Catalytic supercritical water gasification of eucalyptus wood chips in a batch reactor

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Abstract: Eucalyptus wood chips were reacted under supercritical water conditions to evaluate the effect of a $NiFe_2O_4$ catalyst, residence time and temperature parameters. Experiments were performed in a batch reactor at 400, 450 ºC and 500 ºC using three different amounts of catalyst (0, 1.0, 2.0 g) and three different residence times (30, 45, 60 mins). Results showed that eucalyptus wood chips reacted and produced CO_2 as the dominant gas in all cases, followed by H_2 and CH_4. However, the presence of $NiFe_2O_4$ catalyst led to a 60 % increase in H_2 produced, while significantly reducing the solid residue and enhancing the percentage of methyl derivatives in the organic liquid products. The highest H_2 mol % was at 450 ºC, 2 g of catalyst and 60 min of residence time. Analysis of the derived oils showed that they were mostly composed of ketones, aldehydes, methylbenzenes and alkylated phenols. Increasing the reaction temperature to 500 ºC increased the molar composition of methane by 62 % compared to its yield at 450 ºC. In generally, this work showed that $NiFe_2O_4$ acted as an effective heterogeneous catalyst for improved production of H_2 and CH_4 via supercritical water gasification process.

Keywords: supercritical water gasification; heterogenous catalyst; eucalyptus wood chips; hydrogen production.

1. INTRODUCTION

Biomass is one of the promising alternatives for renewable energy sources to ensure economic development with social inclusion and without environmental aggression. Brazil has 5,673,783 hectares of eucalyptus wood plantation and 70.74 million m³ were consumed by the pulp and paper industry in 2016. Moreover, Brazil led the global rankings of forest productivity with an average productivity of 35.7 m3/ha/year for eucalyptus plantations in 2016. In that same year, 47.8 million tonnes of solid waste were generated, with 14.1 million tonnes (29.5 %) from industrial activities (pulp and paper sector) [1]. 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 energy requirements of the process. Therefore, it has become necessary to develop new technologies to generate clean energy using this waste.

Hydrogen from waste biomass is regarded as a clean gaseous fuel and efficient for heat and power generation due to its high energy content [2]. About 4% of hydrogen demand is produced from renewable sources and only biomass can directly generate renewable hydrogen while other sources require electrolysis [3].

An interesting option 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 energy of the feedstock. The process occurs in the presence of a gasification agent (e.g. steam, carbon dioxide, air or oxygen) and at high temperatures (700-1500 °C). Nevertheless, during the gasification process, some of the fuel is not converted into gas and remains as a condensate product (tar), which is one of the major problems to deal with during biomass gasification [4-6]. Supercritical water gasification (SCWG) is a promising technology to ensure a higher hydrogen yield and lower the formation of tar.

The main difference between SCWG and other gasification technologies is related to the gasification medium i.e. supercritical water compared to steam and/or inert gas. SCWG also converts wet biomass, which reduces pre-treatment costs e.g. avoiding expensive dewatering and drying to acceptable moisture contents for conventional gasification or pyrolysis. Further, the high solubility of organic compounds in supercritical water enhances their reactivity, thereby minimizing tar formation and improving SCWG performance. The SCWG process is flexible and can be tuned to enhance the selectivity of gas products. For example, SCWG produces higher hydrogen content at high temperatures (> 700 °C) and higher methane content at lower temperatures (< 600 °C) [7-9]. These advantages make SCWG an even more attractive technology.

Hydrothermal processes have been reported to involve steps including the effective hydrolysis of cellulosic materials in biomass to simpler sugars, which can be easily gasified for hydrogen gas production. Onwudili and Williams [7] investigated the production of hydrogen gas from hydrothermal gasification of glucose in a batch reactor in the presence of the alkali from 200 ºC, 2 MPa to 450 ºC, 34 MPa at constant water loading. This work demonstrated that temperature was a significant parameter for hydrogen and methane production. It was observed that at 350 ºC, 21.5 MPa, half of the optimum hydrogen gas yield had formed and at 450 ºC, 34 MPa, more than 80 % vol of the gaseous effluent was hydrogen gas. In addition, Schmieder et al. [10] studied the SCWG of glucose aqueous solution in a tumbling batch autoclave operated at 600 °C, 20 - 31 MPa, and 120 s of reaction time and obtained low concentrations of CH_4 (< 4 vol %) in the product gas without catalysts.

Even though SCWG increases the selectivity of hydrogen production, it requires high pressure and temperature for a reaction without catalysts. Catalysts are a good solution to improve the efficiency of the gasification process. The choice of catalyst for

SCWG depends on its ability to break C-O and C-C bonds during the reforming process, accelerate the water-gas shift reaction and decrease the activation energy in the SCWG reaction [11]. Thus, catalytic supercritical water gasification (CSCWG) is a favourable option to improve the efficiency of the gasification process, producing a mixture of gases and value-added liquid products, depending on the reaction parameters and conditions.

Both homogenous and heterogeneous catalysts have been tested in SCWG in previous studies. The investigated homogenous ones were mainly alkaline salts such as K_2CO_3, NaOH, KOH, Na_2CO_3 [5]. The mechanism of hydrogen production using alkali salts as catalysts starts with easily breaking the C-C bonds and decreasing the temperature of the degradation of cellulose, producing simpler intermediates, which are then easily converted to hydrogen [7, 12, 13]. On the other hand, ruthenium, rhodium, and nickel have proved to be active metal catalysts for SCWG, offering high catalytic activity, selectivity and recyclability compared to a homogeneous catalyst [11].

