CONTINUOUS HYDROGEN RICH SYNGAS PRODUCTION VIA SUPERCRITICAL WATER GASIFICATION

Rafael Felipe de Rezende[1], Isabela Milhomem Dias[1], Lucas Clementino Mourão[1], Mariana Bisinotto Pereira[2], Christian Gonçalves Alonso[1], Guilherme Botelho Meireles de Souza[1]

[1] *Instituto de Química, Universidade Federal de Goiás, Goiânia, Goiás, Brasil, guilherme_botelho@ufg.br*
[2] *Departamento de Engenharia Química, Universidade Estadual de Maringá, Maringá, Paraná, Brasil*

ABSTRACT

The supercritical water gasification (ScWG) technology is a promising alternative to produce hydrogen rich syngas from renewable sources such as ethanol or residual glycerol from the biodiesel manufacture. The ScWG process can achieve high selectivity towards hydrogen and elevated conversion efficiencies in short reaction times. In this work, the ScWG of mixtures of glycerol and ethanol were investigated in the absence of catalysts. At constant pressure of 25 MPa, the effects of temperature (500 – 700 °C), feed flow rate (10 – 20 mL min^{-1}), organic carbon concentration (15 – 25 g L^{-1}), and ethanol to glycerol ratio were evaluated. At optimized conditions, that is, temperature of 700 °C, feed flow rate of 20 mL min^{-1}, organic carbon concentration of 25 g L^{-1} and ethanol to glycerol ratio of 50:50, a mean total gaseous flow rate and hydrogen molar fraction of 1842.5 N mL min^{-1} and 60.56% were respectively achieved.

Keywords: renewable hydrogen, synthesis gas, low carbon process, supercritical water.

Introduction

The global economy decarbonization ambitions, aligned with the climate neutrality commitments signed during the Paris agreement, has driven a search for novel technologies and processes that can reduce, neutralize, or even turn negative the atmospheric emissions of fossil carbon. The uncontrolled increase in carbon dioxide (CO_2) emissions, considered one of the main contributors to the global warming, is strictly related to human activities, especially the massive use of fossil fuels, which began with the industrial revolution [1]. In this scenario of economic/energetic transition and growing environmental awareness, the reduction of greenhouse gas emission levels is essential to prevent the occurrence of catastrophic effects such as extreme weather conditions, rising ocean levels and disruption of ecosystems [2].

Among several alternatives, the use of hydrogen (H_2) has stood out as one of the main routes for the energetic transition from fossil to renewable sources. Hydrogen is defined as an energy vector, that is, it first requires to be produced using a primary energy source, renewable (such as wind, solar or hydroelectric power) or not. Then, the H_2 must be stored and transported to the place of use, where its latent chemical energy can be fully realized [3]. At this point, the H_2 can be utilized for the production of electricity and heat or directly used in transport systems, without generating compounds that pollute the environment or contribute to the aggravation of climate change, since the sole product of hydrogen combustion reaction is water [4].

Despite all these advantages, the development of efficient and safe systems for the production, storage, and transport of H_2 still remains as the main challenges to be overcome before the so-called global hydrogen economy is established [5]. Thus, to prevail such challenges, especially those intrinsically related to the production of hydrogen from renewable sources, numerous technologies have been investigated [6], amongst them, the supercritical water gasification of biomass [7]. Among several feedstock candidates, from the Brazilian economic standpoint, both ethanol, a renewable biomass, and glycerol, a residual one, stand out due to the large production in the country.

Above its critical point, temperature of 374.3 °C and pressure of 22.09 MPa, water presents specific physicochemical characteristics that favor the oxidation/gasification of organic molecules resulting in the production of various gases, such as H_2, carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4) [8]. Thus, the supercritical water technology enables the use of residual liquid

biomass with high concentrations of organic content, whether industrial effluents or even domestic sewage, as raw materials to produce gases of industrial interest, especially H_2 [9]. Also, it should be noted that the supercritical water technology offers another considerable environmental advantage, as it does not require the use of clean water and allows the treatment of contaminated liquid effluents.

In this sense, the current study investigated the continuous production of a hydrogen rich syngas via the supercritical water gasification of mixtures of glycerol and ethanol as feedstock solutions. At a constant pressure, the effects of temperature, feed flow rate, total organic carbon (TOC) concentration, and ethanol to glycerol ratio on the total gaseous flow rate and hydrogen molar fraction were evaluated. Additionally, at the optimal operational conditions, the process conversion efficiency was evaluated based on the reduction of total organic carbon (TOC) value.

