production and purification

Then, a magnetic rod was inserted, responsible for providing agitation of the medium (600 rpm), with alcohol and diluted catalyst (Fig. 2a). After the reaction time indicated by the experimental delineation, the reaction product was transferred to a separation flask, where it remained for a period of 3 hours and then the glycerol was removed (Fig. 2b). To promote the purification of biodiesel, distilled water heated at 80°C, was added in a proportion equal to one third of the volume of oil used in the transesterification (Fig. 2c). After 24 hours the separation of biodiesel and water was carried out, where the wastewater was discharged and the biodiesel allocated in a laboratory oven at 65 °C for a period of 12 hours, aiming to promote the removal of moisture.

Fig. 2 – (a) Transesterification; (b) Separation of glycerol and biodiesel; (c) Purification of biodiesel.

3.2 Analyses

Kinematic viscosity (ν), Acid Index (AI) and Iodine Index (II) were determined according to ASTM standard methods, while the Saponification Index (SI) was determined according to the AOAC method and the moisture was determined by the loss of moisture by desiccation at 105 °C. The standard methods used in analyzes are shown in Table 2, and the viscometer used was a Saybolt Viscometer Model Q288SR:

Parameter	Standard method
v	ASTM D445 [61]
Moisture	Desiccation loss [62]
AI	ASTM D664-67 [63]
II	ASTM D459-97 [64]
IS	AOCS CD3-25 [65]

Table 2 – Standard method used for each parameter.

The yield was determined based on the volume of biodiesel produced from vegetable oil used in the reaction. The Fatty Acid Methyl Esters (FAME) obtained from the transesterification reaction were identified on a gas chromatograph equipped with a flame ionization detector, Shimadzu QP-2010. The quantitative analysis was performed by area normalization using the GC Solution software compared to the FAME Mix Standard C4C24, Supelco. In table 3 are detailed the chromatographic conditions used in this study are shown:

Parameter	Conditions
Column	(100 m x 0.25 m x 0.25 µm)
Carrier gas	Nitrogen
Volume injected	1 µL
Splitter ratio	1:25
Pressure	44.695 ψ
Flux	1.2 mL min^{-1}
Injection temperature	250 °C
Heating ramp	100 °C (5 min)– 7 °C min^{-1} to 200 °C (5 min)– 5 °C min^{-1} to 230 °C (10 min)
Detector	Flame ionization detector
Detector Temperature	250 °C

Table 3 – Conditions of the chromatographic analysis of methyl esters of fatty acids of biodiesel. Source: Pacheco *et al*. [66]

Statistical analysis of the study results were performed on the IBM SPSS Statistics software by Test F and Tukey Test, both at 5% significance.

4. Results and Discussion

Among the biodiesel produced based on factorial arrangement, P2 and P5 obtained the best result for yield, 96.67% and 98.90%, respectively, differing statistically from the others. However, there was no significant difference between

them and the PC, which gave rise to the factorial arrangement. Only these mentioned biodiesel reached the minimum limit stipulated by the EN of 96.50% yield (Fig. 3):

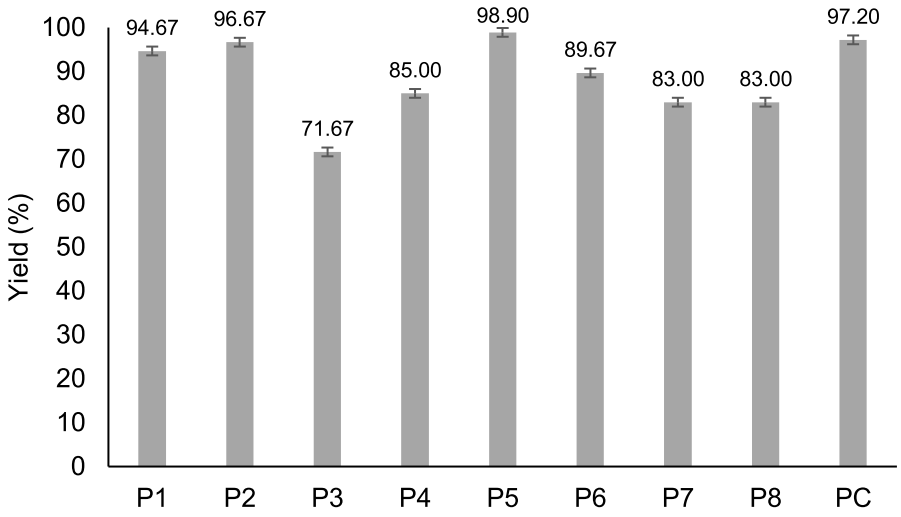

Fig. 3 – Graph of the results of Yield.

Those that achieved yield above the minimum required limit were those that received lower concentration of catalyst, with P2 having a reaction time of 40 minutes and a molar ratio of 9:1 and P5 of 120 minutes and 6:1 molar ratio, evidencing that for a shorter reaction time a larger molar ratio is required whereas for a smaller molar ratio a shorter time period is able to result in a yield within the established standards.

According to the data collected by this study, Brazil has a high oil extraction potential from rice bran, and this potential is concentrated in the southern region, specifically in the state of Rio Grande do Sul. (Table 4):

2018/2019 Harvest [25]	Rice (ton)	Bran (ton)	Oil (m³)
Rio Grande do Sul	7.39E+06	7.32E+05	1.51E+05
South region	8.62E+06	8.54E+05	1.76E+05
Brazil	1.04E+07	1.03E+06	2.13E+05

Table 4 – Potential of oil extraction from rice bran

From the data released by the National Supply Company regarding the 2018/2019 rice crop,[25] the grain and bran oil content found in the literature, [38-40] and the results obtained in this study regarding the yield of transesterification of rice bran vegetable oil for biodiesel production (98.9%), it was possible to determine the national, regional and state biofuel production potential (Fig. 4):

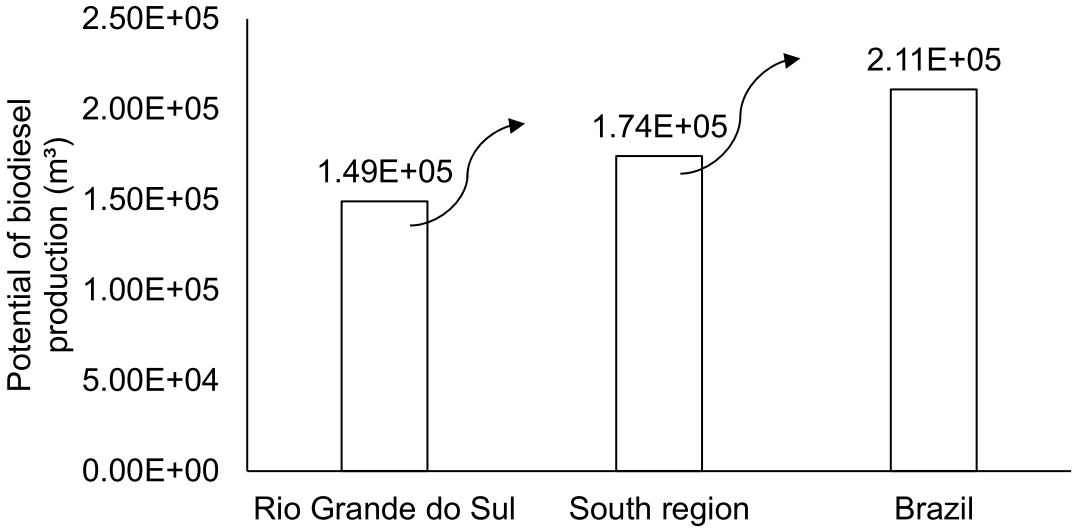

Fig. 4 – Annual potential of rice bran oil biodiesel production.

Based on the results of this study it was found that the state of Rio Grande do Sul has a high production potential of biofuel produced from agricultural waste, rice bran, since the state represents 70.62% of the 2.11E+05 m³ of biodiesel that could have been produced with the bran generated in the 2018/2019 crop.

About the production of biodiesel, according to the maximum and minimum limits established by ASTM, ANP and EN regarding kinematic viscosity for biofuels, only P1 and P7 biodiesel presented non-standard quality averages (Fig. 5). Establishing the ASTM limits as parameter all biodiesel had allowed values. Regarding Brazilian standards, only P7 showed kinematic viscosity above the permitted by ANP. The kinematic viscosity of the fuel oil increases proportionally to the increase in the length of the fatty acid chain and decreases with the increase in the number of unsaturation:[67,68]

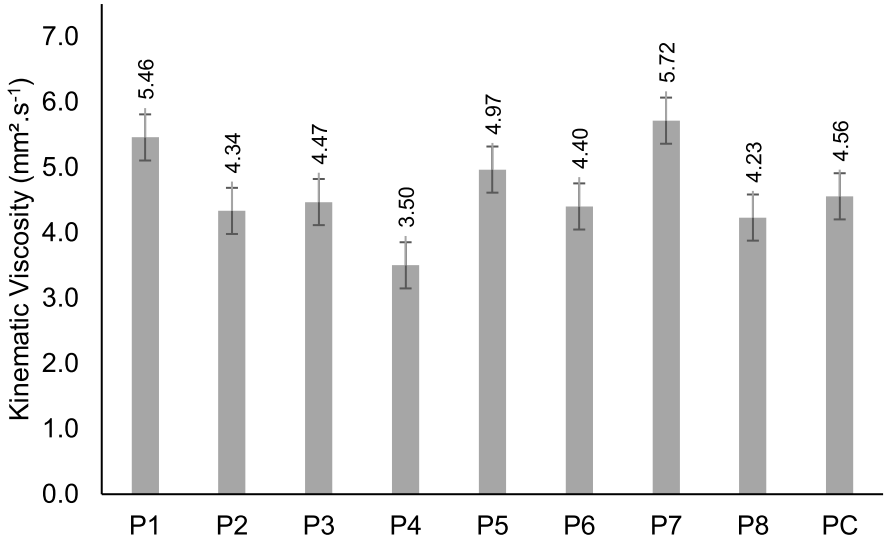

Fig. 5 – Graph of the results of the Kinematic Viscosity analyzes.

The kinematic viscosity at 40 °C for biodiesel from rice bran oil varied, in this study, from 3.50 to 5.72 mm^2s^{-1} (Table 4), while for biodiesel from soybean oil the literature indicates a range of 4.10 – 4.20 mm^2s^{-1}.[66,69,70] Several studies regarding the production of biodiesel from rice bran vegetable oil obtained kinematic viscosity of 4.30 – 4.76 mm^2s^{-1} at 26 °C and 4,12 – 8.45 mm^2s^{-1} at 40 ºC.[22,66,71-74] Mazaheri *et al*. obtained an oil biodiesel from rice bran with kinematic viscosity of 4.42 mm^2s^{-1} using a 35:1 molar ratio of methanol to rice bran oil and 0.5% of catalyst (CaO) for transesterification:[73]

	ν (mm^2s^{-1})	Moisture (%)	AI ($mgKOHg^{-1}$)	SI ($mgKOHg^{-1}$)	II (gI_2g^{-1})	Yield (%)
ANP	2.50 – 5.50	-	≤ 0.80	-	-	-
ASTM	1.90 – 6.00	0.050	≤ 0.50	-	-	-
EN	3.50 – 5.00	-	≤ 0.50	-	≤ 120	≥ 96.50
P1	5.46^{cd}	0.024^{a}	0.11^{c}	133.92^{cd}	95.05^{a}	94.67^{d}
P2	4.34^{ab}	0.020^{a}	0.06^{ab}	137.86^{d}	97.50^{b}	96.67^{de}
P3	4.47^{abc}	0.021^{a}	0.04^{a}	125.86^{b}	99.10^{b}	71.67^{a}
P4	3.50^{a}	0.018^{a}	0.04^{a}	124.44^{b}	97.62^{b}	85.00^{b}
P5	4.97^{acd}	0.030^{a}	0.07^{b}	118.46^{a}	98.27^{b}	98.90^{e}
P6	4.40^{ab}	0.010^{a}	0.06^{ab}	124.82^{b}	101.82^{c}	89.67^{c}
P7	5.72^{d}	0.027^{a}	0.07^{b}	129.12^{bc}	102.74^{c}	83.00^{b}
P8	4.23^{ab}	0.025^{a}	0.07^{b}	118.84^{a}	97.34^{ab}	83.00^{b}
PC	4.56^{ac}	0.018^{a}	0.08^{b}	115.06^{a}	98.83^{b}	97.20^{de}

Table 4 – Results and parameters of the analyzes. Means followed by equal letters, in the same column, does not differ significantly by the Tukey Test at 5% of significance.

Although the standard deviation shown in the graph of Fig. 1 displaces P4 and P5 from the limits of EN, statistically P4 does not differ significantly from P2, P3, P6 and P8, while P2, P3, P6, P8 and PC do not differ from P5, which are within the limits established by the EN. It was observed that the use of the 6:1 molar ratio for P1, P3, P5 and P7 resulted in a higher kinematic viscosity than using 9:1 molar ratio that occurred in the rest of the factorial arrangement. However, still the P3 and P5 biodiesel, with 6:1 molar ratio, were in agreement with all established limits.

Kinematic viscosity is precisely one of the determining factors for the use of reactions such as transesterification in vegetable oils to minimize viscosity, making them suitable for compression ignition engines. Fuel blends for internal combustion engines of diesel oils have similar combustion characteristics and reduced emissions with lower power loss compared to diesel.[75] The high viscosity of vegetable oils and their low volatility causes several problems if used for a long time in compression ignition engines,[18] such as low atomization of fuel, clots, deposits and coke of fuel and dilution of the lubricating oil.[76]

The moisture content of all biodiesel was in the range of 0.01-0.03% with a standard deviation of 0.006%. The ANP, the regulator of biodiesel quality in Brazil, does not stipulate values for this property. However, ASTM D6751 stipulates a maximum value of 0.05%, therefore, the moisture obtained in this study was satisfactory.

The results of the analyzes related to AI and II revealed adequacy of the biodiesel to the existing parameters of ANP, ASTM and EN (Fig. 6 and 7) with great margin, thus, although there was statistical difference among the results, the conditions of the transesterification did not influence in the determination of biodiesel quality regarding these parameters (Table 4). High levels of acidity can lead to corrosion in storage tanks and engines. In addition, AI provides data about oil conservation status and product quality[68],[68] with the possibility of being used to evaluate the degree of degradation of the biodiesel[77].[77] However, the II is related to the degree of chain unsaturation and dependent on the triglyceride source used for biofuel production:[67]

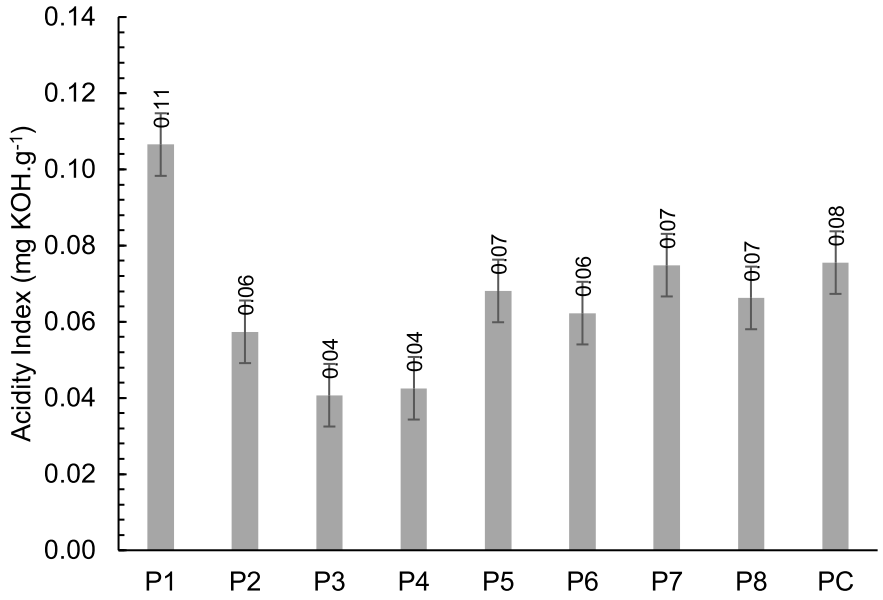

Fig. 6 – Graph of the results of the Acidity Index analyzes.

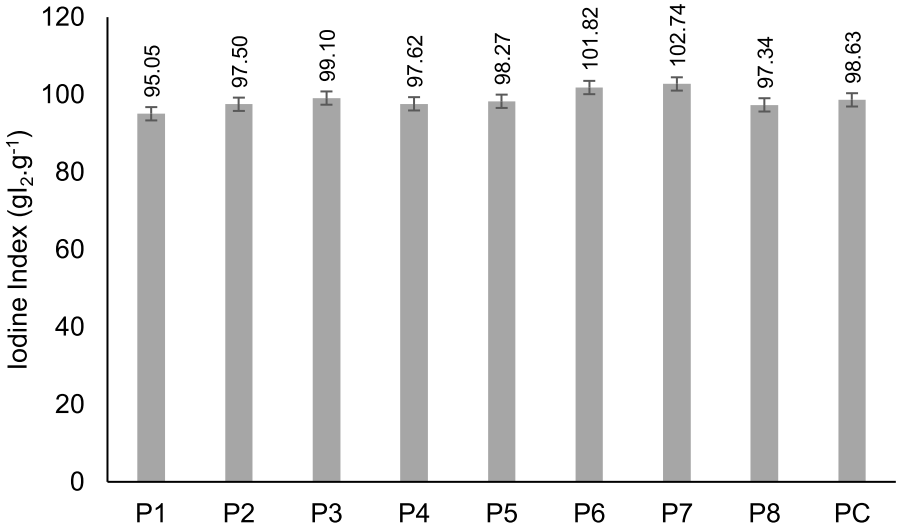

Fig. 7 – Graph of the results of the Iodine Index analyzes.

