

Supercritical Water Gasification of Eucalyptus Wood Chips Using NiFe₂O₄ as a Catalyst

Ane Caroline Pereira Borges¹, Jude A. Onwuidili², Carine Tondo Alves³, Andrew Ingram⁴, Heloysa Martins Carvalho Andrade⁵, Ednildo Andrade Torres¹, and Silvio Alexandre Beisl Vieira de Melo⁶

¹Interdisciplinary Center of Energy and Environmental (CIENAM), Federal University of Bahia (UFBA), Salvador, Brazil

²European Bioenergy Research Institute, Chemical Engineering & Applied Chemistry, Aston University, Birmingham, England

³Energy Engineering, Federal University of Reconcavo of Bahia (UFRB), Feira de Santana, Brazil

⁴Chemical Engineering, University of Birmingham, Birmingham, England

⁵Chemical Institute, Federal University of Bahia (UFBA), Salvador, Brazil

⁶Chemical Engineering, Federal University of Bahia (UFBA), Salvador, Brazil

Abstract. In this work, the supercritical water gasification of eucalyptus wood chips has been investigated in relation to reaction temperature and presence of catalyst. Experiments were performed in a batch reactor at 450 °C and 500 °C with two different feed concentrations. This work wanted to evaluate mainly the gases were formed during the reactions. The gas products were analysed by gas chromatography. According to the results, it was found that eucalyptus wood chips reacted to form mainly H₂, CH₄ gases with little yield of CO₂. Increasing the reaction temperature beyond 500 °C led to the increasing production of both CH₄ (around 31.1 mol%) and H₂ (up to 38 mol%) gases and the liquid sample and solid residue have decreased. Generally, this work suggests that the SCWG has improved significantly the production of H₂ but more experiments still necessary to verify the effects of other experimental parameters and to characterise the liquid sample and solid residue.

1 Introduction

Searching for renewable energy sources to ensure economic development with social inclusion without environmental aggression is a challenge all over the world. An alternative is biomass, a primary and renewable energy source. Brazil has 5,673,783 hectares of eucalyptus planted, 70.74 million m³ of all this eucalyptus was consumed by the pulp and paper industry in Brazil in 2016 [1]. In 2016, Brazil generated 47.8 million tons of solid waste, with 14.1 million tons (29.5 %) from industrial activities (pulp and paper sector). In the paper industry, this waste is burned to generate energy, avoiding the use of fossil fuels but more waste is generated than can be used for the process energy requirements. Nevertheless, it is still necessary to discover new technologies to generate clean energy using this waste.

Hydrogen from waste biomass is considered to be a clean gaseous fuel and efficient for heat and power generation due to its high energy content [2]. A good choice to produce hydrogen-rich-gas is biomass gasification, involving a thermochemical conversion process of a solid into fuel gas, which maintains 70-80% of the original energetic fuel. The process occurs at high temperatures (700-1500 °C) and in the presence of a

gasification agent (air or oxygen, steam, carbon dioxide). However, during the gasification process, some of the fuel is not converted into gas remaining as a condensate product (tar) [3]. Tar formation is one of the major problems to deal with during the biomass gasification process because it is a complex mixture of condensable hydrocarbons with low condensation temperatures [3-5]. A new and promising technology to ensure lower tar formation and higher hydrogen yield is the supercritical water gasification (SCWG). The main difference between SCWG and other gasification techniques is related to the gasification medium i.e., supercritical water compared to inert gas and/or steam. Supercritical water gasification is a process that can also convert wet biomass, which reduces pre-treatment costs. Further, the high solubility of organic compounds in supercritical water enhances their reactivity, which leads to an improvement of the SCWG performance. These advantages make SCWG an even more attractive technology, because one of the major disadvantages of the traditional gasification is the large production of tar. The SCWG also produces higher hydrogen content at high temperatures (> 700 °C) and higher methane content at lower temperatures (< 600 °C) [6,7]. Even though the SCWG increases the selectivity of hydrogen production, it requires high pressure and temperature for the reaction without catalysts. Catalytic supercritical water gasification (CSCWG) is a promising

solution to improve the efficiency of the gasification process, producing a mixture of gases and value-added liquid products depending on the process conditions. The choice of catalyst to gasify lignocellulosic biomass in supercritical water depends on its capability to break C-C bonds, promote water gas shift (WGS) reaction, accelerate the cleavage of the C-O bond, and decrease the activation energy in SCWG reaction [8]. Heterogeneous catalyst has higher selectivity and recyclability compared with the homogeneous catalyst. The transition metals are typical catalysts for CSCWG because they offer high selectivity, high catalytic activity, and high level of carbon conversion to gas at lower temperature [9].