Ru-based catalysts have been reported to offer high selectivity, high catalytic activity and a high level of carbon conversion to gas at lower temperature, however they are very expensive [8, 9, 11]. Hence, many researchers have used cheaper nickel-based catalysis in the SCWG process and most of them found that nickel-based catalyst can accelerate the conversion rate of biomass [9, 14, 15]. Moreover, the chemical and physical structure of Ni catalysts have been reported to significantly change under hydrothermal conditions, leading to improved gasification reactions of biomass. Nakagawa et al. [16] observed that the carbon-supported nickel (Ni/C) catalyst shows high catalytic activity in hydrothermal conditions.

Yoshida et al. [17] gasified lignin, cellulose, and their mixture with a nickel catalyst in a stainless-steel batch reactor at supercritical water at 400 °C, 25 MPa and 25 min of residence time. The gasification efficiency was low for the tests using small amount of catalyst. However, increasing the catalyst loading from 0.04 to 0.08g led to remarkable hydrogen gasification efficiency (HGE) increase (59 %), which demonstrated the importance of the nickel catalyst for the SCWG of cellulose lignin mixture. Sealock Jr. et al. [18] used Harshaw Ni as catalyst for the SCWG of wood at 450 °C and 34 MPa for 150 min. They obtained maximum methane yield of 0.22 (g of CH4)/(g of wood), corresponding to 33 vol % CH_4 in the product gas.

Thus, nickel-based catalysts appear to be good option not only because they generally are cost-effective, but they are also known to promote the water-gas shift reaction and to largely suppress tar formation due to an enhanced ability for cracking organic compounds [11].

In the present work, eucalyptus wood chips conversion by supercritical water gasification (SCWG) was investigated in a batch reactor, in the presence of $NiFe_2O_4$ catalyst previously synthetized by combustion reaction. The SCWG tests were carried out mainly at 450 ºC for three different residence times (30, 45, 60 mins) and three different amounts of catalyst (0, 1.0, 2.0 g) to investigate the influence of the severity of the reaction conditions on biomass gasification under supercritical condition. The influence of the reaction temperature was also investigated at 400, 450 and 500 ºC, respectively. The focus of this work was to evaluate the gas and bio-oil products formed during the reactions as an alternative to converting the vast Eucalyptus waste resource into valuable energy carriers.

2. EXPERIMENTAL

2.1. Materials

Eucalyptus grandis chips, with approximately 30 % moisture content and average particle size of 710 µm, were used as starting biomass material. The biomass was characterised before use. All analyses were performed according to the American Society for Testing and Material (ASTM) Standard Methods and the results summarized in Table 1 [19]. The methodology of these analyses has been discussed in an earlier paper [20].

Table 1. Characteristics of the *Eucalyptus grandis* chips starting biomass

Sample	**Moisture Content (%)**	**HHV (MJ/kg)**	**Proximate Analysis (%)**			**Ultimate Analysis (%)**			
			Volatile Matter	Fixed Carbon	Ash	C	H	N	O*
Eucalyptus wood chips	30	17.50	83.23	16.42	0.5	46.81	6.11	0.12	46.76

*Oxygen was obtained by difference.

The nickel iron oxide ($NiFe_2O_4$) catalyst has a surface area of 32.4 m^2g^{-1} and average particle size of 18.11 nm. Briefly, the catalyst was synthesized by the combustion reaction method using ferric nitrate $Fe(NO_3)_3.9H_2O$, nickel nitrate $Ni(NO_3)_2.6H_2O$ and urea $CO(NH_2)_2$ as fuel. The batches were placed in a vitreous silica basin, homogenized and directly heated up in air on a hot plate to a temperature of around 480 ºC until the ignition took place, producing a nickel iron oxide in a foam form. The obtained material was heated at 480ºC for additional 20 minutes to eliminate any volatile products [21].

2.2. Reactor system and experimental procedure

All experiments were performed in a non-stirred Hastelloy-C reactor purchased from Parr Instruments Co., Inc. USA. The reactor has a 75 cm^3 volume capacity and the maximum operating conditions of temperature and pressure were 600 ºC and 45 MPa, respectively.

In each experiment, the feed material was loaded into the reactor containing distilled water, and then the catalyst was added. The amount of water loading was 20 mL for all tests. The experiments were designed to evaluate some of the main parameters of the process (catalyst, residence time and temperature). For each catalytic SCWG test, 2.22 g (10 wt%) of biomass sample was used without and with two different amounts of catalyst (1.0 g and 2.0 g), three different residence times (30, 45, 60 mins), and three different temperatures (400, 450 and 500 °C), at operating pressures around of 20-22 MPa, 22-25 MPa and 25-30 MPa, respectively.

Once the reactor was loaded, it was sealed and put into an electric furnace fitted with a temperature controller. The reactor was heated rapidly at a rate of 20 °C min^{-1} up to 400, 450 and 500 °C, such that the reaction temperature was attained after just 15 min. At the end of each reaction run, the reactor was rapidly withdrawn from the heater and quickly cooled to ambient temperature by blowing compressed air over the surfaces.

Initial reproducibility tests were carried out for experiment 1 in triplicate, followed by analysis of reaction products. The analysis results showed that the standard deviations for all reaction products were less than 5%. Thus, armed with this confidence, the subsequent experiments were carried out only once or twice. Nevertheless, the analyses of reaction products were carried out in triplicates in all cases.