The AI of biodiesel ranged from 0.04 to 0.11 $mgKOHg^{-1}$, while authors reported in the literature values of 0.13 – 0.50 $mgKOHg^{-1}$ for the biofuel obtained from rice bran oil.[66,73] In general, biodiesel derived from soybean oil presents AI of 0.14 – 0.18 $mgKOHg^{-1}$,[69,70] while studies where the raw material used were bovine tallow indicate higher values, 0.45 – 0.60 $mgKOHg^{-1}$.[49,78] As for II, the range reported in the literature for biodiesel from soybean oil, in general, is 118 – 128 gI_2g^{-1} [69] and for bovine tallow is 50 – 93 mg gI_2g^{-1} .[69,70,78] The biodiesel of rice bran vegetable oil, in this study, presented an II between 95.05 and 102.74 gI_2g^{-1}.

Although there is no regulatory limit regarding SI, it is important factor since it influences in the costs for production and use of biofuel, so that smaller indexes are preferable because they result in lower costs. According to the literature the SI of fatty materials is around 210 mg of $KOHg^{-1}$. The results obtained in this study were in the range of 115.06 – 137.86 $mgKOHg^{-1}$ (Table 4 and Fig. 8), and the two higher SI were found on biodiesel that received only 1.00% of catalyst with a reaction time of only 40 minutes. It is reported in the literature values that can reach 186.64 $mgKOHg^{-1}$ for the same raw material,[22] as for biodiesel from bovine tallow and soybean of 34.9 – 67.6 $mgKOHg^{-1}$ and 195.03 $mgKOHg^{-1}$, respectively:[78,79]

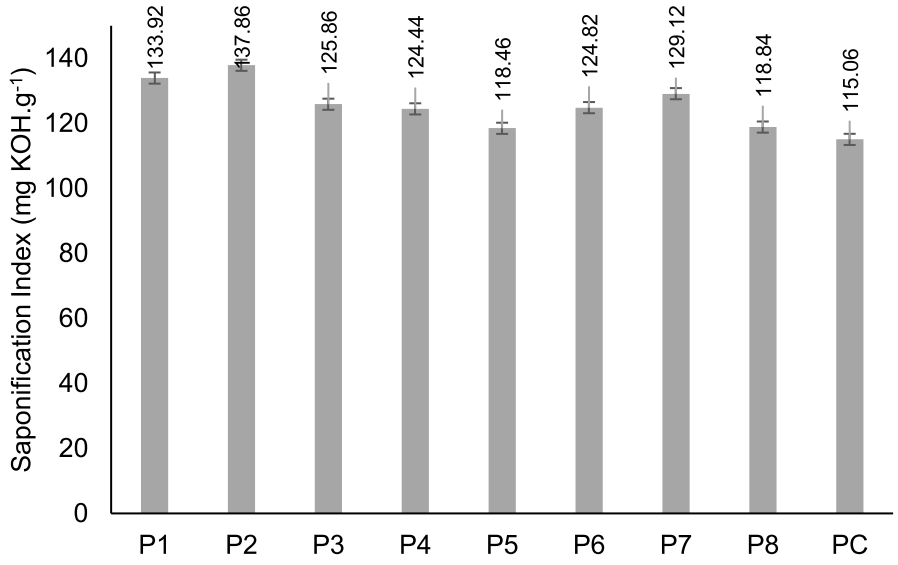

Fig. 8 – Graph of the results of the Saponification Index analyses.

The combinations of factors of the arrangement that resulted in lower yields were those with higher amount of catalyst, 1.5%. According to Lima *et al*., homogeneous alkaline catalysts competitively activate the saponification reactions, which is relatively faster due to the availability of free fatty acids and transesterification.[80] The authors also reported that the concentration change from 0.5% to 1.5% of KOH resulted in a decrease in transesterification yield.

The Fig. 9 shows the chromatograms from which the results of composition of FAME in biodiesel were extracted by quantitative analysis by area normalization using the GC Solution software and compared to the FAME Mix Standard C4C24 (Fig. 9):

Number of Fatty Acid in the chromatograms	Fatty Acid
1	C16:0
2	C18:0
3	C18:1*n*9c
4	C18:2*n*6c
5	C20:0
6	C20:1
7	C18:3*n*3
8	C22:0
9	C24:0

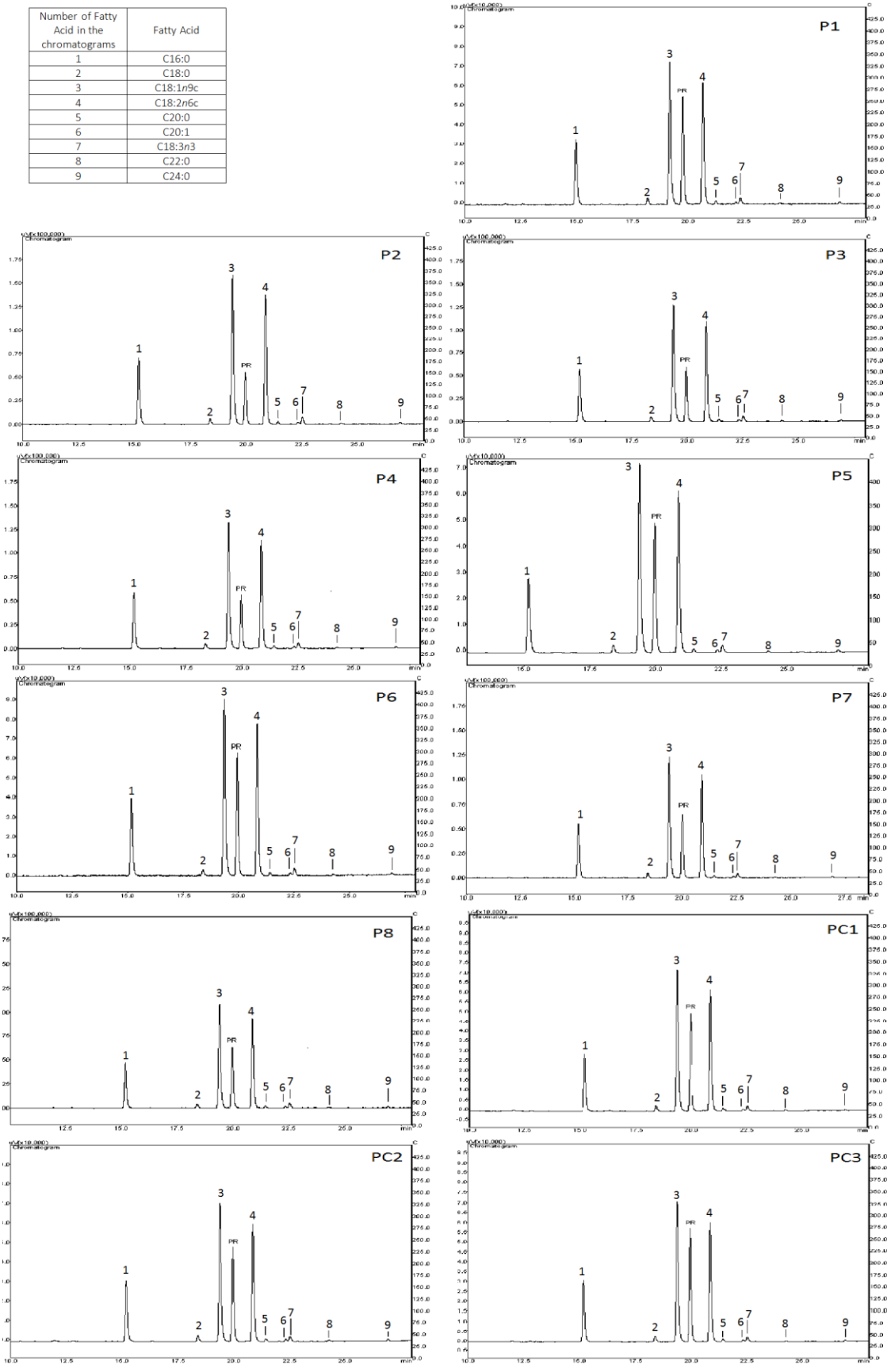

Fig. 9 – Chromatograms of FAME

The composition of FAME in biodiesel indicated that there was no significant difference for the percentage of Palmitic Acid (C16:0), Oleic Acid (C18:1*n*9), Linoleic Acid (C18:2*n*6) and Gadolinic Acid (C20:1), while for Stearic Acid (C18:0), A-linolenic Acid (C18:3*n*3), Eicosanoic Acid (C20:0), Beenic Acid (C22:0) and Lignoceric Acid (C24:0), the different conditions for the reaction of transesterification resulted in different homogeneous subsets within the averages of their respective percentage in the Tukey Test at 5% significance (Table 5):

	C16:0 (%)	C18:0 (%)	C18:1*n*9c (%)	C18:2*n*6c (%)	C20:0 (%)	C20:1 (%)	C18:3*n*3 (%)	C22:0 (%)	C24:0 (%)
P1	19.11^{a}	1.74^{b}	40.88^{a}	34.03^{a}	0.80^{c}	0.51^{a}	1.66^{b}	0.47^{b}	0.75^{b}
P2	18.30^{a}	1.56^{a}	41.30^{a}	34.74^{a}	0.64^{a}	0.56^{a}	1.83^{cde}	0.26^{a}	0.44^{a}
P3	18.76^{a}	1.57^{a}	41.24^{a}	34.60^{a}	0.69^{ab}	0.56^{a}	1.87^{e}	0.23^{a}	0.43^{a}
P4	18.56^{a}	1.49^{a}	41.42^{a}	34.58^{a}	0.69^{ab}	0.59^{a}	1.85^{de}	0.22^{a}	0.46^{a}
P5	17.95^{a}	1.72^{b}	41.35^{a}	34.82^{a}	0.97^{d}	0.66^{a}	1.79^{c}	0.26^{a}	0.43^{a}
P6	18.60^{a}	1.56^{a}	41.02^{a}	34.60^{a}	0.74^{bc}	0.64^{a}	1.81^{cd}	0.28^{a}	0.71^{b}
P7	19.19^{a}	1.71^{b}	41.25^{a}	34.07^{a}	0.80c	0.57^{a}	1.58^{a}	0.33^{a}	0.45^{a}
P8	18.42^{a}	1.73^{b}	41.23^{a}	34.48^{a}	0.81^{c}	0.60^{a}	2.01^{f}	0.33^{a}	0.36^{a}
PC	18.27^{a}	1.75^{b}	41.55^{a}	34.61^{a}	0.77^{bc}	0.67^{a}	1.54^{a}	0.30^{a}	0.48^{a}

Table 5 – FAME chromatography results. Means followed by equal letters, in the same column, did not differ significantly by the Tukey Test at 5% significance.

All biodiesel analyzed presented a majority composition of C16:0, C18:1n9c and C18:2n6c, corroborating with the other results that indicate the efficiency of the transesterification reaction, assuring that the products obtained through the reaction are in fact a biodiesel with similar characteristics to the diesel, since the fossil oil has in its composition hydrocarbons with 15 to 24 carbon atoms as well as the biofuels obtained in this study. In addition, esters of fatty acids affect the physical and chemical characteristics of the biofuel and determine the quality of the final product. High concentrations of saturated fatty acids increase the occurrence of solid residues, leading to problems related to obstructions in diesel engines.[81] High levels of polyunsaturated fatty acids affect storage since they are susceptible to oxidation, whereas high levels of monounsaturated fatty acids may affect beneficial properties.[77]

The sum of the concentration of methyl fatty acids varied from 99.86% to 99.97% among the biodiesel produced. Silva obtained a rice bran refined oil methyl biodiesel of 99.2% yield and composed by 17.6% of C16:0, 51.8% of C18:1*n*9 and 30.5% of C18:2n6.[74] Mazaheri *et al*. reported results where the biodiesel from same raw material showed C18:1 and C18:2 as main components, 38.76% and 37.00%,

respectively.[73] For Giakoumis and Sarakatsanis, in a detailed statistical research related to FAME composition, found 42.35% of C18:1. 34.84% of C18:2 and 18.12% of C16:0 in rice bran biodiesel and 11.4% of C16:0, 23.47% of C18:1 and 53.46% of C18:2 in biodiesel from soybean oil.[71] Silva *et al*., reported a similar result for biodiesel from soybean oil, where C18:2n6c played a dominant role, representing 51.79% of the biodiesel composition, followed by C18:1n9c and C16:0, with 28.75% and 11.13% respectively.[82] As well as for biodiesel from bovine tallow, Silva *et al*. reported majority composition of C16:0 (25.35%), C18:0 (29.10%) and C18:1*n*9 (28.15%).[83]

5. Conclusion

According to this study it is possible to conclude that biodiesel production via methyl transesterification using KOH as a catalyst is viable and capable of producing biodiesel with quality required by ANP, EN and ASTM specifications, considering that:

- For the Acidity and Iodine Indexes and moisture, all the conditions imposed by the factorial arrangement promoted the reactions of transesterification in an efficient way in order to guarantee results in agreement with the specifications of the standards addressed in this study, between 0.04 and 0.11 mg $KOHg^{-1}$ for the Acidity Index and between 95.05 and 102.74 g I_2g^{-1} for the Iodine Index. The results obtained were superior to those found in the literature for biodiesel from rice bran, soybean oil and bovine tallow, since they presented lower values than those reported by other authors. For the analysis of moisture, the results were between 0.01% and 0.03%;
- For the Saponification Index, all combinations of conditions performed in this study promoted better results than those found in the literature for biodiesel from rice bran and soybean oil, ranging from 115.06 to 137.86 mg $KOHg^{-1}$;
- For the Kinematic Viscosity, all the biodiesel produced were within the limits established by ASTM, whereas for the ANP only one exceeded the maximum limit and for the EN two exceeded the maximum limit, and these were produced with molar ratio of 6:1. According to the results obtained in all the biodiesel produced by factorial arrangement, the 6:1 molar ratio was responsible for the higher kinematic viscosities. The variation presented in this study was close to the other studies about biodiesel from rice bran oil, varying from 3.50 to 5.73 $mm^2\ s^{-1}$;

- For the yield of transesterification reaction for production of biodiesel, the conditions presented great influence as regards the framing of the results obtained in the minimum limit determined by the EN, 96.50%. In addition to the Central Point, only two other biodiesel showed yields above 96.50%, which in the production of one of them a molar ratio of 6:1 and 120 minutes of reaction time was used and in the other 9:1 and 40 minutes, both with a catalyst concentration of 1.0%, resulting respectively in 98.09% and 96.67%. The concentration of 1.5% resulted in the lowest yields obtained in the study;
- In contrast to all the results obtained in the study and their respective parameters, in fact for the methodology applied for the production of methyl biodiesel via transesterification with KOH as catalyst, among the variations studied, the best conditions are given in three different combinations: 9:1 of molar ratio, 1.0% catalyst and 40 minutes; 7.5:1 of molar ratio, 1.25% catalyst and 60 minutes; 6:1 of molar ratio, 1.0% catalyst and 120 minutes. The molar ratio of 6:1, 1.0% catalyst and 120 minutes showed the highest yield obtained in this study, 98.09%;
- Brazil, its southern region and the state of Rio Grande do Sul have the annual potential to produce about 2.11E+05, 1.74E+05 and 1.49E+05 m³ of rice bran oil biodiesel, respectively.

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4.2 Artigo 2: Review and optimization of methane production from rice parboiling anaerobic sludge by the addition of crude glycerol: Specific Methanogenic Activity

ABSTRACT

Rice parboiling industries in Brazil have high energetic potential, capable of promoting the energy self-sufficiency of the sector with surplus energy trading. Thus, studies that seek to optimize the production of biofuels from this type of industry become pertinent. The objective of this study was to review SMA tests and to determine the feasibility of glycerol application of rice bran oil methyl biodiesel for the production of methane from the UASB reactor sludge of rice parboiling effluents. No studies have been found in the literature that has addressed the SMA of this type of sludge, nor its co-digestion with glycerol. The SMA test digesters operation with different proportions of crude glycerol (0, 1, 2 e 3%). The highest methane production occurred in the 1% glycerol system, 945.23±5.34 mL, in 168 hours of experiment, a production equivalent to 539.45% of system production without glycerol. From the results obtained in this study was found that the system that showed higher SMA was the one that did not receive the addition of glycerol. Through the study was possible to determine that although the addition of glycerol does not increase the anaerobic sludge SMA of rice parboiling, the byproduct of biodiesel production is able to prolong the duration of the stationary phase of methanogenic bacteria, increasing total methane production at the end of the anaerobic digestion process. In addition, the anaerobic digestion process was efficient for COD removal and pH reduction in all systems, especially in those that had the addition of glycerol.

Keywords: Biodiesel; SMA; biogas; biofuel; bioenergy.