The present work aimed to perform the supercritical water gasification process of eucalyptus wood chips in the presence of a novel NiFe_2O_4 for increased hydrogen production using a batch reactor. The investigation involved study of the influences of biomass concentration

in addition to reaction temperature on the gasification process.

2 Experimental

2.1 Raw Materials

The raw material used was *Eucalyptus grandis* chips with approximately 30 % moisture content and size of 710 μm obtained from Federal University of Bahia. The biomass was characterised before use. All analysis was performed according to the Standard Test Method (ASTM). The characteristics of the wood chips were determined by physico-chemical analyses as ultimate analysis; determination of immediate analysis and Higher Heating Value (HHV). The methodology of these analyses has been discussed in an earlier paper [10]. The results of these analyses are summarized in Table 1.

Table 1. Characteristics of the biomass used.

Sample	Moisture Content (%)	Proximate Analysis (%)			Ultimate Analysis (%)			
		Volatile Matter	Fixed Carbon	Ash	C	H	N	O
Eucalyptus wood chips	30	83.23	16.42	0.5	46.81	6.11	0.12	46.76

The catalyst used, NiFe_2O_4 , was synthesized by combustion reaction method using ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea $\text{CO}(\text{NH}_2)_2$ as fuel. The methodology of that synthesis and characteristics of the catalyst has been discussed in an earlier paper [11].

2.2 Reactor system and experimental procedure

The supercritical water gasification experiments were performed in a non-stirred Hastelloy-C reactor obtained from Parr Instruments Co., Inc. USA. The reactor has 75 ml of volume capacity and the maximum operating conditions of temperature and pressure are 600 °C and 45 MPa, respectively.

In each experiment, first the feed material was loaded into the reactor containing deionized water, then the catalyst was loaded. The amount of water loading was 20 mL at 450 °C and 15 mL at 500 °C, giving corresponding operating pressures of 33 MPa and 28 MPa, respectively.

Experiments were performed using two different amounts of biomass, 2.22 g (10 wt %) and 5.0 g (20 wt %) and amounts of catalyst (1.0 g and 2.0 g). These were designed to evaluate some of the main parameters of the process (temperature, catalyst, feed concentration).

Once the reactor was loaded, it was sealed. It is placed into an electrical furnace fitted with temperature controller. The reactor was heated fast at a rate of 20 °C min^{-1} up to 450 and 500 °C, such that the reaction temperature was reached after just 15 minutes. The reaction time was mostly 30 min. At the end of each reaction, the reactor was rapidly withdrawn from the heater and quickly cooled to ambient temperature with compressed air. After cooling, the gas outlet valve was opened to collect the gas samples. After that, the reactor

was opened to collect the liquid sample and solid residues.

The results have been obtained are only preliminary. It is necessary to carry out experiments in duplicates/triplicates to guarantee a good reproducibility in terms of product balance and physical experiments parameters. In this work only, the gases formed during the reactions were analyzed properly.

2.3 Gas products analysis

The gases were collected from the reactor using a gas sampling bag then 1 μL were sampled into a gas tight syringe and analysed using gas chromatograph (Shimadzu GC-2014 gas chromatograph) fitted with two columns and detectors were used. Usually, two samples were taken per experiment and the average reported. The hydrocarbon gases (methane, ethene, ethane, propene, propane, butane and butene) were separated on a 2 m long by 2 mm diameter and packed with 80 - 100 mesh Hayesep and analysed using a flame ionization detector (FID). The permanent gases (hydrogen, oxygen, nitrogen, and carbon monoxide) were separated on a 2 m packed molecular sieve (60 - 80 mesh) column and analyzed using a thermal conductivity detector (TCD) while a packed Hayesep column of similar dimensions was used for analysing carbon dioxide. The GC was first calibrated with standard gas mixtures (1 % H_2 , 1 % CO , 1 % CH_4 , 1 % CO_2 , 1 % ethene, 1 % ethane, 1 % propane, 1 % propene, 1 % butane and 91 % N_2 as the swing gas) at levels similar to the composition of the produced gases. Argon was used as the carrier gas. The methods of analysis applied are in agreement with previous work [12]. The results from the GC were obtained in volume percent and were converted to moles of each gas using the general gas equation.