2.3. Product Analyses

Figure 1 shows a simplified analyses scheme of the reaction products (gas, liquid and solid residue). After cooling, the gas outlet valve was opened to collect the gas samples. Then, the reactor was opened to collect the liquid sample and solid residues. The liquid and solid products were collected from the reactor by rinsing with distilled water and dichloromethane as an organic solvent. All liquid products and solid residue (SCWG char and catalyst) were filtered to separate the solid residue. Based on thermogravimetric analyses, it was considered that the amount of catalyst remained the same before and after the tests. No analysis of the spent catalysts was carried out. All the product analyses were carried out in Birmingham in the United Kingdom.

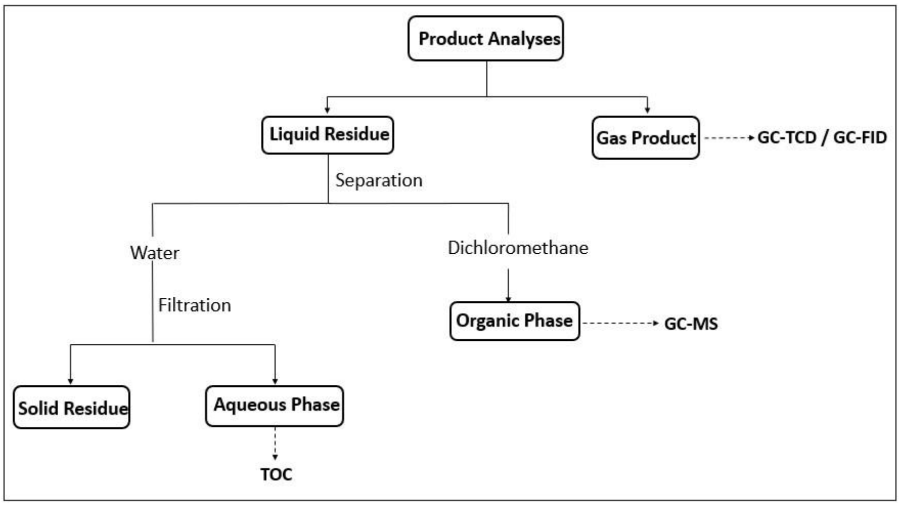

Figure 1. Scheme for products analyses

2.3.1. Gas product

The gas products were analyzed using a GC-2014 gas chromatograph obtained from Shimadzu UK, Milton Keynes. The permanent gases; hydrogen, nitrogen, oxygen and carbon monoxide were separated on a 2 m length by 2 mm diameter 60 – 80 mesh molecular sieve column, fitted to a thermal conductivity detector (TCD) for quantification. Hydrocarbon gases (C_1 to C_4) and CO_2 were separated on a 2 m length by 2 mm diameter Hayesep 80 – 100 mesh column. The hydrocarbon gases were quantified with a flame ionization detector (FID), while CO_2 was quantified with a TCD. For each analysis, 1 mL of the gas sample was injected into the GC using a gas-tight syringe. The injector was held at 60 ºC and the detectors at 220 ºC. The column oven was programmed as follows: initial at 80 ºC, and ramped at 10 ºC min^{-1} to 180 ºC and finally held at 180 ºC for 3 minutes, giving a total analysis time of 13 min.

2.3.2. Liquid product

Analyses of the organic phase (bio-oil)

After collecting the gas sample, the reactor was opened to recover the solid/liquid phase products and put into a clean and dry beaker. The mixture of solid/liquid product was filtered using a vacuum pump. The organic phase (bio-oil) was extracted using dichloromethane (DCM) as an organic solvent. The reactor was rinsed with 10 mL of DCM to extract any remaining tar/solid products from the reactor. Then, the DCM-solid mixture was also filtered over the same filter paper used for the aqueous phase, yielding another liquid phase (bio-oil) and a solid phase. Analyses of organic fractions of the liquid products were performed using a Varian 3800-GC coupled to a Varian Saturn 2200 ion trap MS/MS equipment. The column was a 30 m x 0.25 mm inner diameter Varian VF-5ms (DB-5 equivalent), while the carrier gas was helium, at a constant flow rate of 1 mL min^{-1} [22]. For GC-MS analysis, the samples were prepared by mixing the extracted pyrolysis liquids with more dichloromethane solvent up to a specific constant volume. A sample volume of 1 µL was injected into the GC column via an injection port maintained at 300 °C, with 1:50 split ratio. The GC oven was initially held at 50 °C for 2 min, then ramped at 5 °C min^{-1} to 275 °C, and finally held at 275 °C for 3 min, giving a 50 min analysis time. Helium was used as carrier gas at a constant flow rate of 15 mL min^{-1}. Compounds separated on the column were detected by the mass selective (MS) detector held at 250 °C. The transfer line was also kept at a temperature of 275 ºC. Mass spectra were obtained using 70 eV ionization energy in the molecular mass range of m/z = 35 – 300, with a scan time of 0.35 seconds [22]. A NIST05 MS library was used to assign the main peaks, with similarity indexes >85%.

Analyses of the aqueous phase

After the extraction of the organic phase, an aqueous phase was obtained. Then, 10 mL aliquots of the aqueous phase were collected for the total organic carbon (TOC) determination in a Shimadzu TOC-L CPH-ASI-L analyzer.

The solid phase, mainly consisting of char and/or recovered catalyst, was dried at 105 °C in a vacuum oven for 2 hours, cooled in a desiccator, then re-weighed to determine any mass loss. Combining all the results from the various analyses, the carbon balance of each experiment was computed as a means of evaluating the performance of the SCWG.