ABREVIATIONS

CH_4	Methane
CHP	Combined Heat and Power
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
FS	Fixed Solids
H_2O	Water
H_2S	Hydrogen Sulfide
N_2	Nitrogen
NaOH	Sodium Hydroxide
NO	Nitrogen Oxide
P	Phosphorus
pH	Hydrogen Potential
SMA	Specific Methane Activity

SO_2	Sulfur Dioxide
TS	Total Solids
UASB	Upflow Anaerobic Sludge Blanket
VSS	Volatile Suspended Solids

1. Introduction

The depletion of fossil fuels linked to global warming makes the search for new energy sources urgent, in this context, the development of clean and renewable energies also represents the possibility of reducing greenhouse gas emissions [1]. Petroleum has been used as the main energy matrix, accounting for 33.3% of global energy consumption [1,2,3], with emissions of Carbon Dioxide (CO_2), Nitrogen Oxide (NO) and Sulfur Dioxide (SO_2) originating already from fuel plants [4].

Bioenergy is the energy derived from biomass to be generated from solid, liquid and gaseous biofuel for different uses, such as transportation, heating and electricity generation, allowing greenhouses reduction when replacing fossil fuels [5-7]. The conversion of biomass to biofuel occurs, for example, in the anaerobic digestion of these compounds for biogas generation, or in the lipid transesterification for biodiesel production [5,8,9].

Nadaleti and Przybyla [10] studied the production of syngas and biogas produced from rice husk and parboiled rice effluent, respectively, the authors state that the energy production potential of rice parboiling industries in Brazil is high and capable of promoting the energy self-sufficiency of the sector with surplus energy trading. Thus, studies that seek to optimize the production of these biofuels, as well as those that exploit the viability of production of others, become pertinent.

In this sense, Sinha *et al*. [11] report that rice bran vegetable oil, an agricultural residue from the husking and polishing stages of grain, produces biodiesel with excellent physicochemical properties. Among the biodiesel production techniques, the most widely used on an industrial scale is the transesterification reaction [12], where a triglyceride reacts with a short-chain alcohol in the presence of a base or strong acid (catalyst), producing a mixture of esters of fatty acids (biodiesel) and glycerin - a byproduct [13,14].

Currently, crude glycerol undergoes separation and purification processes to obtain crude glycerin, which has 95% glycerol and is marketed, with low added value, to the cosmetics and cleaning chemical industries [15]. Given that the industrial sector uses

only glycerin, unrefined glycerol is characterized as an environmental liability [16]. Considering that for every 10 kg of biodiesel produced about 1 kg of crude glycerol is generated [17,18], the significant increase in biodiesel production in the last decade has resulted in overproduction and accumulation of the byproduct, making new alternatives necessary for its use [18,19]. Thus, anaerobic digestion is evidenced as a favorable alternative for glycerol application through the co-digestion of this byproduct with other organic substrates aiming at obtaining biogas.

Biogas production occurs through the complex interaction of microorganisms capable of degrading the organic matter present in the system and converting it mainly into Methane (CH_4) and CO_2 [20]. The addition of glycerol may favour anaerobic digestion by serving as an energy source, optimizing the carbon to nitrogen ratio and increasing biogas production and methane concentration [21,22].

However, although several studies have reported the enhancement of biogas production and methane concentration using glycerol in anaerobic co-digestion at certain concentrations [23-27]. The use of biodiesel production by transesterification may negatively influence if added to inadequate proportions to the system, making it appropriate to perform Specific Methane Activity (SMA) tests to determine the concentration at which the inhibition power of a given glycerol to the inoculum appears.

The objective of this study was to review SMA tests and to determine the feasibility of glycerol application of rice bran oil methyl biodiesel production for the Upflow Anaerobic Sludge Blanket (UASB) reactor sludge used in the treatment of rice parboiling effluents, aiming to optimize the system and the methane production potential, delimiting in which glycerol concentrations the sludge SMA inhibition and potentiation potential are presented.

2. Literature Review

According to Ülgüdür *et al*. [28] historically, anaerobic digestion has been applied in the treatment and stabilization of high-strength waste to a profitable outcome and the production of renewable energy. Thus, the process is considered an efficient method for stabilizing the biodegradable components of solid waste while presenting itself as a renewable source of energy in the form of biogas [29-32].

Kong *et al*. [33] report that due to its ability to recover bioenergy from organic waste and its strong tolerance to high organic loads, anaerobic digestion overcomes the

drawbacks of conventional activated sludge processes, making it a conventional process for the treatment of organic wastewater and organic solid waste [34,35]. The anaerobic digestion process is carried out by different bacterial populations so that it has four different phases: hydrolysis, acidogenesis, acetogenesis and, finally, methanogenesis, the phase responsible for the formation of CH_4 rich biogas [36,37].

Produced by mesophilic and thermophilic microorganisms in the absence of oxygen in different environments [38,39], biogas is a source of energy that can be used for fossil fuel substitution in cars, electricity generation and as a heat source [40, 41]. Biofuel is mainly composed of CH_4, from 40 to 75%, and CO_2, from 15 to 60%, and also contains traces of other components, such as water (H_2O), from 5 to 10%, Hydrogen Sulfide (H_2S), 0.005 to 2%, siloxanes, from 0 to 0.02%, halogenated hydrocarbons, <0.6%, Carbon Monoxide (CO), <0.6%, and Nitrogen (N_2), from 0 to 2% [39].

For the conversion of biogas into bioenergy, the high content of CH_4 in its composition is essential, since the gas has high calorific value, whereas a high CO_2 content negatively interferes with being inert in terms of combustion [39]. Thus, for the use of biogas for energy purposes purification processes are performed in order to obtain biomethane, where the fuel has at least 90% of CH_4 in its composition [9].

2.1 Specific Methanogenic Activity

SMA is a commonly used indicator of microbial activity during anaerobic digestion and can be calculated by dividing the maximum methane production rate by biomass during batch anaerobic digestion experiments using specific substrates [42]. According to Batstone *et al*. [43], SMA identifies methane production from acetate above saturation kinetics and is analogous to biomass specific maximum acetotrophic absorption rate.

The test should be performed under controlled laboratory conditions to ensure the maximum biochemical activity of conversion of organic substrates to biogas, enabling the determination of the maximum methane production capacity [44,45]. As described by Hyaric *et al*. [46], SMA tests involve the addition of a specific substrate and a biomass sample confined in a batch reactor and incubated at a controlled temperature, usually mesophilic.

According Abbasi and Abbaasi [36], among the factors that interfere in the process, can be cited the operating condition, temperature and pH. Temperature is an

extremely important factor in anaerobic digestion, so changes in this parameter may alter the activity of enzymes in the microbiome and affect fundamental biological processes such as substrate degradation and methanogenesis [42]. According to Feng *et al*. [47], anaerobic digestion is generally classified into psychrophilic (<20 °C), mesophilic (25-45 °C) and thermophilic (> 45 °C) digestion, anaerobic metabolic rate usually increases with increasing temperature, but mesophilic anaerobic digestion has a better yield on methane production and process stability than thermophilic condition, which explains the common use of mesophilic anaerobic digestion for the treatment of organic waste. Mesophilic granules, used in most anaerobic reactors [42,46,48-51], are more sensitive to sudden temperature changes than thermophilic granules [52-54] and may result in granule disintegration. Given this, careful temperature control is the first prerequisite for maintaining granules in reactors [36].

According to Abbasi and Abbaasi [36], since an acidogenic population is significantly less sensitive to pH fluctuations compared to methanogenic, which require pH to be in the range of 6.3 to 7.8, acid formation prevails on methanogenesis when the pH is low, resulting in the accumulation of volatile fatty acids in the reactor. According to the authors, the pH may change if the concentration of nonionized volatile fatty acids exceeds the buffering capacity of the reactor contents, which may lead to the disintegration of the granules.

Therefore, a pH close to neutrality is required [48]. In a study by Latif *et al*. [55], agitated mesophilic reactors fed sewage activated sludge obtained better performance when operated with the pH between 6.5 and 7.0. During the SMA test, it should be ensured that the biomass contacts the substrate, so the reaction vials are frequently incubated with constant agitation [50,54], although there are no conclusive results in the literature regarding the influence of such a mixture. stirring and the type of stirrer to be used. Thus, manual or mechanical agitation may or may not be adopted during the test [42,46,49].

Thus, the biochemical activities responsible for methane generation are extremely dependent on environmental conditions, and the availability of nutrients is another extremely relevant factor. Several authors report the preparation and addition of nutrient solution, glucose and sodium bicarbonate for the occurrence of maximum metabolic activity of bacteria and simulation of the conditions of anaerobic reactors employed in larger scales [46,48].

However, Liu *et al*. [42] state that there is no consensus on the effectiveness of using the nutrient solution and trace elements in anaerobic sludge SMA testing. The authors performed preliminary experiments on methane production in vials containing only glucose and vials containing in addition to glucose, also supplemental growth factors in the form of concentrated solution (Table 1). Methane production of glucose and glucose mix only, nutrients and trace elements were similar, indicating that supplemental growth factors were an unnecessary addition to the SMA test:

Table 1. Composition of growth factors.

Nutrient	Concentration ($g.L^{-1}$)
NH_4Cl	26.60
KH_2PO_4	10.00
$MgCl_2 \cdot 6H_2O$	6.00
$CaCl_2$	2.27
$FeCl_2 \cdot 4H_2O$	2.00
$CoCl_2 \cdot 6H_2O$	0.49
$MnCl_2 \cdot 4H_2O$	0.10
$NiSO_4 \cdot 6H_2O$	011
$ZnCl_2$	0.05
H_3BO_3	0.05

Source: Liu *et al*. [42].

However, despite the lack of consensus on the use of the nutrient solution and trace elements, Cuff *et al*. [49] mention that as a readily degradable substrate, glucose addition is usually used in SMA tests. The authors also point out that the use of glucose as a standard makes it possible to determine the degradation rate of the general anaerobic process (excluding hydrolysis), as well as the granular sludge SMA. SMA is determined by calculating based on the direct measurement of methane production rate or substrate consumption per unit biomass in VSS and time unit [56,57].

2.1.1 Quantification

Among the different methods for quantifying methane generated in the SMA tests, the most used are those based on the volumetric displacement of fluids. According to

López *et al*. [58], these methods are based on the quantification of methane concentration through displacement of Sodium Hydroxide (NaOH), since NaOH promotes the dissolution of CO_2, allowing the methane produced to be measured (Figure 1):

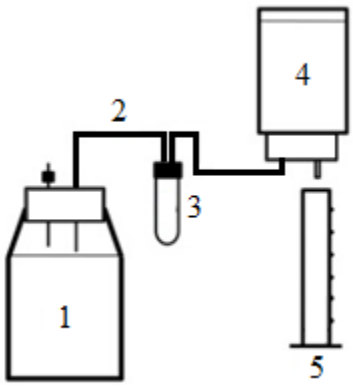

Figure 1. Example of system used for running SMA test. Where: 1 - Mixture of biomass and medium; 2 - Biogas circuit; 3 - Security camera; 4 - Mariotte bottle (containing NaOH); 5 - Tube with methane volume displaced. Source: López *et al*. [58].

Liu *et al*. [42] studied the characterization of SMA during anaerobic digestion with high solids content of sewage sludge and NaOH solution for CO_2 dissolution, however, the authors also used a pH indicator, thymolphthalein. The system of Sepúlveda-Mardones *et al*. [59], promoted the biogas bubbling in an inverted Mariotte flask containing NaOH solution in order to remove CO_2. The displacement of the NaOH solution by the methane accumulated in the free space of the flask was measured daily to obtain the volume of methane produced.

Already in a study by Cuff *et al*. [49], the tests were performed with an automated system (Figure 2) in which methane was semi-continuously computerized quantified after removal of CO2 in NaOH:

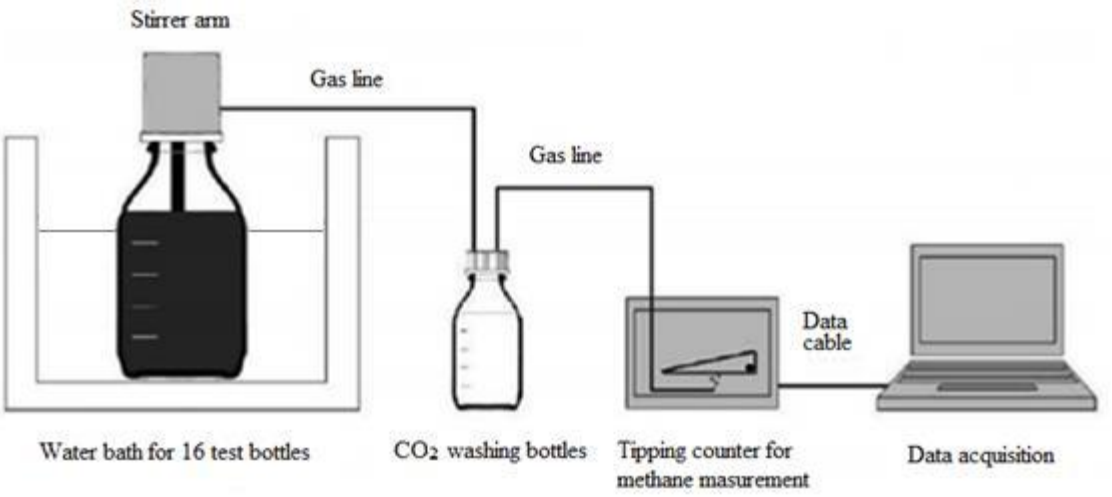

Figure 2. SMA Test System.

Source: Cuff *et al*. [49].

If methane formation is measured continuously, the SMA can still be determined directly from the ratio of the gas volume difference during the observation period, where after a short phase lag in the first hours of the experiment, the substrate is acidified and decomposed into compounds that can be converted by methanogens, with an almost linear increase in gas production corresponding to the time interval chosen for the determination of SMA [49].

After quantification of the generated methane, according to the methodology of Aquino *et al*. [45], the value of SMA can be obtained by a time plot of cumulative methane production, where SMA will be determined by the angular coefficient at the highest slope, expressed as $mLCH_4.gVSSh^{-1}$ and $gCODCH_4.gVSSh^{-1}$.

2.1.2 Applications

In addition to assisting in reactor operation control, SMA also has great utility in determining effluent degradability under anaerobic conditions due to the fact that the removal of equivalent electrons, reduced compounds causing Chemical Oxygen Demand (COD), of the effluent to be treated will only occur with the formation of methane. Thus, SMA allows to establish the maximum capacity of COD removal from the liquid phase, allowing an estimate of the maximum organic load that can be applied, minimizing the risk of anaerobic process imbalance [44,45].

Thus, SMA has high importance for understanding the behavior of the crop regarding its gas production potential [44,57,60]. Although there is no standardized

protocol for the performance of the test in relation to the methodology that should be followed, its importance is recognized in several literature, since in addition to quantifying the anaerobic sludge SMA, it can also be used in the evaluation of inoculum at the start of reactors with different physiological groups present in the sludge, evaluation of the inhibitory effect of toxic elements on anaerobic digestion, evaluation of biomass activity in anaerobic reactors and biodegradability potential [61-68].

2.1.1 Anerobic co-digestion

Considering the high potential of methane production through the anaerobic degradation of various waste from agricultural industries, the SMA test becomes a very important tool to quantify this potential and attest synergy between different substrates and inoculum for the application of anaerobic co-digestion of these residues. Anaerobic co-digesting, a technique that promotes the simultaneous digestion of two or more substrates that have complementary characteristics, stands out as a promising process for biogas production, since it increases the stability and efficiency of the system, enhancing biogas production and methane concentration [69-72].

The technique is able to increase biogas production by 25% to 400% over anaerobic digestion of only one substrate [71], thus increasing the yield of anaerobic digestion through synergisms established by mixing different substrates, such as nutrient supply, C/N balance, availability of organic matter, better buffering capacity and dilution of inhibitory compounds [72-76].

Wu *et al*. [77] evaluated the co-digestion of food waste and grease trap residues through the SMA test, the authors report that the results of the SMA test indicated that the addition of higher concentrations of grease trap residues within an appropriate range elevates the methanogenic activity of co-digestion, reaching 26.9 mLCH4.gVSd^{-1}. Kim *et al*. [78] addressed in their study the synergism of food waste co-digestion with municipal wastewater treatment biosolids, the results of the SMA revealed that co-digestion improved acetogenic, acidogenic and methanogenic activities, with synergistic effects accounting for at least 18-20% of overall methane production, totalling a maximum SMA of 7.3 mL.gVSSh^{-1}.

Li *et al*. [35] studied the co-digestion of feed and activated sludge residues, the authors report that due to the high hydrolysis rate, the maximum yield of CH4 in the thermophilic reactor was 407 mLCH4.gVS^{-1}, a value significantly higher than 350

mLCH4.gVS^{-1} that occurred in a mesophilic reactor. Siddique *et al*. [79] obtained an SMA of 175 mlCH4.gVSSd^{-1} co-digestion for petrochemical wastewater and thickened manure activated sludge. Jiménez *et al*. [52,53] obtained SMA optimization of anaerobic co-digestion of pig manure and rice straw using industrial clay residues as an inorganic additive, 1.31 and 1.38 gCH4COD.gVSSd^{-1} under mesophilic and thermophilic conditions, respectively. Studies have shown that the addition of rice straw and clay improved methane production in anaerobic digestion of pig manure, while rice straw improved cumulative methane production over the long term and clay reduced the inhibitory effect of pig manure. porcine due to ammonia nitrogen adsorption.