3 Results and discussion

The parameters investigated included the influence of feed concentration, feed catalyst and the temperature on the supercritical water gasification of eucalyptus wood chips. Mostly of the experiments were performed at 450

°C and 30 min of residence time, only the test 10 was carried out for 60 min. Only three experiments were performed at 500 °C. The experiments performed, and the gas analysis results obtained from the experiments can be observed in Table 2 and Table 3, correspondingly.

Table 2. List of experiments performed.

Tests	Temperature								
	450 °C						500 °C		
	1	2	3	4	5	6	7	8	9
Catalyst (g)	1.003	1.010	2.007	2.004	-	-	-	1.019	1.004
Biomass (g)	2.246	4.997	5.006	2.221	5.005	2.219	2.223	2.228	2.224

Table 3. Gas analysis results.

Gases	% mols								
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9
C ₂ H ₆	10.408	12.395	4.851	3.910	4.238	2.615	3.615	6.853	4.656
C ₂ H ₂	1.159	0.798	0.319	0.405	0.302	0.372	0.121	0.144	0.188
C ₃ H ₈	4.285	5.105	2.027	1.699	1.602	0.950	1.416	2.804	1.849
C ₃ H ₆	2.429	1.788	0.715	0.985	0.622	0.727	0.257	0.304	0.392
C ₄ H ₁₀	4.015	3.790	0.734	1.111	0.682	0.666	0.658	1.221	0.878
CH₄	17.753	18.951	32.042	22.468	29.947	20.164	34.961	31.766	31.102
H₂	23.476	13.147	24.348	36.898	20.586	18.693	17.677	28.091	38.059
CO₂	17.507	32.991	7.522	3.890	10.534	1.931	7.893	5.540	2.383
N ₂	16.813	8.607	23.396	25.631	19.235	39.137	22.440	22.311	19.114
CO	2.156	2.428	4.046	3.004	12.252	14.746	10.962	0.966	1.378

3.1 Effect of feed concentration and catalyst concentration

The effect of feed concentration on gasification of eucalyptus wood chips, in supercritical water gasification was carried out in the presence of NiFe₂O₄ at 450 °C for 30 min reaction time. The wood sample concentrations used were 10 wt% and 20 wt%. The concentration of eucalyptus wood chips and the presence of catalyst especially have a significant effect on the gasification process. It can be observed that increasing feed concentration the CH₄ (33 %) gas product yield rises significantly (Table 3). In general, the concentration of the other gaseous products (CO, CO₂, and hydrocarbons) usually increase at higher concentrations of feed samples, as some researchers have reported [13,14,15]. But it was not noticed during the experiments. It could be explained by the presence of the catalyst, which probably helped to keep the predominance of water gas shift and methanation reactions instead of the alternative reaction pathways during the reaction at higher biomass.

Nickel catalyst is a good option not only because of the cost-effective but is also known promote water-gas shift reaction and to largely suppress tar formation by cracking it. Many researchers have been introducing it into a supercritical water gasification reaction to understand better the activity and stability of its. Most searches found that using nickel catalyst the conversion