2.4. Evaluation of results

The experimental and thermodynamic results were evaluated according to Eqs. (1) to (3):

Molar composition of the gas product (x_i):

$$x_i\ [\%] = \frac{ni}{n\ (total)} x100 \qquad (1)$$

Carbon gasification efficiency (CGE):

$$\text{CGE}\ [\%] = \frac{mass\ of\ carbon\ in\ gaseous\ products}{mass\ of\ carbon\ in\ feed} x100 \qquad (2)$$

Hydrogen gasification efficiency (HGE):

$$\text{HGE}\ [\%] = \frac{mass\ of\ hydrogen\ in\ gaseous\ products}{mass\ of\ hydrogen\ in\ feed} x100 \qquad (3)$$

The carbon balance was calculated considering the carbon content in the gaseous products, in solid residue and in the liquid (aqueous and organic) products based on the following equations:

$$\%\ \text{carbon}_{\text{(gas phase)}} = \frac{\text{mass of carbon in GC analysis (g) x 100}}{mass\ of\ eucalyptus\ wood\ in\ feed} \qquad (4)$$

$$\%\ \text{carbon}_{\text{(aqueous phase)}} = \frac{\text{mass of carbon in TOC (g) x 100}}{mass\ of\ ecalyptus\ wood\ in\ feed} \qquad (5)$$

$$\%\ \text{carbon}_{\text{(solid residue)}} = \frac{\text{m (char) (g) x 100}}{mass\ of eucalyptus\ wood\ in\ feed} \tag{6}$$

$$\text{m}_{\text{(char)}} = \text{m}_{\text{solid residue}} - \text{m}_{\text{catalyst}} - \text{m}_{\text{ash}} \tag{7}$$

Assuming a 100% balance, the carbon content in the organic phase was calculated by the difference:

$$\%\ \text{carbon}_{\text{(organic phase)}} = 100 - (\text{carbon}_{\text{(gas)}} + \text{carbon}_{\text{(solid residue)}} + \text{carbon}_{\text{(aqueous phase)}}) \tag{8}$$

3. RESULTS AND DISCUSSION

The effects of catalyst loading and residence time on the supercritical water gasification of eucalyptus wood chips were investigated. Most of the experiments were carried out at 450 ºC, but two tests were also performed at 400 and 500 ºC to evaluate the temperature effect on the % mol of the gas mixture of H_2 and CH_4. The list of the performed experiments and the respective carbon balance are shown in Table 2. A careful look at the results in Table 2 reveals that by increasing the amount of catalyst at the same temperature and residence time, the yield of solid residue decreased while the yield of gas products increased. In general, the presence of the $NiFe_2O_4$ catalyst led to an increase in the conversion of biomass into liquid and mainly gas products. For example, without catalyst, the conversion of eucalyptus ranged from 64-73%, whereas with the catalyst the conversion was between 83 and 95.5%.

Table 2. Experimental data and carbon balance

Exp.	Hold time (min)	Temperature (°C)	Eucalyptus wood chips (g)	Catalyst (g)	Gas (wt%)	Solid residue (wt%)	Liquid (wt%)	Biomass Conversion (%)
Test 1	30	450	2.2162	-	38.09	35.94	25.96	64.05
Test 2			2.1995	0.9999	58.28	12.45	29.26	87.54
Test 3			2.2015	1.9948	53.92	10.89	35.20	89.12
Test 4	45	450	2.1985	-	36.59	28.25	35.16	71.75
Test 5			2.2071	1.0054	52.67	16.65	30.69	83.36
Test 6			2.2252	1.9975	52.57	7.15	40.27	92.84
Test 7	60	450	2.2031	-	34.34	27.28	38.39	72.73
Test 8			2.2083	1.0009	45.41	15.27	39.42	84.83
Test 9			2.2019	2.0048	48.19	4.51	47.30	95.49
Test 10		500	2.2093	1.9996	65.94	13.77	20.29	86.23
Test 11		400	2.2229	1.9977	41.33	18.91	39.76	81.09

3.1. Gas analyses

The gas production of eucalyptus biomass waste via SCWG was investigated with and without adding $NiFe_2O_4$ as a mixed oxide catalyst. The maximum total gas produced was 65.94% at 500 °C and 60 min in the presence of catalyst (1.9996 g). The mole fraction of the produced gases in these conditions indicates that approximately 17.51 % was hydrogen and 24.12 % was methane, as shown in Table 3.

Table 3. Composition of the gaseous product and TOC analyses

Tests	Compound (% mol)						TOC (mg/L)
	CH_4	C_2-C_4	H_2	CO	CO_2	H_2O	
1	16.03	3.82	9.27	8.17	62.51	0.19	1607
2	10.59	3.44	13.11	2.60	70.09	0.16	1580
3	11.49	3.50	19.93	3.30	61.66	0.11	1621
4	18.52	4.16	10.36	7.15	59.54	0.26	1613
5	15.28	4.57	17.96	1.01	61.04	0.14	1479
6	10.78	3.96	20.85	0.64	61.60	0.16	1432
7	21.77	5.37	12.58	6.01	53.98	0.30	1376
8	15.40	4.45	16.59	0.65	62.76	0.16	1321
9	18.16	4.06	22.96	0.60	54.06	0.16	1275
10	24.12	6.17	17.51	0.46	51.64	0.10	1375
11	9.15	3.07	9.52	2.27	75.81	0.18	1584

Analysing the results of gaseous products presented in Table 3, it can be observed that the highest % mol of H_2 (around 23 %) was obtained during Test 9. Similar experiments, at 400 and 500 ºC using 2 g of $NiFe_2O_4$ and 60 min, were designed to evaluate the effect of temperature on the composition of the gaseous product, especially on the % mol of H_2 and CH_4.

The presence of the catalyst improved hydrogen % mol in the gas products compared to the non-catalytic experiments (Tests 1, 4 and 7). These results suggest that the catalyst promoted both the steam reforming of methane and the water gas shift reaction, respectively leading to a decrease of CH_4 % mol and of CO % mol in the gaseous products.