Apparatus and experimental procedure

The apparatus used to conduct the ScWG experiments is depicted in **Fig. 1**. The experimental runs were conducted using a tubular reactor built in Inconel 625, a material with high resistance to pressure, oxidation, and corrosion, with inner diameter (I.D.) of 11 mm, and length (L) of 373 mm. The aqueous solution was prepared to achieve the desired total organic carbon using ethanol, glycerol, or a mixture of both. A high-pressure isocratic pump (1) was used to continuously feed the ethanol: glycerol solution (A) at a pre-defined flowrate from the feedstock reservoir. Prior to reaching the reactor, the solution was pre-heated in a helicoidal tubular heat exchanger (3) to a temperature of 350 °C using a split oven (5) equipped with two ceramic resistances of 1000 W. Another set of oven-resistances system was used to keep the tubular reactor (4) at the desired temperature. A temperature controller (TC1) was used to adjust the heating rate, achieve the desired temperatures, and continuously monitor it. A constant pressure of 25 MPa was maintained and monitored using, respectively, a back-pressure regulator (10) and a mechanical pressure gauge (7). The mixture of liquid and gaseous products was cooled in a heat exchanger (6) refrigerated by a chiller. The generated liquid (B) and gaseous (C) products were continuously recovered in the phase separator (11).

The total gaseous products flow rates were determined by drum-type gas meter (model TG3/5, Ritter) and analyzed on a gas chromatograph (model Nexis™ GC-2030, Shimadzu) equipped with a methanizer, and TCD and FID detectors. The liquid products flow rate was measured using an analytical balance and the total organic carbon was analyzed by TOC analyzer (model TOC-L, Shimadzu).
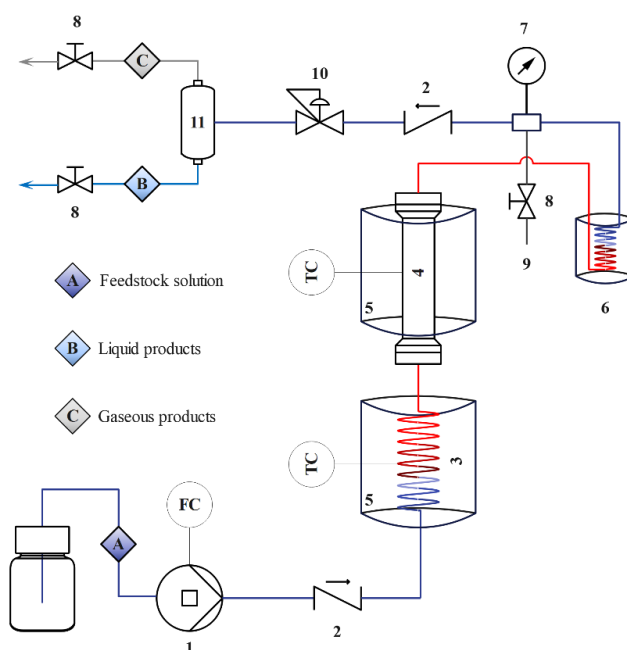

Figure 1 - Schematic representation of the ScWG system.

Results and discussions

Initially, the influence of the temperature (500, 600 and 700 °C) and feed flow rate (10, 15 and 20 mL min⁻¹) on the supercritical water gasification of an equivalent aqueous solution of ethanol and glycerol (50:50) was investigated. For this, the pressure, the pre-heater temperature, and the TOC concentration were kept constant at 25 MPa, 350 °C and 10 g L⁻¹, respectively. The obtained results in terms of total gaseous flow rate and molar composition are presented in **Table 1**.

Table 1 - Influence of the temperature and feed flow rate on the ScWG process.

Temperature (°C)	Feed flow rate (mL min⁻¹)	Composition (mol%)						Total gaseous flow-rate (N mL min⁻¹)
		H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	
500	10	62.00%	11.30%	3.40%	23.00%	0.0%	0.36%	414.4
	15	61.84%	10.79%	3.91%	23.17%	0.02%	0.28%	519.0
	20	63.36%	9.92%	4.62%	21.91%	0.03%	0.16%	569.0
600	10	64.70%	9.50%	1.50%	23.90%	0.00%	0.30%	517.8
	15	63.05%	9.84%	2.25%	24.59%	0.00%	0.28%	650.4
	20	63.07%	9.79%	3.71%	23.18%	0.04%	0.22%	754.5
700	10	66.60%	6.60%	0.80%	25.70%	0.00%	0.30%	626.2
	15	65.66%	7.85%	1.83%	24.38%	0.00%	0.28%	752.8
	20	64.45%	8.04%	2.31%	24.98%	0.01%	0.20%	913.4