Meneses-Reyes *et al*. [80] study the oil-extracted Chlorella Vulgaris biomass and glycerol bioconversion to methane via continuous anaerobic co-digestion with chicken litter, in different concentrations. The best SMA response, 270 mLCH4.gVS^{-1}, was obtained with 30% oil-extracted microalgae, 3% glycerol and 67% chicken litter. The co-digestion SMA was 39.0% higher than that obtained for individual chicken litter digestion, so the authors point out that these biodiesel production residues can be used as raw material to improve methane production through anaerobic digestion. Oliveira *et al*. [81] studied the optimization of biogas production from Sargassum sp using a design of experiments to assess the co-digestion with glycerol and waste frying oil. The biochemical potential of macroalgae methane was 181 LCH_4.kgDQO^{-1}, and co-digestion with glycerol and waste frying oil increased the potential by 56% and 46%, respectively.

The use of a co-substrate such as glycerol in anaerobic digestion may favour the process of biogas and CH_4 production, as microorganisms can use it as a carbon source promoting the necessary balance of the medium C/N ratio [21,22,82-84]. The lack of economic subsidies necessary for the purification of the biodiesel byproduct makes it essential to search for new applications for surplus glycerol, such as its increase as a co-substrate in the anaerobic digestion of organic waste and/or effluents for biogas generation [85].

2.2 The rice sector as an energy source

Brazil is the ninth largest rice producer in the world. The country closed the 2017/18 crop with about 12 million tons of rice produced and has estimates for 2018/19 production of approximately 11.2 million tons [86]. Per capita consumption of grain on the national scene is around 25 kg for a year, consolidating rice as a major sector of the

country's economy [87,88]. The state that supplies most of the rice production in the country is the Rio Grande do Sul, which is responsible for the production of 70.1% of the 2017/2018 national harvest, totalling over 8 million tons of grain [86 .

Rice processing involves several processes, varying according to the methods adopted by the industries. The main processes are receipt, grain storage, soaking and gelatinization (in the parboiling industries), kiln, dryer, husking, honing, final storage and shipping [89]. In general, the main productive cost of the rice industries is the consumption of electricity, which can exceed 40% of the total, thus having great influence on the profitability of the industries that develop such activity [90]. Among the processes of industrial processing of grain, those that have the greatest influence on the demand for electricity are the husking, which represents 52% of demand, followed by the parboiling stage, with 28% of the general consumption [91]. Of all rice consumed in Brazil, about 25% of rice is parboiled rice [92].

The processing of parboiled rice not only involves the removal of husk and bran as in the case of white rice. Parboiling also involves a specific unit where the grain is soaked in 60 °C water tanks for about four hours, followed by vaporization and drying steps [93]. Thus, while white rice processing is responsible for the generation of rice bran and husk only, agricultural residues from the husking and polishing stages, the parboiled rice processing still promotes high effluent generation [94,95].

The critical point of effluent generation in a parboiled rice industry occurs in the soaking stage, as it uses a large volume of water that in turn retains grain properties during bathing [96]. For each kilo of parboiled rice, 2 to 4 litres of effluent is generated [5,97]. The generated effluent is characterized by high loads of organic substances and nutrients, such as N and Phosphorus (P) [87,98], which when disposed of in water bodies without proper treatment, can cause eutrophication [98,99].

Nadaleti [100] conducted a case study in a parboiled rice industry where the energy potential from systems operating on a Combined Heat and Power (CHP) generator set using hydrogen synthesis gas produced from Rice hulls and biogas from the anaerobic effluent treatment in UASB reactors present in the Effluent Treatment Plants (ETP) of the parboiling industries. The author determined a potential to produce more than 2.17E + 04 MWh of electricity considering only the use of biogas generated. Thus, according to Nadaleti and Przybyla [10] and Nadaleti [100], the potential for energy production from

effluents and waste from rice parboiling industries in Brazil can promote the energy self-sufficiency of this sector.

In addition, another energy source in the sector is grain bran that contains 15 to 23% vegetable oil [101]. Due to the enzymatic systems present in the bran, triglycerides are rapidly hydrolyzed to Free Fatty Acids, increasing the acidity content, thus, the viability of oil extraction for refining for human consumption occurs only when the acidity content is reduced. [94]. In a study by Zullaikah *et al*. [101], already at zero storage time, the percentage of FFA of rice bran was above the pre-established by ANVISA [102].

Thus, rice milling offers a source of low-cost triglycerides that can promote biodiesel production [11,95,103]. Sinha, Agarwal and Garg [11] report that rice bran vegetable oil produces biodiesel with excellent physicochemical properties due to its natural antioxidants. Considering that biodiesel generation on an industrial scale is mainly carried out through the transesterification of vegetable oils using homogeneous catalysts [94,104,105], the possibility of producing biodiesel from rice bran vegetable oil would result in a large supply of glycerol in the sector, since in transesterification triglycerides, or triacylglycerols, present in the composition of oils, react with an alcohol generating esters and glycerol [94,105].

The production of 10 kg of biodiesel generates about 1 kg of glycerol [106], thus the supply of glycerol grows linearly with the increase in biofuel production. In 2017 alone, Brazil produced over 4 million cubic meters of biodiesel [107], generating over 400,000 tons of glycerol. By 2021 world biodiesel production is expected to lead to the generation of 3 million tonnes of glycerol [108].

2.2.1 Anaerobic sludge from rice parboiling

Few studies found in the literature indicate significant biogas production potential using the anaerobic sludge from ETP UASB of rice parboiling industries (Figure 3) as inoculum of the anaerobic digestion process. According to studies by Nadaleti *et al*. [109], anaerobic digestion in effluent batch and anaerobic sludge from parboiled rice production at 35 °C promoted the production of 5,198 dm^3 of biogas over a period of 276 hours (18.83 $dm^3.h^{-1}$). Lourenço *et al*. [110] conducted studies on the effluent and sludge co-digestion of the UASB ETE from parboiling rice with fruit peels in batches at 35 °C, the authors obtained 11,730 dm^3 of biogas during 168 hours (69.82 $dm^3.h^{-1}$) of orange peel co-digestion and 8,490 dm^3 with the banana peel (50.55 $dm^3.h^{-1}$). Nadaleti *et al*. [111]

studied the effluent co-digestion of dairy industry, also in batch and at 35 ° C, for 252 hours and obtained total production of 1.50 dm^3 of methane. For all studies cited, 2.15 dm^3 volume reactors and 30% headspace reactors were used:

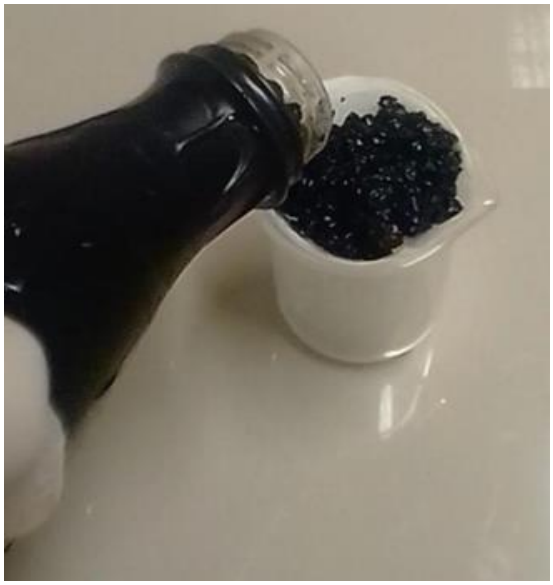

Figure 3. UASB sludge from an ETP of a rice parboiling industry

However, no studies have been found in the literature that have addressed the SMA of this type of sludge, nor its glycerol co-digestion. As shown in Table 2, Lourenço [112] performed the characterization of UASB sludge and effluent from a rice parboiling industry located in southern Rio Grande do Sul (Brazil) and obtained the following results:

Table 2. Characterization of sludge and effluent

Effluent		Sludge	
COD (mg O_2L^{-1})	8595.04	Humidity %	70.79
P ($mg.L^{-1}$)	8.11	P ($g.kg^{-1}$)	16.11
Mn ($mg.L^{-1}$)	0.13	Mn ($mg.kg^{-1}$)	704.23
N ($mg.L^{-1}$)	89.44	N ($g.kg^{-1}$)	29.45
Zn ($mg.L^{-1}$)	0.09	Zn ($mg.kg^{-1}$)	182.88
Fe ($mg.L^{-1}$)	0.70	Fe ($mg.kg^{-1}$)	1636.25
C (mg/L)	2303.00	%C	15.51
C/N	25.75	C/N	5.27
pH	4.48	pH	7.78

3. Experimental

3.1 Material and Methods

The determination of crude glycerol potentiating and inhibiting power concentrations of rice bran oil methyl biodiesel production in the anaerobic digestion process of the UASB Reactor sludge from the Effluent Treatment Plant of a rice parboiling industry in Rio Grande do Sul was performed based on the adaptation of the methodology developed by Nadaleti in 2016, in the patent application process, and statistical analysis of the results.

The SMA test digesters were conditioned at 35 °C, in a heating bath with thermostat, and fed sludge, of distilled water, glucose solution (80 g/L), of sodium bicarbonate (Table 3) and different proportions of crude glycerol (0, 1, 2 e 3%), for each glycerol concentration a triplicate was performed. The digesters used have a usable volume of 625 mL of which 20% is reserved to operate as headspace:

Table 3. Digester content

Sludge (mL)	14
Distilled water (mL)	473
Glucose solution (mL)	13
Sodium bicarbonate (g)	1

3.1.1 Volumetric quantification of methane generation

The quantification system developed by Nadaleti at 2016, operates from the use of NaOH solution 5%, and phenolphthalein indicator to promote biogas washing, dissolution of CO_2 in NaOH, resulting in the purification of biogas and thus allowing the quantification of the methane generated. The digester receives a connection to the meter, so it promotes the transport of biogas to the NaOH solution present in the measurement system, sealing the connections with colorless acetic silicone, prevent future losses of CH_4 to the atmosphere. Inserting a tube into the bottom of the meter, where a butterfly-type needle is attached, allows capillary escape of the phenolphthalein with NaOH solution, quantified by weighing the collection bottle, using correction factor according to the average weight of NaOH solution 5% and phenolphthalein. Figure 4 shows the complete system:

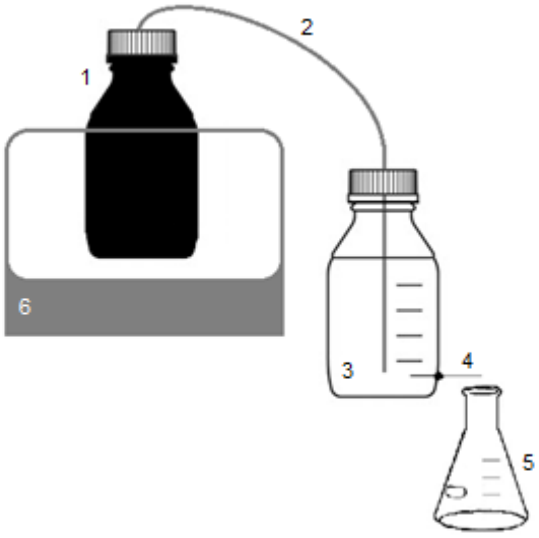

Figure 4. System used to quantify methane production

1. Digester; 2. Connection; 3. Phenolphthalein with NaOH; 4. Needle; 5. Collection bottle; 6. Heating Bath

The quantification of the methane volume produced was performed everyone hour during the first twelve hours of the experiment and, thereafter, every twelve hours for a period of seven days.

3.1.2 Analyzes

COD, Hydrogen Potential (pH) and total solids, fixed and volatile, were analyzed from inlet and outlet samples of the digesters. The COD and pH were determined based on the methodology by *Standard Methods for the examination of water & wastewater* [113], while total, fixed and volatile solids were determined by methods A, B and C, respectively, of NBR 10664 [114]. Statistical analysis of the study results was performed on the IBM SPSS Statistics software by Test F and Tukey Test, both at 5% significance.

3.1.3 Determination of the SMA

According to the methodology by Aquino *et al*. [45], the value of the SMA can be obtained by a time graph of cumulative methane production, where the SMA will be determined by the angular coefficient in the highest slope, being expressed in $mLCH_4.gVSSh^{-1}$ and $gCODCH_4.gVSSh^{-1}$. Therefore, the conversion of volumetric

methane production to COD is required by the stoichiometric coefficient of methane oxidation (Equation 1):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1)$$

Thus, Equation 1 determines the equivalence of 1 mol of methane to 2 moles of O2 or 64 g of COD. Whereas 1 mol of gas at CNTP (0 ° C and 1 atm) occupies 22.7 L, 1 g of COD consumed equals 0.354 L of methane produced at CNTP. Once the experiment was performed at 35 °C, Equation 2 was used to correct the methane volume equivalent to 1 g COD:

$$\left(\frac{P_1V_1}{T_1}\right)_{CNTP} = \left(\frac{P_2V_2}{T_2}\right)_{LAB} \quad (2)$$

Where:

P_1: CNTP pressure, equal to 1, in atm;

V_1: 1 mol volume of a gas in CNTP, in L, equal to 22.7;

T_1: CNTP temperature, equal to 273.15, in K;

P_2: Pressure in the laboratory, equal to 1, in atm;

V_2: Gas volume in the laboratory, in L;

T_2: Gas temperature in the laboratory, equal to 308.15, in K.

Thus, was determined that 1 mol of a gas at 35 °C (308.15 K) occupies a volume of 25.60865825 L, so 1 g of COD consumed corresponds to 0.3993596925 L of CH_4. Equations 2 and 3 were used to determine the SMA in terms of $mLCH_4.gVSSh^{-1}$ and $gCODCH_4.gVSSh^{-1}$, respectively:

$$SMA = \frac{\Delta V}{M_i \Delta t} \quad (3)$$

$$SMA = \frac{\Delta V}{M_i \Delta t 0.3993596925} \quad (4)$$

Where:

ΔV: Variation in the volume of methane produced over a given period, in mL

M_i: Microorganism mass added to reactor, in gVSS;

Δt: Time interval, in h.

3.2 Results and Discussion

The addition of glycerol promoted an increase in the pH of the input samples according to the increase of its concentration (Figure 5). Thus, while the system without glycerol had at its entrance a pH of 8.73, the system with 3% of glycerol reached a pH of 10.30:

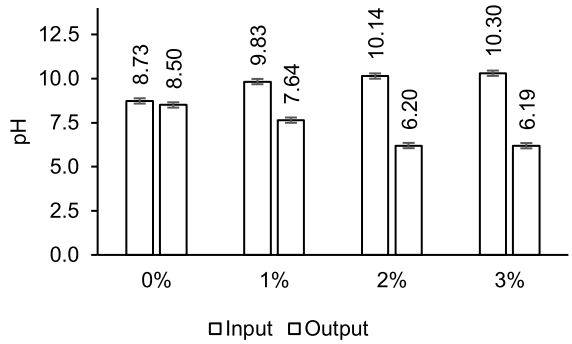

Figure 5. Graph of pH analyses results

In all systems, the anaerobic digestion process promoted in the test SMA, resulted in a pH reduction. Digestion was more pronounced in those with higher values at the system entrance. According to literature, the development of methanogenic bacteria is favored at pH tending to neutrality [115]. Therefore, the satisfactory anaerobic digestion range occurs between 6.0 and 8.0, and is inhibited below 6.0 or above 8.5 [41].

Table 4 presents the results regarding the analyzes of total, fixed and volatile suspended solids, there was no significant difference between the systems for any of the three analyzes by the F test at 5% significance:

Table 4. Results of the analyzes solids

	TS ($mg.L^{-1}$)		FS ($mg.L^{-1}$)		VSS ($mg.L^{-1}$)	
	Input	Output	Input	Output	Input	Output
0%	350.77	288.23	250.31	198.13	100.46	90.10
1%	371.51	314.62	264.81	227.79	106.70	86.83
2%	353.16	316.69	252.19	216.83	100.97	99.86
3%	364.86	334.14	260.19	240.09	104.67	94.05

Such analyzes are necessary for the determination of SMA once it is expressed in $gCODCH_4.gVSS^{-1}$ in a given time interval, the inoculated sludge mass and conventional gravimetric measurement of volatile suspended solids must be known are usually adopted as the total bacterial concentration and active biomass added to the reactor [116].

According to the results of the COD analyzes (Figure 6) was the 1% glycerol system, with the removal of 12728.89±153.96 $mg.L^{-1}$ of COD, corresponding to a removal of 76.99% of COD in relation to the system. The 0%, 2% and 3% systems removed 1809.78±99.24 $mg.L^{-1}$, 7520.00±161.88 $mg.L^{-1}$ and 3520.00±144.40 $mg.L^{-1}$ COD. Thus, all removals are significantly different from each other by the Tukey test at 5% significance:

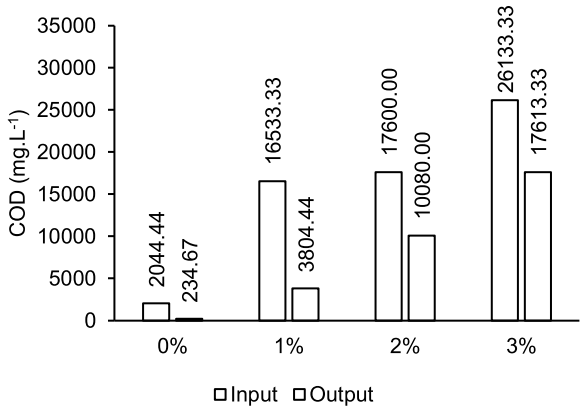

Figure 6. Graph of COD analyzes results.