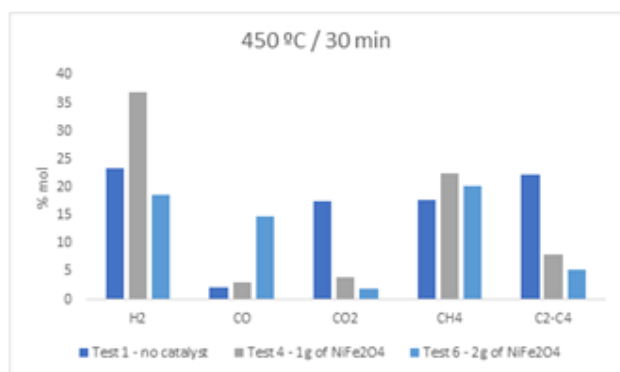
of biomass can be accelerated. Researchers [8, 16, 17] have done experiments to evaluate the hydrothermal gasification performance using Ni as a catalyst. According to these authors, chemical and physical structure of Ni catalyst importantly changes at hydrothermal conditions, these changes can improve the gasification reactions of biomass under supercritical even subcritical water conditions. According to the “Fig. 1 (A)” the presence of catalyst during the experiments at 450 °C increased potentially the H₂ and CH₄ gas product yields by 49.3 % and 10.2 %, respectively. The results were consistent with earlier literature reports [8, 12, 16, 17].

About the liquid obtained from each experiment, at lower feed concentration the liquid samples were clear. As the feed concentration was increased, a dark brownish oil layer was present in the liquid sample. This indicated that the range of reaction temperature and reaction time were not enough to complete degraded the biomass used during the experiments.

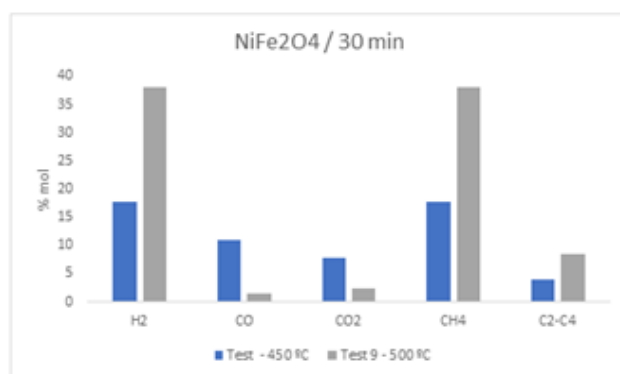
3.2 Effect of temperature

“Fig. 1 (B)” illustrates the effect of reaction temperature increasing from 450 to 500 °C on the composition of gas products from hydrothermal gasification of eucalyptus wood in the presence of NiFe₂O₄ catalyst. The feed of biomass was kept at 2.2 g (10 wt %). According to the “Fig 1 (B)”, the temperature has a significant effect on

the gas yields, the higher temperature favour gaseous production, especially H₂ and CH₄ yields due to the promotion of free-radical reactions which stimulate gas formation. The highest hydrogen yield (around 38 %) was obtained by conversion of eucalyptus wood chips at 500 °C. even during the experiments carried out without catalyst.



(A): Influence of NiFe₂O₄ at 450 °C for 30 min of residence time



(B): Effect of reaction temperature

Fig. 1. Effect of the catalyst (A) and reaction temperature (B).

3.3 Possible uses of gas products

The gasification process led to the production of hydrogen and methane fuel gases, which have various existing applications. First, the gas product can be fed into a gas engine for electricity production and combusted directly for clean energy in the form of heat for the cellulose industry. Second, the gas products are obtained at high pressure, which makes separation using e.g. pressure-swing absorption or membranes, highly applicable. Hydrogen may be obtained pure and used in hydrogen fuel cells, while methane can be used in gas engines to produce electricity. Pure methane can also be fed into domestic gas networks for homes or converted to syngas for further processing. All these added value activities from the SCWG process can potentially increase the economic and environmental viability of the cellulose and other biomass process industries

4 Conclusions

According to the preliminary results, it was observed that the supercritical water gasification is a viable process for convert eucalyptus biomass in H₂ and CH₄. It was found that eucalyptus wood chips decompose to H₂, CH₄ gases with little yield of CO₂. Increasing the reaction temperature beyond 500 °C led to the increasing production of both CH₄ (around 31.1 %) and H₂ (around 38 %) gases and the liquid sample and solid residue have decreased. It was also observed the influence of the catalyst. The NiFe₂O₄ increased the C-C bonds decomposition of eucalyptus. Using the nickel ferrite led to the increasing production of H₂ (49 %). This work proposes that the supercritical water gasification has improved expressively the production of H₂ but more experiments still necessary to verify the effects of other parameters and to characterise the liquid sample and solid residue.