As observed, a similar mean H_2 molar fraction, superior to 61%, was achieved in all evaluated conditions. In this sense, the total gaseous flow-rate was selected as the parameter to define the optimal operational conditions and to carry on the additional experiments. The highest total gaseous flow-rate of 913.4 N mL min⁻¹ was achieved at a temperature of 700 °C and feed flow rate of 20 mL min⁻¹. It is clear that both higher temperatures and feed flow rate positively favors the ScWG of the ethanol and glycerol solution. However, the temperature effect is slightly more prominent. Therefore, only the feed flow rate of 20 mL min⁻¹ was fixed, and the temperature parameter continued to be evaluated in the following experiments.

Then, the effects of the total organic carbon concentration (15 – 25 g L⁻¹) were evaluated. For this, an equivalent mixture of ethanol and glycerol (50:50) was used as feedstock solution. At constant conditions of pressure, pre-heater temperature, and feed flow rate, respectively, 25 MPa, 350 °C and 20 mL min⁻¹, the obtained results are showed in **Table 2**.

Table 2 - Influence of the temperature and TOC concentration rate on the ScWG process.

Temperature (°C)	TOC concentration (g mL⁻¹)	Composition (mol%)						Total gaseous flow-rate (N mL min⁻¹)
		H_2	CH_4	CO	CO_2	C_2H_4	C_2H_6	
500	15	57.87%	13.06%	10.05%	18.80%	0.03%	0.20%	803.7
	20	60.46%	11.51%	5.48%	22.32%	0.03%	0.19%	1040.2
	25	63.53%	9.13%	3.62%	23.51%	0.02%	0.19%	1291.9
600	15	61.86%	11.40%	6.49%	20.14%	0.01%	0.10%	1077.4
	20	60.09%	11.54%	5.39%	22.76%	0.03%	0.19%	1332.4
	25	62.57%	9.80%	4.35%	23.01%	0.03%	0.25%	1619.0
700	15	56.85%	12.56%	13.37%	16.89%	0.06%	0.26%	1024.3
	20	57.19%	12.97%	9.47%	19.83%	0.07%	0.47%	1425.4
	25	60.56%	10.47%	6.59%	21.90%	0.06%	0.43%	1842.5

The results showed that higher values of both temperature and TOC concentration intensified the ScWG process and increased the total gaseous flow rate values achieved. It was also observed that lower residence times (higher feed flowrates) lead to an inhibition of methane formation. Thus, the TOC concentration of 25 g mL^{-1}, corresponding to a total gaseous flow-rate of 1842.5 N mL min^{-1}, was selected to carry on the next experiments.

Finally, to understand the effects of the ethanol to glycerol ratio, additional experiments were carried out under constant conditions of the pressure (25 Mpa), pre-heater temperature (350 °C), flow rate (20 mL min^{-1}) and the TOC concentration (25 g L^{-1}). As stated before, the temperature parameter continued to be evaluated. The results are summarized in **Table 3**.

Table 3 - Influence of the temperature and ethanol to glycerol ratio on the ScWG process.

Feedstock solution ratio	Temperature (°C)	Composition (mol%)						Total gaseous flow-rate (N mL min^{-1})
		H$_2$	CH$_4$	CO	CO$_2$	C$_2$H$_4$	C$_2$H$_6$	
100% EtOH	500	52.25%	13.17%	16.09%	0.85%	0.27%	0.22%	22.1
	600	47.02%	22.96%	23.17%	6.01%	0.18%	0.16%	876.4
	700	51.79%	19.31%	16.30%	11.92%	0.23%	0.37%	1338.1
75% Ethanol 25% Glycerol	500	51.76%	5.22%	10.27%	4.00%	0.25%	0.22%	31.9
	600	47.68%	19.53%	24.37%	8.23%	0.23%	0.26%	973.7
	700	52.87%	15.73%	13.86%	16.01%	0.19%	0.41%	1483.9
25% Ethanol 75% Glycerol	500	51.06%	8.95%	32.97%	6.50%	0.38%	0.23%	494.2
	600	52.14%	11.27%	20.82%	15.05%	0.19%	0.43%	1264.3
	700	57.29%	8.60%	11.35%	21.18%	0.22%	0.66%	1737.1
100% Glycerol	500	52.49%	6.31%	31.21%	9.87%	0.36%	0.28%	678.1
	600	54.62%	7.55%	19.72%	16.81%	0.16%	0.41%	1370.5
	700	58.12%	6.33%	12.50%	22.42%	0.21%	0.76%	1765.6