These results corroborate with the results of volumetric quantification of methane generated in the systems and the literature, since anaerobic treatment processes directly relate COD removal to methane production [117]. Analyzing the results of volumetric quantification of methane generated in the first 12 hours of methanogenic activity at one-

hour intervals (Figure 7), it is observed that the absence of glycerol promoted a higher production peak, reaching 35.25±5.33 mL in the first hour. Thus, only in the system with 3% glycerol, the production peak did not occur in a time equal to 1 hour, having happened only with 5 hours of experiment and reaching 29.23±4.01 mL of methane produced. The systems with 1% and 2% had their production peaks totaling 7.48±2.29 mL and 19.82±4.24 mL, respectively. However, after the peak presented in the first hour of the experiment the system without glycerol addition had decay and stabilization of methanogenic activity (Figure 7), so that in the interval between 12 and 24 hours of experiment had production of only 1.56±0.09 mL of methane and between 36 and 48 hours of experiment the production was already less than 1 mL (Figure 8):

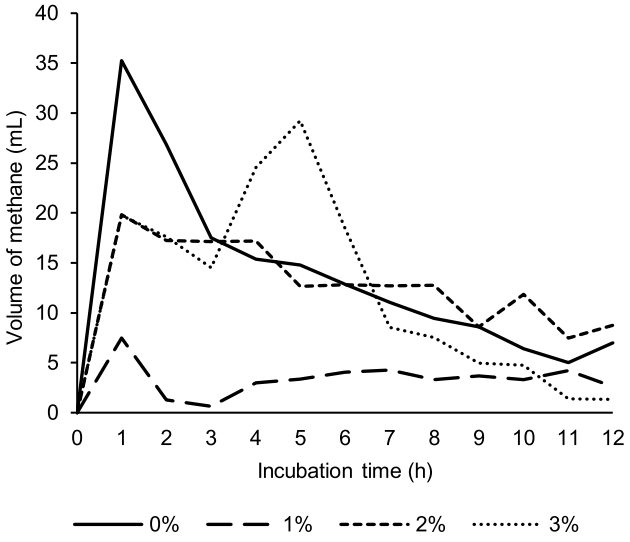

Figure 7 – Graph of methane production in the first 12 hours of experiment.

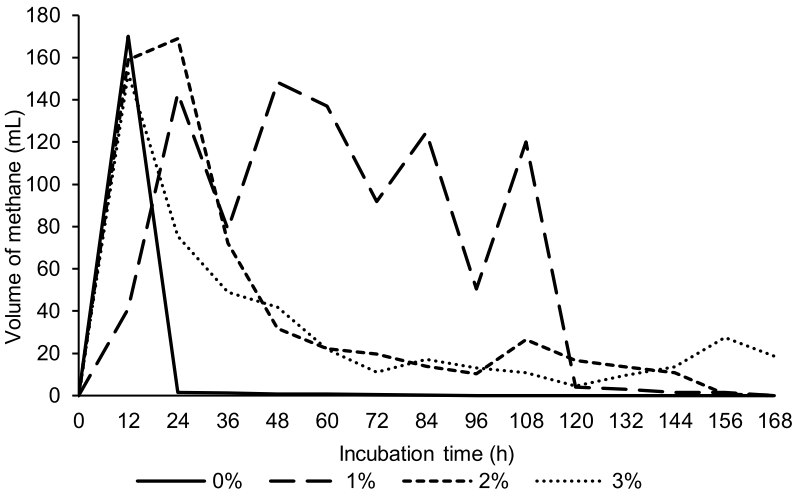

Figure 8 – Graph of methane production over the 168 hours of experiment.

Similar decay was observed in the system with 3% glycerol, however, the same occurred gradually throughout the experiment also after the first 12 hours of the experiment. In the 1% glycerol system the decay of methane production occurred only after 120 hours of activity (Figure 8).

In order to obtain the data for the calculation of the SMA, a graph (Figure 9) of the accumulated methane volume over the time interval, in days, in which the experiment took place was plotted. It is important to note that all results differed significantly from each other by the Tukey test at 5% significance. Thus, we can see from the graph that in fact the highest

methane production occurred in the 1% glycerol system, totaling a volume of 945.23±5.34 mL of methane, a production equivalent to 539.45% of system production without added glycerol:

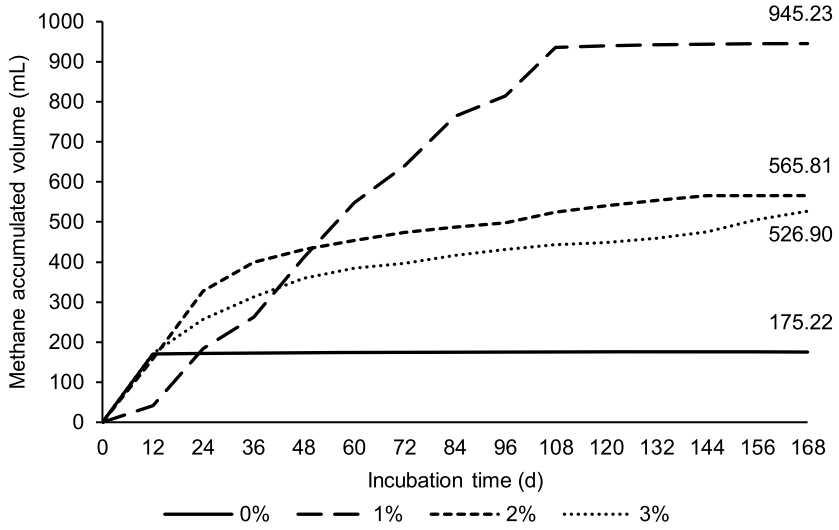

Figure 9 – Graph of methane production accumulated over 168 hours of experiment.

The addition of higher glycerol concentrations in the anaerobic digestion process resulted in inhibition of methanogenic bacteria, since the systems with 2% and 3% glycerol presented lower production than the system with 1%. Thus, from the accumulated methane production and the graphs of Figures 7 and 8 is possible concluded that the system with 1% glycerol allowed a larger stationary phase to the population of methanogenic bacteria present in the systems, enabling the phase of decline to occur only after 120 hours of activity. While in the system without added glycerol the decline phase occurred at the end of the first 12 hours, probably due to the low carbon supply in the system when compared to the other. The systems with 2% and 3% glycerol, despite to have glycerol as carbon source, entered the decline phase, respectively, with 24 and 12 hours, since excess glycerol causes toxicity to the system. Thus, is possible to seen that the glycerol potential to increase methanogenic activity when added at a concentration of 1% is relevant, since such system, even being out of the pH recommended by the literature (Figure 5), obtained superior production to the system without glycerol, which had a higher pH close to that recommended in the literature.

The application of biodiesel byproduct as a substrate for anaerobic digestion of starch effluent, in a study by Lins *et al.* [118], promoted a 94% higher yield when compared to anaerobic digestion of the same effluent without the addition of glycerol. The same authors found a 46% increase in methane production with the addition of glycerol to the anaerobic

digestion process. Larsen [26] found that while the addition of 2% glycerin in anaerobic digestion of Manipura (starch effluent) promotes the growth of biogas production, the addition of 3% can generate a decrease in production.

The addition of glycerol also favours the production of biogas in its co-digestion with swine manure. Aguilar-Aguilar *et al*. [23] report maximum biogas production on digestion of 4 g/L crude glycerol and 5 g/L swine manure for 35 days, totalling 521.5 mL of biogas generated per gram of initial COD. Araújo [24] states that the use of crude glycerin as co-substrate is also efficient in the production of biogas via anaerobic digestion of sheep manure, promoting greater energy intake when compared to digestion without the addition of it.

Silva *et al*. [119] studied hydrogen and methane production in a two-stage anaerobic digestion system of food waste co-digestion, sewage sludge and glycerol. The authors determined that the addition of glycerol to food waste and sewage sludge increased yields of H_2 and CH_4. With a stable production and higher energy yield were obtained with the addition of 1% glycerol, contributing to reduce the lag phase of bacterial culture and methanogenic instability with 3% addition. Veroneze *et al*. [120] determined that the addition of glycerin at doses up to 5% does not represent an increase in biogas production using anaerobic reactors with swine manure in relation to digestion without the addition of glycerin, however, glycerin doses higher than 5% impair biofuel production.

According to Bertozzo [25], the anaerobic co-digestion process of dairy cattle manure and crude glycerin provides higher biogas production than individual waste digestion, when added at daily loads less than 2.5%. Siqueira [27], who also studied the addition of different crude glycerin concentrations in dairy cattle manure, concluded that the addition of 4% glycerol resulted in higher biogas production and that the addition of 6% caused process instability due to the probable accumulation of volatile fatty acids. Such discrepancy may be related to the chemical composition of glycerol and crude glycerin, as it varies according to the type of catalyst and alcohol employed in biodiesel production, as well as transesterification efficiency and biodiesel recovery and purification [121].

The addition of 2.5% glycerol resulted in higher specific biogas production (1654.1 $L.kgVS^{-1}$ added) while adding 2.6% to the highest maximum specific methane production (1058,9 $L.kgVS^{-1}$ added), increasing methane generation by more than 36% compared to glycerin-free treatment. Larger reductions in TS (60.97%) and VS (73.6%) were observed with ideals addition levels of 2.2 and 2.4% glycerol. The addition of glycerol to 2.1% using glycerin with 40% of glycerol resulted in the largest reduction (55.4%) of COD.

Zahedi *et al*. [123] evaluated the effect of glycerol supplementation on anaerobic digestion of real urban solid waste in batch, exploring the effect of five glycerol concentrations (0%, 0.1%, 0.25%, 0.5% and 1%). The authors reveal that with the addition of 0.25% v/v crude glycerol to the feed, the methane production rate increased by 48%, with increased TVS removal from 65±7% to 81±7% and methanogenic activity from 110E−12±17E−12 LCH_4 per cell to 156E−12±24E-12 LCH_4 per cell. The addition of 0.5% or 1% was not viable for the waste thermophilic process, as it caused inhibition of methanogenic activity.

According to Aquino *et al*. [45], SMA can be determined according to the angular coefficient in the most inclined section of the graph refers to the accumulated methane volume over a given incubation time interval. Thus, the SMA of each system shown in Figures 10 and 11 was determined from the highest production intervals shown in the graph of Figure 8:

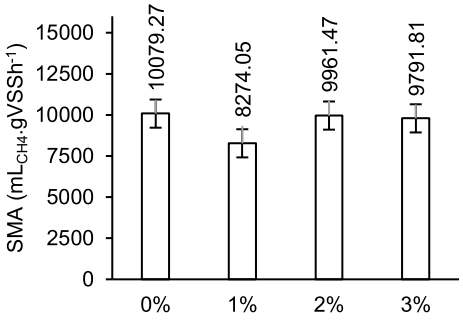

Figure 10. Graph of SMA in $mLCH_4.gVSSh^{-1}$.

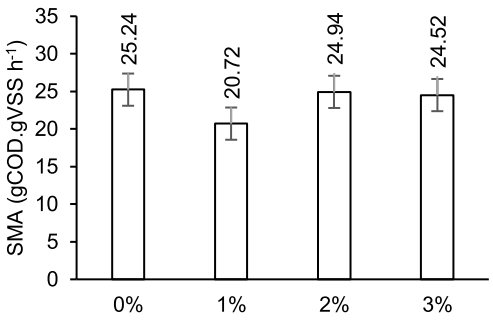

Figure 11. Graph of SMA in $gCOD.gVSS\ h^{-1}$.

From the results obtained in this study was found that the system that showed higher SMA was the one that did not receive the addition of glycerol, while the smallest one received 1% glycerol since it presented the lowest production peak when compared to the others. It is noteworthy that despite this result, in terms of methane production throughout the experiment, the addition of 1% glycerol was precisely what resulted in the largest volume of gas generated, since it was the only one able to provide greater carbon availability and absence of toxicity from glycerol concentration.

This data is extremely important regarding the application of anaerobic co-digestion of rice parboiling effluent and glycerol using the sludge tested in this study as inoculum in order to promote methane production for power generation. It should also be considered that there are no literature data about anaerobic sludge SMA from rice parboiling.

In a study conducted by Nadaleti [11], was determined that the energy production potential from methane generated in anaerobic digestion of effluents from the parboiled rice industries, using sludge from the same origin as the present study, in southern Brazil is 2.2E+07 kWh.year^{-1} for electric and 3.1+07 kWh. year^{-1} for thermal energy. It is noteworthy that the state of Rio Grande do Sul is located in the southern region of the country and was responsible for more than 70% of the national crop 2017/2018 [86].

In 2017, the industrial sector was responsible for the largest consumption of electricity in the state of Rio Grande do Sul, 33%, and in the same year, electricity consumption increased by 3.9% over the previous year [124]. In general, industries have been experiencing an increase in their production costs due to the use of electricity, thus, while the sector is highly dependent on electricity, corporate energy management has a strong focus on strategies for optimizing contracting and consumption [125].

Zhao [125] emphasizes the importance of strengthening the productive autonomy of the industry in order to promote financial returns, enabling environmental liabilities susceptible to reuse or energy readjustments to be the solution of the problem. This possibility has not been explored by the industrial sector throughout Brazil, since in what concerns the energy consumption of the sector, there was not practically change in the matrix regarding the participation of renewable and non-renewable sources [124,126].

According to classification of Energy Research Company, the rice processing industries are classified as food and beverage Industries, this category accounts for 9% of the final energy consumption of the national industrial sector [124], whereas that in the southern region, as in RS, the consumption is even higher, where the manufacture of food products is responsible for the highest consumption of electricity, 23.4% [124,127].

Considering that the production potential with the addition of 1% was 539.45% higher than the system without glycerol addition, the potential determined by Nadaleti [11] mentioned above can be significantly increased with the addition of the byproduct of rice bran vegetable oil biodiesel production, showing a higher capacity than highlighted by Nadaleti and Przybyla [10]. The authors addressed the production potential of synthesis gas and biogas produced from rice husk and parboiled rice effluent, respectively, the authors state that the energy production potential of the rice parboiling industries in Brazil is high and able to promote their energy self-sufficiency, with surplus energy trading.

4. Conclusion

The review of the SMA tests on the rice industry found that there are few experimental studies on the production of biogas and methane from the anaerobic sludge of rice parboiling. This is the first study to report the SMA of this type of sludge, as well as its glycerol co-digestion.

Through the study was possible to determine that although the addition of glycerol does not increase the anaerobic sludge SMA of rice parboiling, the byproduct of biodiesel production is able to prolong the duration of the stationary phase of methanogenic bacteria to increase total methane production at the end of the anaerobic digestion process.

Therefore, the addition of 1% glycerol promoted the longer stationary phase period resulting in 539.45% generation, greater than the system without glycerol, totaling a volume of 945.23±5.34 mL of methane produced in 168 hours of the experiment. In addition, the anaerobic digestion process was efficient for COD removal and pH reduction in all systems, especially in those that had the addition of glycerol.

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4.3 Artigo 3: Generation of biodiesel, biogas, thermal and electric energy from waste and effluent of rice parboiling industries in Brazil

ABSTRACT

Studies claim that the energy potential of effluent and rice husk generated in the processing of grain in rice parboiling industries in Rio Grande do Sul can promote energy self-sufficiency in the sector, through the production and use of syngas and biogas. However, there is no potential in the literature in the state when considering the possibility of producing biodiesel through oil extracted from rice bran and the use of the glycerol generated, whether crude or purified, as a co-substrate in the production of methane at the UASB for the treatment of effluent parboiling of rice. Thus, the objective of this study was to determine the potential for biodiesel production, via methyl basic transesterification of rice bran vegetable oil, and methane, via anaerobic co-digestion of the effluent from rice parboilization and glycerol from biodiesel production, as well as for the production of thermal and electric energy derived from biofuels in the rice industries of the state of Rio Grande do Sul. According to the results obtained, a production potential of 8.34E+02 $m^3.d^{-1}$ of bran oil biodiesel was found and a potential 8.44E+04 $Nm^3.d^{-1}$ of methane through the individual digestion of the effluent in Rio Grande do Sul. Through the addition of 1% crude glycerol in the digestion process, Rio Grande do Sul has a potential to reach a production of 4.55E+05 $Nm^3.d^{-1}$. Thus, the state reaches a potential of 2.93E+06 $kWh.d^{-1}$ of electric energy and 5.55E+06 $kWh.d^{-1}$ of thermal energy through the production and use of biodiesel and methane as energy sources.

Keywords: rice; bran; wastewater; biodiesel; biogas; methane; bioenergy.