Detailed feasibility studies will be carried in collaboration with the cellulose industry in Brazil, to evaluate the potential yields of these gases and associated costs of the process in a typical cellulose plant in consideration for technology take-up.

Acknowledgment

The authors would like to thank CAPES - Coordenação de Aperfeiçoamento de Pessoal de Nível Superior and FAPESB - Fundação de Amparo A Pesquisa do Estado da Bahia, of the Ministry for Education of Brazil, for their support of this research.

References

1. Indústria Brasileira de Árvores - IBÁ. Relatório Anual IBÁ 2017. Brasília, 2017.
2. Reddy, S.N.; Nanda, S.; Dalai, A.K.; Kozin, J.A. Supercritical water gasification of biomass for hydrogen production. *International Journal of Hydrogen Energy*, v.39, p. 6912-6926, 2014.
3. Hernández, J.J.; Ballesteros, R.; Aranda, G. Characterisation of tars from biomass gasification: Effect of the operating conditions. *Energy*, v. 50, p. 333-342, 2013.
4. Dudynski, M.; Van Dyk, J.; Kwiatkowski, K.; Sosnawska, M.. Biomass gasification: Influence of torrefaction on syngas production and tar formation. *Fuel Processing Technology*, v. 131, p. 203-212, 2015.
5. Devi L, Ptasiński KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy*, v. 24, 2003.
6. Kruse, A. Hydrothermal biomass gasification. *The journal of supercritical fluids*, n. 47, p. 391-399, 2009.
7. Behenia, I. Treatment of aqueous biomass and waste via supercritical water gasification for the production of CH₄ and H₂. 2013. 108f.. University of Western Ontario London. Ontário-Canadá, 2013.
8. Elliot, D.C. Catalytic hydrothermal gasification of biomass. *Biofuels Bioproducts and Biorefining* 2(3), p. 254-65, 2008.

9. Guo, Y., Wang, S. Z., Xu, D. H., Gong, Y. M., Ma, H. H., Tang, X. Y. Review of catalytic supercritical water gasification for hydrogen production from biomass. *Renewable and Sustainable Energy Reviews*, v.14, p.334-343, 2010.
10. Borges, A. C. P.; Alves, C. T.; Torres, E. A. . Torrefied Eucalyptus Grandis Characterization as a Biomass to Using in Industrial Scale. *Chemical Engineering Transactions*, v. 49, p. 283-288, 2016.
11. Borges, A. C. P.; Alves, C. T. ; Fiuza, R. ; Andrade, H. M. C. ; Ingram, A. ; Vieira de Melo, S.A.B. ; Torres, E. A. . Preparation of heterogeneous catalysts by combustion reaction for water gas shift reaction. In: IMRC 2017 - XXVI International Materials Research Congress, 2017, Cancun. XXVI International Materials Research Congress, 2017.
12. Muangrat, R.; Onwudili, J.A.; Williams, P.T. Influence of alkali catalysts on the production of hydrogen-rich gas from the hydrothermal gasification of food processing waste. *Applied Catalysis B: Environmental* v. 100, p. 440–449, 2010.
13. Hao XH, Guo LJ, Mao X, Zhang XM, Chen XJ. Hydrogen production from glucose used as model compound of biomass gasified in supercritical water. *Int J Hydrogen Energy* v. 28, p. 55-64, 2003.
14. Onwudili JA, Williams PT. Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass. *International journal of hydrogen energy*, v. 34, p. 5645-5656, 2009.
15. Kruse A, Gawlik A. Biomass conversion in water at 330-410 °C and 30-50 MPa identification of key compounds for indicating different chemicals reaction pathways. *Ind Eng Chem Res*, v. 42, p. 267-279, 2003.
16. Elliot, D.C., Sealock, Jr.Lj, Baker, E.G.. Chemical processing in high-pressure aqueous environments. Development of catalyst for gasification. *Industrial & Engineering Chemistry Research*, v. 32 (8), p. 1542-1548, 1993.
17. Waldner, M.H; Vogel, F. Renewable production of methane from woody biomass by catalytic hydrothermal gasification. *Industrial & Engineering Chemistry Research*, v. 44 (13), p. 4543-4551 2005.