In comparison with the equivalent solution, lower total gaseous flow-rate values were observed for all different ratios evaluated, including when all organic carbon present in the feedstock solution was originated from pure ethanol or pure glycerol. It was noticed that higher ratios of ethanol favored the formation of CH$_4$, especially at 600 °C. On the other hand, at higher concentrations of glycerol, higher molar fractions of CO$_2$ were observed.

Conclusions

At the optimized operational conditions, that is, temperature of 700 °C, pressure of 25 Mpa, pre-heater temperature of 350 °C, feed flow rate of 20 mL min^{-1} and an equivalent mixture of ethanol and glycerol (50:50) with TOC concentration of 25 g L^{-1} as feedstock solution, a total volumetric gaseous flow rate of 1842.5 N mL min^{-1} was achieved and H$_2$ molar fraction of 60.56%. Future research will comprise the evaluation of homogeneous catalysts to enhance both the production of gases and the hydrogen process selectivity focused on the requirements of the Fischer-Tropsch synthesis reaction, as well as thermodynamic simulations to better understand the experimental results.

Acknowledgments

References

[1]   C. Even, D. Hadroug, Y. Boumlaik, and G. Simon, "Microalgae-based Bioenergy with Carbon Capture and Storage quantified as a Negative Emissions Technology," *Energy Nexus*, vol. 7, p. 100117, Sep. 2022, doi: 10.1016/j.nexus.2022.100117.

[2]   T. E. Akinola, P. L. Bonilla Prado, and M. Wang, "Experimental studies, molecular simulation and process modelling\simulation of adsorption-based post-combustion carbon capture for power plants: A state-of-the-art review," *Applied Energy*, vol. 317. Elsevier Ltd, Jul. 01, 2022. doi: 10.1016/j.apenergy.2022.119156.

[3]   P. P. Edwards, V. L. Kuznetsov, and W. I. F. David, "Hydrogen energy," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 365, no. 1853, pp. 1043–1056, Apr. 2007, doi: 10.1098/rsta.2006.1965.

[4]   O. Faye, J. Szpunar, and U. Eduok, "A critical review on the current technologies for the generation, storage, and transportation of hydrogen," *International Journal of Hydrogen Energy*, vol. 47, no. 29. Elsevier Ltd, pp. 13771–13802, Apr. 05, 2022. doi: 10.1016/j.ijhydene.2022.02.112.

[5]   T. Borsboom-Hanson, S. R. Patlolla, O. E. Herrera, and W. Mérida, "Point-to-point transportation: The economics of hydrogen export," *Int J Hydrogen Energy*, Aug. 2022, doi: 10.1016/j.ijhydene.2022.07.093.

[6]   V. Madadi Avargani, S. Zendehboudi, N. M. Cata Saady, and M. B. Dusseault, "A comprehensive review on hydrogen production and utilization in North America: Prospects and challenges," *Energy Convers Manag*, vol. 269, p. 115927, Oct. 2022, doi: 10.1016/j.enconman.2022.115927.

[7]   L. Ferreira-Pinto, M. P. Silva Parizi, P. C. Carvalho de Araújo, A. F. Zanette, and L. Cardozo-Filho, "Experimental basic factors in the production of H2 via supercritical water gasification," *International Journal of Hydrogen Energy*, vol. 44, no. 47. Elsevier Ltd, pp. 25365–25383, Oct. 04, 2019. doi: 10.1016/j.ijhydene.2019.08.023.

[8]   G. B. M. de Souza *et al.*, "Supercritical water technology: an emerging treatment process for contaminated wastewaters and sludge," *Reviews in Environmental Science and Biotechnology*, vol. 21, no. 1. Springer Science and Business Media B.V., pp. 75–104, Mar. 01, 2022. doi: 10.1007/s11157-021-09601-0.

[9]   T. S. S. Ribeiro *et al.*, "Treatment of hormones in wastewater from the pharmaceutical industry by continuous flow supercritical water technology," *J Environ Chem Eng*, vol. 9, no. 5, Oct. 2021, doi: 10.1016/j.jece.2021.106095.