1. Introduction

Brazil's high agro-industrial activity highlights the country as the ninth largest rice producer in the world (FAO 2018), so that the grain is consolidated as an important component of the national economy (Queiroz *et al*. 2007). According to the National Supply Company (CONAB 2019), the country achieved production of around 12 million tons of rice produced in the 2017/18 harvest, with the Rio Grande do Sul being the state responsible for making up most of this production (IBGE 2018).

Nadaleti and Przybyla (2018) and Nadaleti (2019), claim that the potential for energy production from the effluent and husks generated in the grain processing in rice parboiling industries in Brazil is capable of promoting energy self-sufficiency in the sector, through the production and use of syngas and biogas. Thus, the relevance of the study of the application of residues, such as husk and grain bran, and effluent from rice processing to produce biofuels as a source of clean and renewable energy is highlighted.

Its sources are in the form of crop biomass and agricultural waste, solid urban waste and effluents with a high content of organic matter. The production of liquid biofuels occurs mainly using different agricultural raw materials from oil and leguminous crops to obtain bioethanol and biodiesel (Ramos *et al*. 2017; González-González *et al*. 2018). For the production of biodiesel, the technique usually applied for industrial-scales is that of transesterification of the oils extracted from the biomasses to obtain Fatty Acids (FA), such a process guarantees the oil characteristics similar to those of diesel oil (Lima Filho *et al*. 2017).

In the transesterification reaction, a triglyceride reacts with hort-chain alcohol in the presence of a catalyst producing biodiesel and glycerin (Singh and Singh 2010; Visentainer 2013). Crude glycerin is considered a by-product of the reaction and contains approximately 95% glycerol in its composition, for every 10 kg of biodiesel produced, about 1 kg of glycerol is generated (Fontinele *et al*. 2017; Silva *et al*. 2017), or that is, the increase in biodiesel production in the last decade resulted in the high accumulation of the by-product, evidencing the need for new alternatives for its application (D'Aurea *et al*., 2017; Silva *et al*., 2017).

Anaerobic digestion is evidenced as a favorable alternative for the application of glycerol, by co-digesting the by-product with other organic substrates to obtain biogas and methane (CH_4) through the complex interaction of microorganisms capable of degrading the organic matter present in the system and convert it, mainly, into CH_4 and Carbon Dioxide (Schiwingel *et al*. 2016). Furthermore, anaerobic digestion is a valuable source of bioenergy capable of offering a competitive solution regarding the global dependence on fossil fuels (González-González *et al*. 2018).

In this context, anaerobic co-digestion, simultaneous digestion of two or more residues and/or organic effluents, becomes an area to be explored due to its potential to increase the efficiency of the conventional technique, with the main improvement being in production biogas and CH_4 concentration (Anjum *et al*. 2017; Hagos *et al*. 2017; Maragkaki *et al*. 2017). Thus, the increase in glycerol can favor anaerobic digestion by balancing the ratio of carbon to nitrogen (C/N) and thus increase the production of biogas and CH_4 (Meier *et al*. 2016; Kurahashi *et al*. 2017).

Methane production from residues of the rice parboiling industries is still little explored by academic studies (Nadaleti *et al*. 2018; Lourenço *et al*. 2019; Nadaleti *et al*. 2019). In addition, has studies on the potential for methane production through this

same type of effluent in Rio Grande do Sul (Nadaleti 2017), in the southern region of the country (Nadaleti 2019) and in the city of Pelotas, in the state of Rio Grande do sul (Silveira 2019). In the literature, there is no potential in these industries when considering the use of glycerol, whether crude or purified, as a co-substrate in the production of methane at the UASB for the treatment of rice parboiling effluent or the potential for production of rice bran oil biodiesel.

Considering Rio Grande do Sul the Brazilian state responsible for the largest national production of rice, the state becomes attractive from the scientific point of view regarding the realization of research that explores the production of biofuels from the rice industry, evaluating the production potential of bioenergy in the state. From the above, the objective of this study was to determine the potential for biodiesel production, methyl basic transesterification of rice bran vegetable oil, and methane, anaerobic co-digestion of the effluent from rice parboiled and glycerol from biodiesel production, as well as well as the production of thermal and electric energy derived from the biofuels of the rice industries in the state of Rio Grande do Sul, located in the southern region of Brazil.

2. Theoretical framework

2.1 Energy scenario in Brazil and Rio Grande do Sul

In 2018, Brazil reached a total of 416.1 million tons of Carbon Dioxide equivalent in its emissions from the national energy matrix. In this context, the industrial sector stood out as the second-largest source of emissions, 18.8% of the total (EPE 2019). Also, according to data from EPE (2019), fossil fuels represented 54.70% of the country's internal energy supply. Updating the national energy matrix by replacing it with renewable and clean energy sources becomes an emergency (González-González *et al*. 2018).

In this context, regarding the participation of renewables in the generation of electricity, these sources accounted for 83.3% of the country's electricity matrix in 2018 (EPE 2019). However, the growing use of renewable energy occurs through hydroelectric plants, 66.6% of national production (EPE 2019). However, despite the high efficiency in energy generation, its construction and operation result in several negative environmental impacts (Ziembowicz *et al*. 2018). In this sense, there is a search for the adoption of the use of biomass in the national energy matrix.

The industrial sector represents about 27.5% of the economy and 22.44% of the final energy consumption of the state of Rio Grande do Sul, in the sector the agroindustry, the chemical industry, the metalworking and the leather/footwear are the main highlight (Rio Grande do Sul 2011; BERS 2015). In 2017, the industrial sector reached the highest consumption of electricity in the state up to that time, 33%, and in the same year electricity consumption increased by 3.9% in relation to the previous year (EPE 2018).

Considering that the sector is highly dependent on electric energy, corporate energy management turns to strategies for optimizing contracting and consumption (Zhao 2011), since industries suffer an increase in their production costs due precisely to the use of energy electrical (CNI, 2016). In this context, Zhao (2011) points to the productive autonomy of the industry that promotes financial returns through environmental liabilities liable to reuse or energy use. Brazil, in general, has not explored this possibility in the industrial sector throughout Brazil, in recent years there has been no significant change in the energy consumption matrix of the sector regarding the participation of renewable and non-renewable sources (EPE 2018; Salazar 2012).

2.2 Rice sector in Brazil and Rio Grande do Sul

The country closed the 2017/18 crop with about 12 million tons of rice produced and has estimates for production for 2018/19 of approximately 11.2 million tons (CONAB, 2019). The state that supplies most of the rice production in Brazil is Rio Grande do Sul, which was responsible for the production of 70.1% of the 2017/2018 national harvest, totaling an offer of more than 8 million tons of grain (CONAB 2019).

Of all the rice consumed in the country, about 25% of the rice is of the parboiled type (Paraginski *et al*. 2014). Parboiling also involves a specific unit where the grain is soaked in 60 °C water tanks for about four hours, followed by the vaporization and drying steps (AGEITEC 2016).

2.2.1 Rice bran

Rice processing industries are classified as Food and Beverage Industries, being this category responsible for 9% of the final energy consumption of the national

industrial sector (EPE 2018). In the southern region of Brazil, as well as in the state of RS, consumption is even higher, 23.4% (BERS 2015; EPE 2018). The processing of the grain involves several processes, varying according to the methods adopted by the industries (ABIAP 2013). In general, the main production cost is the consumption of electricity, which can exceed 40% of the total, directly influencing the profitability of the segment (Velasquez *et al*. 2012).

The processes that have the greatest influence on the demand for electricity are the stripping, 52%, followed by the parboiling stage, 28% (Rocha 2010). Nadaleti (2019) carried out a case study in one of these industries that were based on the energy potential from systems that operate with a CHP (Combined Heat and Power) generator set using hydrogen synthesis gas from rice husks and the biogas from anaerobic effluent treatment. The author determined the potential to produce at least 2.17E+04 MWh of electricity considering only the use of the biogas generated. Although the author considered only the use of the shell and the effluent, there is still a third residue that can be used for energy.

During rice hulling and polishing, rice bran is generated, an agricultural residue that is usually used to produce animal feed (Evangelista 2011; Pereira 2013). The residue contains 15 to 23% oil (Zullaikah *et al*. 2005; Sinha *et al*. 2008) consisting of about 68 to 71% triacylglycerols, 2 to 3% diglycerols, 5 to 6% monoglycerols and 2 to 3% free fatty acids (Pestana 2008).

Rice bran oil is one of the most nutritious vegetable oils (Lai *et al*. 2005; Silva 2008; Lin *et al*., 2009), is widely consumed in Asian countries, however in Brazil its food use is not widespread, low occurrence (Goffman *et al*. 2003; Pestana, 2007; Walter, 2009). It has about 80% unsaturated AG, however the oil has no propensity for oxidation due to the presence of natural antioxidants in its composition (Xu and Godber 1999; Krishna 2002; Choi *et al*. 2007; Chotimarkorn and 2008). Furthermore, due to the presence of active lipase, rice oil has a high content of Free Fatty Acids (FFA) (Pereira *et al*. 2015) (Table 1):

Table 1 Fatty acids constituting bran and rice oil
Source: Tortosa and Barber (1979)

FA	(%)
C14: 0 Miristic	0.1-2.4
C16: 0 Palmitic	12.3-20.5
C16: 1 Palmitoleic	0.1-0,2
C18: 0 Stearic	1.1-3.0
C18: 1 Oleic	37.1-52.8
C18: 2 Linoleic	27.0-40.7
C18: 3 Linolenic	0.5-2.3
C20: 0 Archaic	0.3-0.7
C22: 0 Behenic	0.5-1.0
C24: 0 Lignoceric	0.4-0.9

The triglycerides present in the bran are rapidly hydrolyzed in free FA due to the enzymatic systems present in the bran, such a process results in elevating the acidity content (Evangelista 2011). Thus, the extraction of oil for refining for human consumption becomes relevant only when the acidity content is reduced, since, according to ANVISA (1999), the percentage of AGL in vegetable oils used in human consumption must be maximum $0.3g.100g^{-1}$. In a study by Zullaikah *et al*. (2005), at zero storage time, the percentage of GA free from rice bran was above the pre-established by ANVISA (1999).

Thus, rice processing offers a low-cost source of triglycerides capable of promoting biodiesel production (Lai *et al*. 2005; Sinha *et al*. 2008; Oliveira 2012; Pereira 2013). According to Sinha *et al*. (2008), vegetable oil from rice bran produces biodiesel with excellent physical-chemical properties, due to its natural antioxidants (Sinha *et al*. 2008), allowing its use in mixtures with other oilseeds or with mineral diesel (Evangelista 2011).

In January 2008, by means of Law 11,097/2005, the addition of 2% biodiesel to diesel in Brazil became mandatory, with a gradual increase forecast (Brasil, 2005). According to the schedule established by Law No. 13,263/2016, in March 2019, biodiesel started to make up 10% of the mixture (Brazil, 2016). As a result of the gradual increase, biodiesel production grows in the country, in 2017 production in the country grew 24.7% in relation to the previous year, reaching the amount of 5,350,036 m^3 (EPE, 2019). The most widely used technique for large-scale production of biodiesel is the transesterification reaction, a chemical reaction between the raw material and alcohol in the presence of a catalyst (Sajid *et al*. 2016).

2.2.2 Wastewater from rice parboiling

The critical point in the generation of effluents in a parboiled rice industry occurs in the flooding stage, since it uses a large volume of water that retains grain properties during the process (Amato *et al*. 1989). For each kilo of parboiled rice, 2 to 4 L of the effluent is generated (Bastos *et al*. 2010; Santos 2012).

If disposed in water bodies without proper treatment, the effluent can have negative environmental impacts on the environment, such as the eutrophication process (Okunuki *et al*. 2004; Faria *et al*. 2006), this is due to its high level of organic load and nutrients (Faria *et al*., 2006; Queiroz *et al*., 2007). According to Bastos *et al*. (2010) there is high variability in the characterization of the rice parboiling effluent, such variation occurs due to seasonal aspects related to grain production. Different studies show effluents from the same industrial sector with high variation in their characterization (Table 2):

Table 2 Characterization of the raw effluent from rice parboiling in different studies

Parameter	Gerber *et al*. (2018)	Isoldi *et al*. (2003)	Bastos *et al*. (2010)	Queiroz and Koetz (1997)	Queiroz *et al*. (2007)	Nadaleti *et al*. (2018)
COD ($mgOL^{-1}$)	398.70	2539.60	4206.8	1019.19	4206.80	6447.50
P ($mgPL^{-1}$)	7.90	-	-	-	-	-
KTN* ($mgNL^{-1}$)	23.10	120.90	78.10	-	32.44	-
Ph	6.30	-	4.64	4.59	4.60	3.47
TSS** (mgL^{-1})	153.40	-	-	89.01	-	-
C/N	-	21.00	53,.8	37.90	72.73	-

* Kjeldahl Total Nitrogen
** Total Suspended Solids

The production of biogas and methane via anaerobic digestion of organic substrates, such as effluents from rice parboiling, is reported as one of the most energy efficient and environmentally friendly techniques for generating biofuels, reducing greenhouse gas emissions when replacing fuels fossils (Weiland 2010). Anaerobic co-digestion is a technique that promotes the simultaneous digestion of two or more substrates that have complementary characteristics, standing out as a promising process for biogas production by increasing the stability and efficiency of the system, enhancing the production of biogas and the efficiency of methane (Capodaglio *et al*. 2016; Anjum *et al*. 2017; Hagos *et al*. 2017; Maragkaki *et al*. 2017).

Thus, the technique is capable of increasing biogas production by about 25-400% in relation to the anaerobic digestion of only one of the substrates (Hagos *et al*,

2017), increasing the efficiency of the anaerobic digestion of solid and effluent residues by synergisms established by mixing different substrates, such as the supply of nutrients, the balance of the C/N ratio, the availability of organic matter, the best buffering capacity and the dilution of inhibitory compounds (Agdag and Sponza, 2007; Xie *et al*., 2011; Mazareli 2015; Capson-Tojo *et al*. 2017; Maragkaki *et al*., 2017). The use of a co-substrate such as glycerol in anaerobic digestion can increase the efficiency of the production of biogas and CH_4, since microorganisms can use it as a carbon source (Jones and Woods 1986; Mata-Alvarez *et al*. 2000; Meier *et al*. 2016; Kurahashi *et al*. 2017; Yen and Brune, 2007).

3. Material and Methods

3.1 Biodiesel

The quantification of the theoretical potential of rice bran oil production was carried out based on data from the literature (Zullaikah *et al*., 2005; Sinha *et al*. 2008) and on the operating licenses of the rice industries of Rio Grande do Sul granted by the State Foundation for Environmental Protection (FEPAM). The potential for biodiesel production from such oil, on the other hand, was calculated based on results obtained in pre-existing studies regarding the efficiency of the methyl transesterification of vegetable oil and the Lower Heat Power (LHP) of the biofuel, determined from its composition (Lourenço 2020).

3.2 Methane

From the data obtained in the operating licenses of the rice industries of Rio Grande do Sul granted by the State Foundation for Environmental Protection (FEPAM), three different methodologies were applied to calculate the methane generation potential for the rice parboiling industries in Biofuels and bioenergy from waste and effluent of rice industries: Potential of the state of Rio Grande do Sul-BR the Rio Grande do Sul from anaerobic digestion of rice parboiling effluent:

- Speece (2001)

$$COD_{CH_4} = Q_{ww} * [(S_O - S) - ((Y_{obs} * K_{solid}) * (S_O - S))] \quad (1)$$

Where:

COD_{CH_4}: DQO convertida em metano (kgDQO$_{CH4}$d^{-1});
Q_{ww}: effluent flow (m³/y);
S_O: COD concentration in the affluent (in kgCODm^3);
S: COD concentration filtered in the effluent (kgCODm^3);
Y_{obs}: coefficient of production of solids in the system (kgCOD$_{lodo}$kgCOD$_{aplicada}^{-1}$), igual a 0,11;
K_{solid}: conversion factor of total volatile solids into COD (kgCODkgTVS^{-1}), equal to 1,42.

Conversion of COD$_{CH4}$ from kgCOD$_{CH4}$.d^{-1} to m^{3}CH$_4$.d^{-1}:

$$\mathrm{Q_{CH_4}} = \frac{\mathrm{COD_{CH_4}}}{\mathrm{K(t)}} \quad (2)$$

Where:

$\mathrm{Q_{CH_4}}$: volume of methane produced (m^3.d^{-1});
$\mathrm{K(t)}$: reactor operating temperature correction factor (kgCODm^3).

Temperature correction factor:

$$\mathrm{K(t)} = \frac{\mathrm{P\,K}}{\mathrm{R\,T}} \quad (3)$$

Where:

P: atmospheric pressure (atm);
K: COD corresponding to 1 mol of CH$_4$ (CODmol^{-1}),equal to 64g;
R: constante universal dos gases (atmL(mol.K)$^{-1}$), equal to 0,08206;
T: reactor operating temperature (K).

- Metcalf & Eddy (2003)

$$\mathrm{X_m} = \mathrm{COD_{af}} - \mathrm{COD_{ef}} - \mathrm{COD_{SSV}} - \mathrm{COD_{CH_4}} \quad (4)$$

Where:

$\mathrm{X_m}$reactor operating temperature (kgCOD.m^3);
$\mathrm{COD_{af}}$: affluent COD in the reactor (kgCOD.m^3);
$\mathrm{COD_{ef}}$: effluent COD in the reactor (kgCOD.m^3);

$\mathrm{COD_{SSV}}$: COD associated with volatile organic matter suspended in the reactor (kgCOD.m^{-3});
$\mathrm{COD_{CH4}}$: amount of oxygen needed to completely oxidize methane to carbon dioxide and water, equal to 0.35 (m^{3}CH$_4$(kgCOD^{-1})).