Hao et al [23] used a continuous flow tubular reactor at 650 ºC and 25 MPa, Na_2CO_3 catalyst to obtain improved hydrogen yields of nearly 40% from glucose. The lower gasification yield of hydrogen obtained in the present work could be related to the combined use a raw biomass instead of a model compound (glucose), in a batch reactor at lower temperatures.

3.1.1. Effect of catalyst loading

The use of a suitable catalyst allows faster gasification of the intermediate products in order to avoid the formation of polymeric materials and eventual carbonizations. It can be noticed that the composition of gases changed with the change of the amount of catalyst.

The effect of the catalyst loading on gasification of eucalyptus wood chips was evaluated through a series of experimental runs carried out in the presence of $NiFe_2O_4$ at 450 ºC for three different residence times (30, 45 and 60 mins). 10 wt % of eucalyptus wood sample was used for all experiments. Figure 2 illustrates the effect of the catalyst on the SCWG.

Increasing the amount of $NiFe_2O_4$ catalyst, significantly increased the H_2 gas mol % while reducing the CH_4 gas mol % (Figure 2). Analysing Table 3, it can be observed that increasing the $NiFe_2O_4$ loading from 0 to 2 g at 30 min caused the highest increment of H_2 mol % (53 %). Though, observing the results at 45 min, it can be noticed that loading more catalyst caused a 42% decrease in the methane gas fraction.

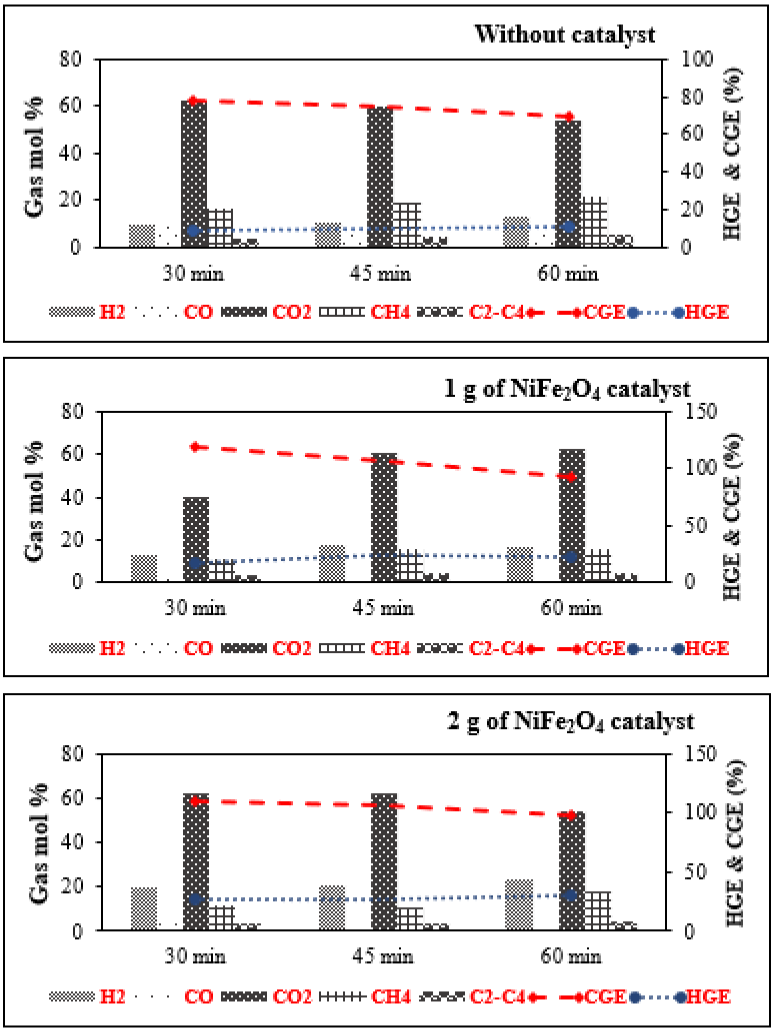

Figure 2. Effect of catalyst and residence time on SCWG of eucalyptus wood chips at 450 °C

In terms of mole percent, the three predominant gases were carbon dioxide, hydrogen and methane for all evaluated conditions. The mole percent of hydrogen was highest using 2 g of $NiFe_2O_4$ at 450 °C and 60 min. Onwudili and Williams [7] reported that carbon dioxide was also the dominant reaction product in absence of catalyst, but the in presence of ruthenium oxide catalyst CO_2 mol % decreased and the methane mol % increased. The differences in the results reported by Onwudili and Williams [7] and this work may be due to differences in feed type and loading, catalyst composition and temperature reaction.

The amount of carbon monoxide and hydrocarbon gases was quite small for the experiments performed in the presence of $NiFe_2O_4$. The lesser amount of CO mol % obtained in the presence of iron oxide catalyst may suggest that the consumption of CO during methanation was faster that the reduction of CO_2 to CO [24], which can be explained by the competition for CO for methanation and hydrogen production via water gas shift reaction [25]. According to Onwudili & Williams [7] and Bjerre & Soerensen [26] the formation of CO and CO_2 could be explained because the carbonylation pathways of carboxylic acids are the usual intermediates formed during the SCWG of several organic compounds.

Similar results have been reported by Ross et al. [27]. In their work, the effect of various catalysts on the SCWG of algae was studied. The catalysts used were NaOH, Ru/Al_2O_3 and Ni/Al_2O_3, and for all these catalysts small amounts of carbon monoxide and C_2-C_4 hydrocarbon gases were produced.