Volume occupied by 1 mole of methane gas considering the reactor temperature:

$$\mathrm{V_{CH_4}} = \frac{\mathrm{nRTz}}{\mathrm{P}} \quad (5)$$

Where:

$\mathrm{V_{CH_4}}$: volume occupied by 1 mole of methane gas (L);
n: number of moles of methane;
R: ideal gas constant (atmL(molK)$^{-1}$), equal to 0,082057;
T: temperature (K);
Z: compressibility factor of methane;
P: pressure (atm).

Deviation from the ideality of a real gas:

$$\mathrm{Z} = \frac{\mathrm{V_{Real}}}{\mathrm{V_{Ideal\,gas}}} \quad (6)$$

Where:

$\mathrm{V_{Real}}$: actual molar volume calculated from the Van der Waals equation of state;
$\mathrm{V_{Ideal\,gas}}$: ideal molar volume of methane.

COD equivalent converted to methane under anaerobic conditions:

$$CH_{4_{equivalent}} = \frac{\mathrm{V_{CH_4}}}{\mathrm{O_{CH_4}}} \quad (7)$$

Where:

$CH_{4_{equivalent}}$: methane equivalent to converted COD (m^{3}CH$_4$(kg.COD)$^{-1}$);
$\mathrm{O_{CH_4}}$: mount of oxygen required to oxidize 1 mole of methane, equal to 64 (gCODmol^{-1}).

$$Q_{CH_4} = COD_{CH_4} * CH4_{equivalent} \quad (8)$$

Where:

Q_{CH_4}: methane gas production ($m^3.d^{-1}$).

- UNFCCC (2012)

$$Q_{CH_4} = Q_{ef} * COD_{ef} * Bo_{CH_4} * MCF * CFU * \eta * COD \quad (9)$$

Where:

Q_{CH_4}: amount of methane ($kgCH_4h^{-1}$);
Q_{ef}: effluent flow (m^3h^{-1});
COD_{ef}: COD of the effluent ($kgDQOm^{-3}$);
Bo_{CH_4}: maximum capacity for mass methane production ($kgCH_4(kgDQO)^{-1}$), equal to 0,25;
MCF: methane correction factor, referring to anaerobic reactors, UASB reactors and fixed bed reactors, equal to 0.8.
CFU: correction factor due to uncertainty, equal to 0.9;
ηCOD: COD removal efficiency for UASB reactors, equal to 0.7.

The data referring to the substrate characterization were determined based on the methodology of Standard Methods for the Examination of Water & Wastewater (2005) and NBR 10664 (ABNT, 1989). The gas production potential from the co-digestion of the effluent with crude glycerol from the transesterification of rice bran vegetable oil was determined based on the results obtained through the results for the digestion of only the effluent and the results of Lourenço (2020) on Specific Methanogenic Activity (SMA) of sludge from a UASB of the effluent treatment plant of a rice parboiling industry from the addition of 1, 2 and 3% of crude glycerol from methyl transesterification of the oil. The data referring to the substrate characterization were determined based on the methodology of Standard Methods for the Examination of Water & Wastewater (2005) and NBR 10664 (ABNT, 1989).

3.3 Energetic potential

In order to determine the energy potential of Rio Grande do Sul from biodiesel from rice bran vegetable oil and methane from the rice parboiling industries, the theoretical PCI of both biofuels 51.55 $MJ.m^{-3}$ for methane (Silveira *et al*. 2019) and

55.77 $MJ.m^{-3}$ for biodiesel, and that of biodiesel was determined from the concentrations of methyl esters found in the composition of the rice bran oil biofuel according to Lourenço (2020). Thus, the potential for producing electric and thermal energy from biofuels, methane and biodiesel, were calculated based on Equations 10 and 11 (Nadaleti 2017):

$$CE = \bar{Q} * LCV \quad (10)$$

Where:

CE_{CH4}: chemical energy production ($MJ.d^{-1}$);
$\bar{Q}_{CH4}$: volume of fuel ($m^3.d^{-1}$);
LCV_{CH4}: lower calorific value of biofuel ($MJ.m^{-3}$).

$$E = CE * \eta M * C \quad (11)$$

Where:

E: energy ($kW.d^{-1}$);
ηM: engine efficiency (%), equal to 85 for thermal energy and 45 for electrical energy for the CHP engine powered by methane (Silveira 2019), 80 for thermal energy and 20 for electric energy for the mCHP engine powered by biodiesel (Krishna *et al*. 2010)
C: conversion from MJ to kWh, equal to 0.2778.

4. Results and Discussion

4.1 Biodiesel

The data presented in Table 3 were obtained as follows: Raw rice, the data were collected from the operating license of each of the rice industries present and active 63. the Rio Grande do Sul; Bran, was calculated based on an average of 9.9% corresponding to the content of agricultural waste in the composition of the grain (Zullaikah *et al*. 2005; Sinha *et al*. 2008); Oil, was calculated based on an average of 19% corresponding to the oil content present in the bran composition (Zullaikah *et al*. 2005; Sinha *et al*. 2008) considering a density of 0.921 $ton.m^3$ for rice bran vegetable oil (Paucar-Menacho *et al*. 2007); Biodiesel, was calculated based on the 98.9% yield obtained by Lourenço (2020) through the methyl transesterification of refined rice bran oil at 80 °C, 6:1 molar ratio of oil to alcohol, 1% potassium hydroxide as a catalyst and a reaction time of 120 minutes:

Table 3 Theoretical potential for bran generation and production of vegetable oil from rice and biodiesel

Industry	Crude rice ($ton.d^{-1}$)	Bran ($ton.d^{-1}$)	Oil ($m^3.d^{-1}$)	Biodiesel ($m^3.d^{-1}$)	Industry	Crude rice ($ton.d^{-1}$)	Bran ($ton.d^{-1}$)	Oil ($m^3.d^{-1}$)	Biodiesel ($m^3.d^{-1}$)
1	2.47E+02	2.44E+01	5.04E+00	4.98E+00	35	6.90E+00	6.84E-01	1.41E-01	1.39E-01
2	4.93E+01	4.88E+00	1.01E+00	9.96E-01	36	1.48E+01	1.46E+00	3.02E-01	2.99E-01
3	1.18E+02	1.17E+01	2.42E+00	2.39E+00	37	3.45E+01	3.42E+00	7.05E-01	6.97E-01
4	4.44E+01	4.39E+00	9.06E-01	8.96E-01	38	6.41E+01	6.35E+00	1.31E+00	1.29E+00
5	1.25E+03	1.24E+02	2.55E+01	2.53E+01	39	1.15E+02	1.14E+01	2.35E+00	2.32E+00
6	4.93E+02	4.88E+01	1.01E+01	9.96E+00	40	1.97E+01	1.95E+00	4.03E-01	3.98E-01
7	1.82E+02	1.81E+01	3.73E+00	3.69E+00	41	1.66E+01	1.64E+00	3.38E-01	3.35E-01
8	3.95E+02	3.91E+01	8.06E+00	7.97E+00	42	1.49E+02	1.48E+01	3.04E+00	3.01E+00
9	5.09E+03	5.04E+02	1.04E+02	1.03E+02	43	8.88E+01	8.79E+00	1.81E+00	1.79E+00
10	4.42E+02	4.37E+01	9.02E+00	8.93E+00	44	1.56E+02	1.54E+01	3.18E+00	3.15E+00
11	3.95E+02	3.91E+01	8.06E+00	7.97E+00	45	2.30E+02	2.28E+01	4.70E+00	4.65E+00
12	4.46E+02	4.42E+01	9.11E+00	9.01E+00	46	1.08E+02	1.07E+01	2.22E+00	2.19E+00
13	3.84E+02	3.80E+01	7.83E+00	7.75E+00	47	4.69E+02	4.64E+01	9.57E+00	9.47E+00
14	2.47E+02	2.45E+01	5.05E+00	5.00E+00	48	4.11E+01	4.07E+00	8.39E-01	8.30E-01
15	4.44E+01	4.39E+00	9.06E-01	8.96E-01	49	5.48E+01	5.42E+00	1.12E+00	1.11E+00
16	4.93E+01	4.88E+00	1.01E+00	9.96E-01	50	4.93E+01	4.88E+00	1.01E+00	9.96E-01
17	1.05E+03	1.04E+02	2.15E+01	2.13E+01	51	2.96E+01	2.93E+00	6.04E-01	5.98E-01
18	2.56E+02	2.54E+01	5.24E+00	5.18E+00	52	7.40E+01	7.32E+00	1.51E+00	1.49E+00
19	5.92E+03	5.86E+02	1.21E+02	1.20E+02	53	9.86E+01	9.76E+00	2.01E+00	1.99E+00
20	1.04E+03	1.03E+02	2.12E+01	2.09E+01	54	4.44E+01	4.39E+00	9.06E-01	8.96E-01
21	1.18E+02	1.17E+01	2.42E+00	2.39E+00	55	1.63E+02	1.61E+01	3.32E+00	3.29E+00
22	6.85E+02	6.78E+01	1.40E+01	1.38E+01	56	3.29E+01	3.25E+00	6.71E-01	6.64E-01
23	2.80E+02	2.77E+01	5.72E+00	5.66E+00	57	4.93E+02	4.88E+01	1.01E+01	9.96E+00
24	2.30E+02	2.28E+01	4.70E+00	4.65E+00	58	1.97E+01	1.95E+00	4.03E-01	3.98E-01
25	2.52E+02	2.50E+01	5.16E+00	5.10E+00	59	4.93E+01	4.88E+00	1.01E+00	9.96E-01
26	1.44E+01	1.42E+00	2.94E-01	2.91E-01	60	4.79E+01	4.75E+00	9.79E-01	9.68E-01
27	6.58E+01	6.51E+00	1.34E+00	1.33E+00	61	4.93E+02	4.88E+01	1.01E+01	9.96E+00
28	6.90E+02	6.84E+01	1.41E+01	1.39E+01	62	3.47E+02	3.44E+01	7.09E+00	7.01E+00
29	1.64E+04	1.63E+03	3.36E+02	3.32E+02	63	2.63E+01	2.60E+00	5.37E-01	5.31E-01
30	1.38E+02	1.37E+01	2.82E+00	2.79E+00	64	6.85E+01	6.78E+00	1.40E+00	1.38E+00
31	3.01E+01	2.98E+00	6.16E-01	6.09E-01	65	9.27E+01	9.18E+00	1.89E+00	1.87E+00
32	4.11E+01	4.07E+00	8.39E-01	8.30E-01	66	7.89E+01	7.81E+00	1.61E+00	1.59E+00
33	1.10E+02	1.08E+01	2.24E+00	2.21E+00	67	1.97E+02	1.95E+01	4.03E+00	3.98E+00
34	7.40E-01	7.32E-02	1.51E-02	1.49E-02	68	9.86E+01	9.76E+00	2.01E+00	1.99E+00
					TOTAL	**4.13E+04**	**4.09E+03**	**8.44E+02**	**8.34E+02**

According to the results obtained, a production potential of 8.34E+02 $m^3.d^{-1}$ of biodiesel from rice bran vegetable oil in Rio Grande do Sul was verified, totaling 3.05E+05 m^3 per year. Thus, rice bran presents itself as a great opportunity to be explored for the production of biofuel in the state of the Rio Grande do Sul and in Brazil, since it is not presented as a source of national biodiesel production in the National Energy Balance (EPE, 2019).

Such state potential is equivalent to an amount of 5% of Brazilian biodiesel production in 2018, surpassing the annual production of biodiesel from chicken and

pork fat, as well as canola oil, peanuts, cotton and palm. In Brazil, soybeans are highly regarded as a raw material for biofuel, accounting for 63% of production, followed by beef tallow with 12%, thus the potential for producing biodiesel from vegetable oil from rice bran is surpassed only by soybean oil, beef tallow and a category called “other fatty materials” (without further specifications) (EPE, 2019).

It should be noted that the use of rice bran to produce biodiesel does not represent a new occupation and land use, since the bran is already generated on a large scale in the country during the processing of the grain. This possibility stands out for promoting the diversification of the sources of the bioenergetic matrix and relieving the occupation and use of the soil for soy planting in the country. Currently, 44.37% of the area planted or destined for harvest in Brazil is used for soy production, totaling 3.48E+07 hectares (IBGE, 2020).

Considering the annual production potential determined in the present study and that for every 10 kg of biodiesel produced, about 1 kg of glycerol is generated (Fontinele *et al*., 2017; Silva *et al*. 2017), in such a production scenario they would be generated annually 3.05E+04 m^3 of crude glycerol from methyl transesterification of rice bran oil. The incorrect disposal of glycerol can promote negative environmental impacts, since when in contact with water it becomes a soap responsible for hindering the oxygenation of the medium through its precipitation (Bertozzo, 2013).

In this context, the importance of its application in the anaerobic digestion process of the rice parboiling effluent is given, in order to increase the production of methane and promote an environmentally appropriate destination for the by-product of biodiesel production. The use of a co-substrate such as glycerol in anaerobic digestion increases the efficiency of the biogas and CH_4 production process, by promoting the necessary balance of the C/N ratio (Jones; Woods 1986; Mata-Alvarez *et al*. 2000; Meier *et al*. 2016; Kurahashi *et al*. 2017; Yen and Brune, 2007). Several studies report the efficacy of using glycerol in anaerobic co-digestion with other compounds, such as starch wastewater (Lins *et al*. 2014; Larsen 2009), pig manure (Aguilar-Aguilar *et al*. 2017), sheep manure (Araújo 2012) and bovine waste (Bertozzo 2013; Siqueira 2012).

However, it is important to note that there is a maximum limit on the concentration of glycerol to be added to the system, since it can present toxicity to anaerobic microorganisms. In addition, the chemical composition of glycerol and crude glycerin varies according to the type of catalyst and alcohol used in the production of

biodiesel, as well as the efficiency of transesterification and the recovery and purification of biodiesel, thus being able to present more or less toxicity to the environment. medium (Yang *et al*. 2012).

4.2 Methane

In order to obtain results that more accurately correspond to the methane production potential in the Rio Grande do Sul from the anaerobic digestion of the rice parboiling effluent, the effluent characterization of an industry in the sector located in the city of Pelotas was carried out. located in the south of the state. Thus, Table 4 presents the results obtained regarding the characterization necessary for the application of the methodologies of Speece (2001), Metcalf and Eddy (2003) and UNFCCC (2012):

Table 4 Characterization of rice parboiling effluent

COD ($Kg.m^{-3}$)	8.60
TS ($Kg.m^{-3}$)	49.20
VSS ($Kg.m^{-3}$)	42.80
COD_{VSS} ($Kg.m^{-3}$)	0.86

Based on the production data of parboiled rice in the industries of the state of Rio Grande do Sul obtained in the respective operating licenses and considering that for each kilo of parboiled rice an average of 3 liters of effluent is generated (Bastos *et al*., 2010; Santos *et al*. 2012) and the application of the methodologies of Speece (2001), Metcalf and Eddy (2003) and UNFCCC (2012), it was possible to obtain the daily generation of effluent in the state and the potential of methane generation from digestion anaerobic treatment (Table 5). The UNFCCC methodology shows inferior results because it is more conservative, with reducing factors linked to uncertainties (Nadaleti *et al*., 2019):

Table 5 Theoretical potential for effluent generation and methane production

Industry	Parboiled rice ($ton.d^{-1}$)	Wastewater ($m^3.d^{-1}$)	Methane ($Nm^3.d^{-1}$)		
			Speece (2001)	Metcalf and Eddy (2003)	UNFCCC (2012)
1	2.47E+02	7.40E+02	1.48E+03	1.40E+03	1.22E+03
2	1.78E+01	5.33E+01	1.07E+02	1.01E+02	8.79E+01
3	1.18E+02	3.55E+02	7.12E+02	6.74E+02	5.86E+02
4	1.48E+01	4.44E+01	8.90E+01	8.43E+01	7.33E+01
5	2.65E+02	7.94E+02	1.59E+03	1.51E+03	1.31E+03
6	4.93E+02	1.48E+03	2.97E+03	2.81E+03	2.44E+03
7	6.41E+01	1.92E+02	3.86E+02	3.65E+02	3.18E+02
8	2.47E+02	7.40E+02	1.48E+03	1.40E+03	1.22E+03
9	4.73E+03	1.42E+04	2.85E+04	2.70E+04	2.34E+04
10	1.78E+02	5.33E+02	1.07E+03	1.01E+03	8.79E+02
11	3.95E+02	1.18E+03	2.37E+03	2.25E+03	1.95E+03
12	2.27E+02	6.81E+02	1.36E+03	1.29E+03	1.12E+03
13	3.84E+02	1.15E+03	2.31E+03	2.18E+03	1.90E+03
14	2.47E+02	7.42E+02	1.49E+03	1.41E+03	1.22E+03
15	3.78E+01	1.13E+02	2.27E+02	2.15E+02	1.87E+02
16	4.93E+01	1.48E+02	2.97E+02	2.81E+02	2.44E+02
17	3.95E+02	1.18E+03	2.37E+03	2.25E+03	1.95E+03
18	1.97E+02	5.92E+02	1.19E+03	1.12E+03	9.77E+02
19	5.92E+03	1.78E+04	3.56E+04	3.37E+04	2.93E+04
20	1.24E+02	3.73E+02	7.47E+02	7.08E+02	6.15E+02
21	2.96E+01	8.88E+01	1.78E+02	1.69E+02	1.47E+02
22	6.85E+02	2.05E+03	4.12E+03	3.90E+03	3.39E+03
23	1.27E+02	3.80E+02	7.61E+02	7.21E+02	6.27E+02
TOTAL	**1.52E+04**	**4.56E+04**	**9.14E+04**	**8.65E+04**	**7.52E+04**

Based on the above, the state of Rio Grande do Sul has a total of 23 active rice parboiling industries, which currently have a minimum potential to generate 7.52E+04 $Nm^3.d^{-1}$ and an average of 8.44E+04 $Nm^3.d^{-1}$ of methane through the individual digestion of the effluent. Nadaleti (2017) obtained an average production potential of 1.7E+04$Nm^3.d^{-1}$ of methane when estimating, with the same methodologies (Speece 2001; Metcalf and Eddy 2003; UNFCCC 2012) the production potential of biofuel in the parboiled rice industry in the Rio Grande do Sul. However, it is important to note that although the author in question carried out a survey of 34 industries in the sector in 2017, according to the operating licenses in force that year, it was considered a COD of 5.387 $Kg.m^{-3}$ and the maximum effluent flow allowed by the environmental agency described in the licenses. The present study chose to use the theoretical value since there was no consistency between the maximum allowed flow and the maximum production of parboiled rice allowed in most of the consulted licenses.