From this, it seems that the $NiFe_2O_4$ catalyst has probably activated the decomposition reactions of intermediates to produce light gases and helped to keep the predominance of the water-gas shift reaction instead of alternative reaction pathways during the reaction with the higher amount of catalyst.

The presence of $NiFe_2O_4$ catalyst also prevented the polymerization of carbon species, thus forming less tars and/or chars. Analyzing the results of carbon balance in the Figure 3, it can be noticed that the best condition to the least formation of solid residue

(4.51 %) and the highest gas production (48.19 %) was achieved from the experiments using 2 g of catalyst at 450 ºC and 60 min. However, analyzing all the results obtained (Table 2), the highest gas production was 65.94 % in Test 10 (500 ºC, 60 min and 2 g of $NiFe_2O_4$). Interestingly, Test 10 from which the highest gas production was achieved, gave the highest % mol of CH_4 rather than H_2, which may imply the occurrence of a different mechanism at higher temperatures, since methanation reactions are exothermic [25, 28].

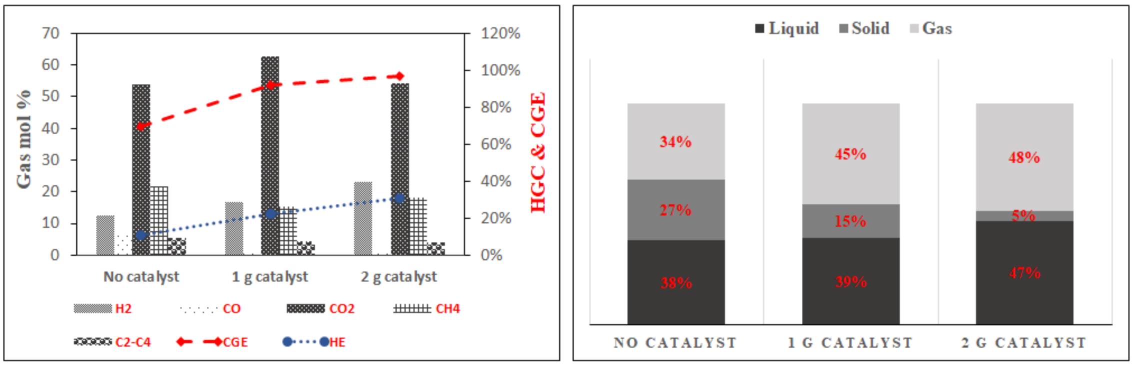

Figure 3. Effect of catalyst loading on SCWG of eucalyptus wood chips at 450 ºC and 60 min hold time

In Figure 3, the effect of the catalyst on both carbon and hydrogen yields can be observed. As desired, the addition of $NiFe_2O_4$ promoted the hydrogen gas yield expressively. Moreover, the hydrogen gasification efficiency (HGE, the ratio of total hydrogen in the product gas to the total hydrogen in the dry feed) increased corresponding to the gas yield behaviour.

CGE values were consistently higher during the catalytic tests, with values between 69.64 wt% and 97.03 wt% for experiments at 450 ºC, 2 g of $NiFe_2O_4$ and 60 min hold time, compared to HGE values, which varied between 11.1wt% and 30.62 wt%. For the non-catalytic tests, the CGE values obtained were quite similar, varying between 69.64 to 77.52 wt%. Hence, the $NiFe_2O_4$ catalyst was able to convert most of the carbon compounds in the eucalyptus wood chips feed into gas.

In the work of Yildirir, Onwudili, Williams [29], refuse derived fuel (RDF) was gasified under supercritical water condition at 500 ºC and 29 MPa pressure using a heterogeneous $RuO_2/\lambda\text{-}Al_2O_3$ as catalyst and the obtained results were compared with the use of NaOH homogenous catalyst. The presence of 20 wt% $RuO_2/\lambda\text{-}Al_2O_3$ catalyst achieved carbon gasification efficiency up to 93 %, compared to 75 % when NaOH was used for the same reaction time of 60 min. Compared with this work, 2 g $NiFe_2O_4$ catalyst gave CGE of 133.37 %. The better results obtained using heterogeneous catalysts ($NiFe_2O_4$ and $RuO_2/\lambda\text{-}Al_2O_3$) demonstrate the high ability of transition metal to break C-C and C-O bonds during the SCWG, promoting high carbon conversion to gas at lower temperatures.

3.1.2. *Effect of residence time*

The effect of residence time was studied at a constant temperature of 450 ºC without catalyst, 1 g of $NiFe_2O_4$ and 2 g of $NiFe_2O_4$ catalyst while increasing the residence time from 30 to 60 min. Figure 2 shows the effect of residence time on supercritical water gasification of eucalyptus wood chips in the evaluated conditions.

In all cases, the % mol of hydrogen gas increased as the reaction time increased from 30 to 60 min. CH_4 and C_2-C_4 gases mol % also showed significant increases at longer residence times as reported by other researchers [29, 30]. The mol % of CO and CO_2 decreased, probably because $NiFe_2O_4$ catalysed the methanation of the carbon oxides [25].

There was also evidence that the catalyst might have significantly promoted CO and CO_2 methanation. For instance, the CH_4 content in the product increased from 16.03 mol% at 30 min to 21.77 mol% at 60 min for the tests without catalyst; from 10.59 mol% at 30 min to 15.40 mol% at 60 min for the runs with 1 g of $NiFe_2O_4$ catalyst and, from

11.49 mol% at 30 min to 18.16 mol% at 60 min for the runs with 2 g of $NiFe_2O_4$ catalyst, as shown in Table 3.

Analysing the effect of residence time, it can be observed that the mol % of hydrogen increased with the reaction time, but this parameter was not dominant to achieve higher % biomass conversion and higher formation of H_2. The carbon balance for SCWG of eucalyptus wood chips at 450 ºC and 2 g of $NiFe_2O_4$ catalyst (Figure 4) shows that the proportion of gas was fairly constant at 45-55 wt % while the proportion of liquid products increased, and the proportion of solid residue decreased with increasing reaction time. Comparing the experiments carried out with 2 g of catalyst to those without catalyst, for the same residence time, the gas mol % of H_2 increased (53 % at 30 mins, 50 % at 45 mins and 45 % at 60 mins), as shown in Table 3. Despite the hydrogen yield increased with increasing reaction time, the observed increase was lower than that caused by the temperature increase. Similar results have been reported by Ross et al. [27] and Hao et al. [23], who found that increasing the reaction time does not enhance the gasification of algae and glucose considerably.

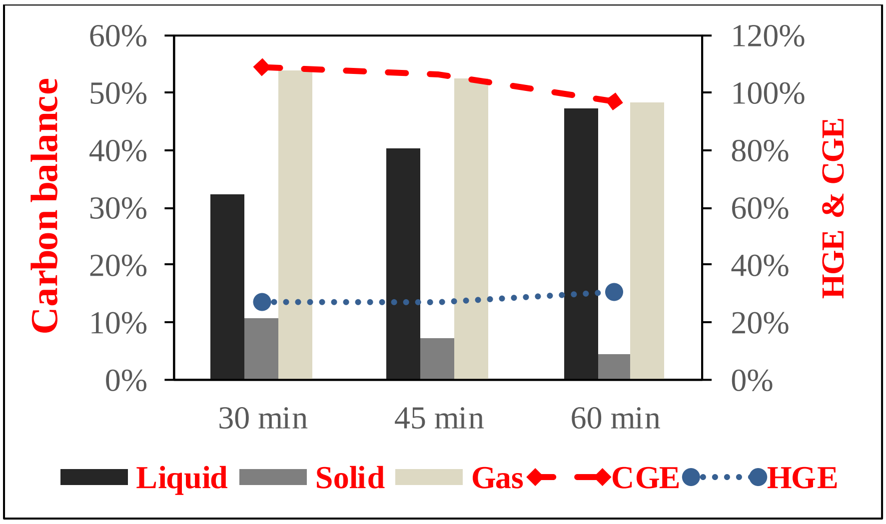

Figure 4. Carbon balance of SCWG of eucalyptus wood chips at 450 ºC and 2 g of $NiFe_2O_4$ catalyst

Louw et al. [31] reported that, during a SCWG of a primary paper sludge in the presence of nickel catalyst, H_2 content decreased and CH_4 content increased with an increase in the hold time to 120 min, which could be attributed to increased methanation at longer residence times at lower temperatures.

3.1.3. *Effect of temperature*

Figure 5 illustrates the effect of the reaction temperature (400, 450 and 500 ºC) on the composition of the gas products from the SCWG of 10 wt% of eucalyptus wood for 60 mins, using 2 g of $NiFe_2O_4$ catalyst.

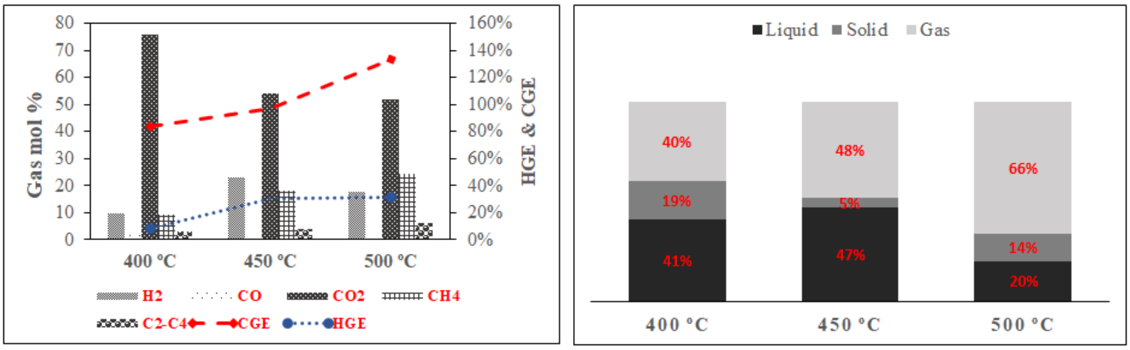

Figure 5. Effect of temperature on SCWG of eucalyptus wood chips, 60 min and 2 g of $NiFe_2O_4$ catalyst

According to Figure 5, the temperature has a significant effect on the gas yields. The highest temperature favoured the gas production, especially CH_4 and H_2 due to the promotion of free-radical reactions that stimulate the formation of gas [32]. Increasing the temperature, the water density decreases, consequently the ionic product increases which favour the free radical mechanisms [33]. The increase of the free radical concentration favours the decomposition of the biomass constituents, which are complex molecules and require energy for the endothermic reactions.

Although the experiments carried out at 500 ºC produced the highest amount of gases (around 66 wt %), the highest amount of hydrogen (around 23 mol %) was obtained by the conversion of eucalyptus wood chips at 450 ºC. An increase in reaction temperature from 400 to 500 ºC led to a higher CH_4 production (24.12 mol %). Since methanation is an exothermic process, it seems that a different mechanism was responsible for the increased methane formation at higher temperatures. Hence, the most probable explanation would be that the catalyst enhanced the hydrogenolytic demethylation of methylated components in the liquid products. It could be also observed that the carbon gasification efficiency and the hydrogen gasification efficiency increased with temperature, which agreed with results reported by previous researchers [34-36].