Regarding the co-digestion of the effluent from the parboiling of rice with crude glycerol: considering the results obtained by Lourenço (2020) as SMA of the sludge from a UASB of the effluent treatment plant of a rice parboiling industry with the addition of 1, 2 and 3% crude glycerol from methyl transesterification of refined rice bran oil, the results shown in Fig. 1 was determined. The study by Lourenço (2020) determined an increase of 539.45% in methane production when added 1% of glycerol compared to SMA without glycerol, 322.91% with 2% glycerol and 300.71% with 3% glycerol:

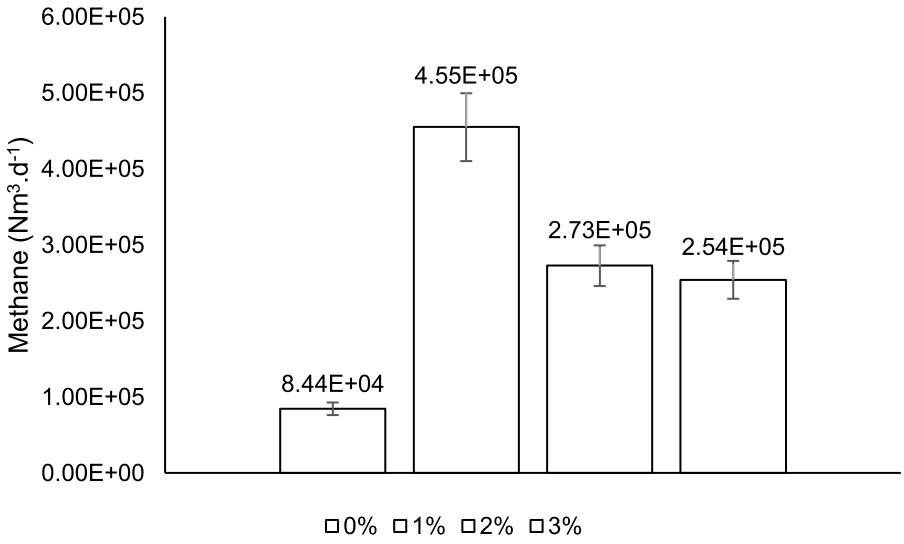

Fig. 1 Average potential of methane production through co-digestion of effluent from rice parboiling with crude glycerol from methyl transesterification of rice bran oil

Thus, through the addition of 1% crude glycerol in the anaerobic digestion process of the rice parboiling effluent, Rio Grande do Sul has the potential to reach an average production of 4.55E+05 $Nm^3.d^{-1}$, totaling 1.66E+08 Nm3 per year. A positive difference of 3.70E+05 $Nm^3.d^{-1}$ in relation to the individual digestion of the effluent. A study published by Nadaleti *et al*. (2019) in relation to methane production from the anaerobic digestion of the sugarcane vinasse determined that the entire southern region of Brazil has potential to generate 2.33E+06 $Nm^3.d^{-1}$, while the country has a total potential of 4.03E+07 $Nm^3.d^{-1}$. In this context, the co-management proposed in the present work, with residues from the rice sector, is capable of providing an energy source from biomass that offers greater efficiency, due to the high supply of residues

by the sector, differently from what occurs in the case of vinasse. The region has low sugar cane production due to the unfavorable climatic conditions of its production (Rosseto 2017).

Even the production of methane from the individual digestion of the effluent from rice parboiling is still little explored by academic studies. Among the few reports in the literature, according to Nadaleti *et al*. (2018), the ideal temperature for biogas production via anaerobic digestion in batches of effluent and anaerobic sludge from the UASB at the Effluent Treatment Station (ETE) for the production of parboiled rice is 35 °C, the authors obtained a production of 5,198 dm³ of biogas in a period of 276 hours. Lourenço *et al*. (2019) carried out studies on the co-digestion of effluent and sludge from the UASB of the ETE for the parboiling of rice and fruit peels in batches at 35 °C, the authors obtained 11,730 dm³ of biogas during 168 hours of co-digestion with orange peel and 8,490 dm³ with the banana peel. Nadaleti *et al*. (2019) studied co-management with effluent from a dairy industry, also in batch and at 35 ° C, for 252 hours and obtained a total production of 1,500 dm³ of methane. Reactors of 2,150 dm³ in volume and 30% headspace were used for all the studies mentioned.

4.3 Energy potential

According to the biofuel production estimate, it was possible to determine the potential for generating electric and thermal energy from biodiesel and methane, and for methane four scenarios were considered: Methane [0%], where methane production was From the individual digestion of the effluent, for Methane [1%] the co-digestion of the effluent with 1% glycerol was considered, for Methane [2%] with 2% glycerol and for Methane [3%] with 3% (Fig. 2 and 3):

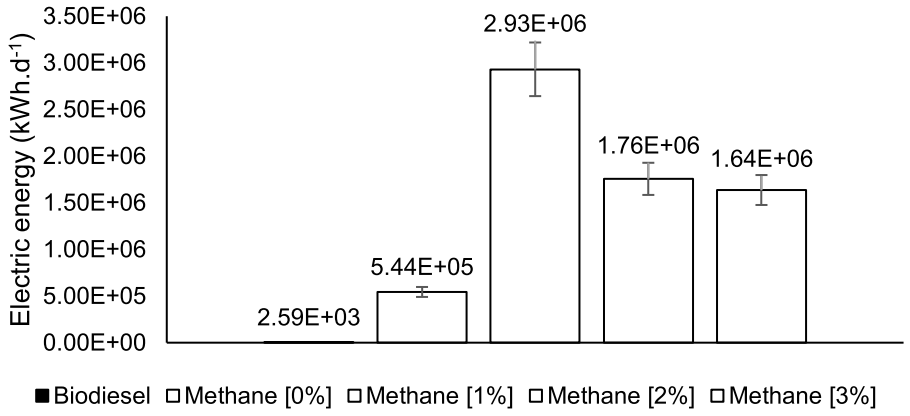

Fig. 2 Potential for electricity generation

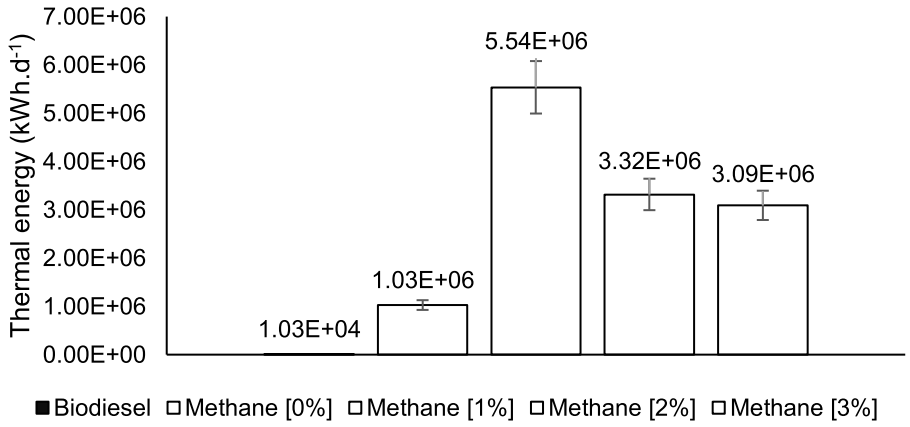

Fig. 3 Potential for termal energy generation.

Thus, considering a scenario where there was the production of biodiesel and methane, with the use of 1% glycerol, the state would be able to reach 2.93E+06 $kWh.d^{-1}$ of electricity and 5.55E+06 $kWh.d^{-1}$ of thermal energy. In the study carried out by Nadaleti (2017) on the production of energy from biogas produced in the individual digestion of the effluent, the state's potential reached a potential of only 5.95E+04 $kWh.d^{-1}$ for electricity and 8.49E+04 $kWh.d^{-1}$ for thermal. The author also determined the energy generation potential from the rice husk synthesis gas production, obtaining a total of 2.00E+06 $kWh.d^{-1}$ of electric energy and 5.48E+06 $kWh.d^{-1}$ of thermal energy from a production potential of 9.0E+06 $Nm^3.d^{-1}$ of syngas.

Silveira *et al*. (2019) studied the potential for energy production from synthesis gas and methane in the rice industries of Pelotas and region, a city located in the south of Rio Grande do Sul, the author determined potential of 5.75E+04 $kWh.d^{-1}$ of thermal energy and 3.01E+04 $kWh.d^{-1}$ of electric energy for methane and 2.08E+06 $kWh.d^{-1}$ of

thermal energy and 1.23E+06 kWh.d^{-1} of electric energy for syngas. The author also carried out the energy balance for the industries, based on the chemical energy required for the parboiling of the grain, 1,055 MJ.ton^{-1} (Nadaleti 2017), a total of 9.86E+05 MJ.d^{-1} was determined. chemical energy required in the region and a potential of 7.67E+06 MJ.d^{-1} of chemical energy offered for the production potential of biofuels, so that the possibility of energy self-sufficiency of the industries was verified. It is important to note that such self-sufficiency was only achieved through the energetic potential of syngas, since it was responsible for 7.40E+06 MJ.d^{-1} of that potential, while methane contributed only 1.32E+05 MJ.d^{-1}.

When considering the chemical energy required for 1.06E+03 MJ.ton^{-1} grain parboiling determined by Nadaleti (2017), that a Rice Bran Oil Extraction System has a demand of 3.70E+02 MJ.ton^{-1} (2017) and the potencial of produce eletric energy from biodiesel and methane (from codigestion of wastewater and 1% of glycerol), the energy use of only the biofuels covered in the present study is able to promote the sector's self-sufficiency (Table 6). It should be noted that there is still the possibility of raising the energy potential of the sector adding the energy production potential of the syngas from the gasification of rice husks highlighted in the aforementioned studies, raising its potential to generate revenue from the sale of surplus energy. Thus the sector explore new sources of energy use from its waste and effluents, contributing to the diversification of the state's industrial energy matrix, besides ending the purchase of energy from concessionaires and reducing its negative environmental impacts by having the perspective of adopting a system that covers waste-to-energy technology, and thus, the use of green energy.

Table 6 Demand for chemical energy to produce parboiled rice and extraction of bran oil throughout Rio Grande do Sul and state potential for chemical energy generation from the production of biodiesel and methane

Parboiled rice (ton.d^{-1})	1.52E+04
Bran (ton.d^{-1})	1.50E+03
Energy demand (MJ.d^{-1})	**1.67E+07**
Biodiesel potential (MJ.d^{-1})	1.71E+04
Methane potential from codigestion with 1% of glycerol (MJ.d^{-1})	2.35E+07
Total energy potential (MJ.d^{-1})	**2.35E+07**

Waste to energy technology presents itself as a potentially sustainable and environmentally friendly solution to deal with the growing generation of waste in

general, offering the possibility of ecologically correct and economically viable energy generated through biological and thermal processes responsible for extracting the energy stored in waste streams (Rajaeifar *et al*., 2019). In this context, the use of waste in energy technologies, such as the production of biogas is one of the best options to meet the global energy demand. Among the different sources of renewable energy, biogas is often presented as the best alternative, as it can be used directly in various applications (Khalil *et al*. 2019). In addition, the solid by-product of the digestion process can be used as an organic fertilizer or organic substrate in greenhouse cultivation (Nasir *et al*., 2013).

The energy recovery of these residues and effluents makes it possible to maintain or even reduce the carbon cycle of the waste produced, as well as reducing the emission of greenhouse gases considering the substitution of fossil fuels for biofuels. Thus, while non-renewable energy is increasing the world's environmental degradation, renewable energy helps to reduce and control it (Sharif *et al*. 2018). In addition, the use of waste and effluents reduces the environmental liabilities presented by them and, in some cases, reduces expenses related to the environmentally appropriate final disposal.

5. Conclusion

According to the results obtained, production potential of 8.34E+02 $m^3.d^{-1}$ of biodiesel from rice bran vegetable oil was found and an average potential to generate 8.44E+04 $Nm^3.d^{-1}$ of methane through of the individual digestion of the effluent in Rio Grande do Sul. Through the addition of 1% crude glycerol in the anaerobic digestion process of the rice parboiling effluent, the Rio Grande do Sul has a potential to reach an average production of 4.55E+05 $Nm^3.d^{-1}$. Thus, the state reaches a potential of 2.93E+06 $kWh.d^{-1}$ of electric energy and 5.55E+06 $kWh.d^{-1}$ of thermal energy through the production and use of biodiesel and methane as energy sources.

The state's potential for biodiesel production is equivalent to an amount of 5% of Brazilian biodiesel production in 2018. In this context, rice bran presents itself as a great opportunity to be explored to produce biodiesel in the state and in Brazil as a whole, since it is not presented as a source of national biodiesel production in the National Energy Balance.

However, the energy utilization of only the biofuels addressed in the present study is not able to promote the sector's self-sufficiency, and it is still necessary to explore the energy production potential of the syngas from the gasification of rice husks in order to guarantee its self-sufficiency and fully explore the sources of energy use available in the sector's waste and effluents, contributing to the diversification of the state's industrial energy matrix and reducing its expenses with the purchase of energy from concessionaires and reducing its negative environmental impacts by adopting waste-to-energy technology and the use of green energy.

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5. CONSIDERAÇÕES FINAIS

O presente estudo produziu biocombustíveis utilizando como matéria-prima resíduos sólidos e líquidos gerados nos processos do beneficiamento de arroz, a fim de estimar o potencial de geração de bioenergia do setor arrozeiro no Rio Grande do Sul. Nesse contexto, a primeira hipótese desse estudo foi comprovada ao constatar-se a viabilidade de produção de biodiesel via transesterificação básica metílica, gerando biocombustível com a qualidade exigida pelas especificações ANP, EN e ASTM. Sendo que a razão molar de 6:1, 1,0% de catalisador e 120 minutos apresentou o maior rendimento obtido neste estudo, 98,09%.

Acerca da segunda hipótese, foi possível determinar que apesar da adição de glicerol não elevar a AME do lodo anaeróbio da parboilização de arroz, o subproduto da produção de biodiesel é capaz de prolongar o período de duração da fase estacionaria das bactérias metanogênicas, elevando a produção total de metano. A adição de 1% de glicerol promoveu o maior período de fase estacionária resultando em geração 539.45% maior que o sistema sem glicerol, totalizando um volume de 1.35E-04 $m^3.d^{-1}$.

Por fim, verificou-se que o potencial estadual de produção de biodiesel equivale a um montante de 5% da produção brasileira de biodiesel no ano de 2018. Tal potencial somado ao ofertado pelo metano, produzido na codigestão efluente com 1% de glicerol, é capaz de promover a autossuficiência do setor, comprovando-se a terceira hipótese. Foi estimado um potencial de 2.93E+06 $kWh.d^{-1}$ de energia elétrica e 5.55E+06 $kWh.d^{-1}$ de energia térmica através da produção e uso do biodiesel e do metano (em codigestão com 1% de glicerol) como fontes de energia.

Além de garantir maior segurança energética ao setor, visar o uso de todas as fontes de aproveitamento energético disponíveis nos resíduos e efluentes permitiria completar o ciclo da tecnologia *waste-to-energy*. Nesse contexto, temos a possibilidade de explorar o potencial de produção de energia do gás de síntese na gaseificação das cascas de arroz, contribuindo para a diversificação da matriz energética industrial do estado, elevando ganhos com a venda de energia excedente e reduzindo impactos ambientais negativos. Assim, recomenda-se a abordagem simultânea dos três biocombustíveis em trabalhos futuros, assim como a produção do biogás em escala laboratorial e piloto, a fim de otimizar sua produção a partir dos dados obtidos nesse estudo.

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