3.2. Liquid analysis

The highest yield of liquid products was observed at 400 ºC, which corresponded to the lowest percentage of gases. This indicates greater formation of tar in these conditions, as a result of the rapid depolymerization of the eucalyptus wood chips at low temperature [10].

In Table 3, the total organic carbon (TOC) contents of the aqueous liquid phase obtained after gasification are presented. The results show that increasing the amount of catalyst and the reaction time led to a decrease in the TOC values.

Analysing the effect of the reaction time (at 450 ºC) on TOC, a reduction is observed with increasing reaction time. Hence, as the residence time increases, the aqueous liquid produced contains a lower amount of total organic carbon by conversion to gas or to water-insoluble organic products. The maximum TOC amount was measured for the tests performed without a catalyst (Test 1 and 4) and the test at 400 ºC (Test 11), where the TOC values were between 1500-1700 mg L^{-1}. Comparing these results to those obtained by Casteloa et al. [37], ~4000 mg/l as the lower value of TOC, after 16 h of reaction time, they are rather lower. The minimum TOC amount was 1275 mg/L obtained in Test 9. Therefore, it can be said that the consumption of TOC was moderately fast, with a 21 % reduction after 60 mins of residence time.

Semi-quantitative analyses of each liquid organic fraction were carried out according to a method reported in literature [38-40] to indicate the concentrations of components in the liquid organic products. The area % of each identified compound was expressed as a percentage of the total area of selected peaks in the chromatograms. The results obtained in relation to the use of the catalyst at 450 °C and 60 min can be seen in Table 4, where the residence time, molecular formula and relative peak area %, are respectively listed with each identified component. This method was chosen because it was a fast way of obtaining enough information on the components of the bio-oils, which was not the focus of this present research.

Some of these compounds have also been identified as the main products of biomass hydrothermal conversion [28, 35, 41, 42]. According to Onwudili & Williams [28] the oil components can be classified as aliphatic (ketones, aldehydes, alcohols and carboxylic acids), alkylbenzenes (ethylbenzene, xylenes, and various methyl benzenes), phenols (phenol, alkylated phenols), and polycyclic aromatic hydrocarbons (PAH) (naphthalene and alkylated naphthalenes, biphenyls, fluorene, acenaphthene). Table 4 shows that the major liquid organic compounds identified in the oils produced during SCWG of eucalyptus feedstock were ketones, aldehydes, methyl benzenes and alkylated phenols. 2,4-dimethylphenol compound was the component with the highest area %. In addition, most of the cyclic compounds (benzofuran, 1,2-dimethyl cyclopropane, 2-methyl cyclopropane-, spiro [2.4] hepta-4,6-diene, o-xylene) were identified from experiments without catalyst. For the experiments performed with catalyst, polycyclic aromatic compounds were not detected or their % area decreased. This has also been reported elsewhere [35, 41].

Table 4. Chemical composition of organic liquid production from SCWG of eucalyptus wood chips at 450 ºC and 60 min

Residence time (min)	Compound	Formula	Relative peak area (%)		
			No catalyst	1 g of catalyst	2 g of catalyst
1.74	Cyclopropane, 1,2-dimethyl-,	C_5H_{10}	8.22	4.36	2.73
2.64	Kurchessine	$C_{25}H_{44}N_2$	-	-	0.65
4.64	Toluene	C_7H_8	-	2.35	1.46
4.64	Spiro[2.4]hepta-4,6-diene	C_7H_8	2.83	-	-
7.22	o-Xylene	C_8H_{10}	2.86	2.09	-
8.78	3-Furaldehyde	$C_5H_4O_2$	9.44	-	-
13.37	2-Cyclopenten-1-one, 3-methy	C_6H_8O	3.61	-	-
15.04	Cyclopentene, 3-methyl-	C_6H_{10}	-	5.15	-
15.04	2-Cyclopenten-1-one, 2,3-dim	$C_7H_{10}O$	5.26	-	3.95
15.49	Benzofuran, 2-methyl-	$C_{10}H_8O_3$	1.81	-	-
16.27	Cyclopropane,ethynyl-	C_5H_6	5.52	7.37	6.37
17.62	Phenol, 2-methyl-	C_7H_8O	6.93	7.47	6.48
18.55	Benzofuran, 4,7-dimethyl-	$C_{10}H_{10}O$	4.36	-	-
18.63	Phenol, 4-methyl-	C_7H_8O	2.61	4.16	4.51
18.69	Phenol, 3-methyl-	C_7H_8O	8.56	14.61	12.44
19.75	Phenol, 2-ethyl-	C_6H_5OH	-	-	5.25
19.91	2,4-Dimethylphenol	$C_8H_{10}O$	10.69	18.89	16.40
20.87	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	-	3.30	2.87
20.95	Phenol, 3,5-dimethyl-	C_6H_5OH	2.40	5.51	-
21.02	Phenol, 4-ethyl-	$C_8H_{10}O$	-	2.57	-
21.09	Phenol, 3-ethyl-	$C_8H_{10}O$	-	5.75	5.99
21.69	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	-	-	5.56
22.98	Phenol, 2,3,6-trimethyl-	$C_9H_{12}O$	-	-	2.29
23.16	Benzeneacetic acid, .alpha.-	$C_8H_8O_2$	2.78	8.14	7.08
23.29	Phenol, 3-propyl-	C_6H_5OH	-	5.54	5.78
23.29	Phenol, 2-propyl-	C_6H_5OH	-	-	2.02
25.19	1-Methoxycycloheptatriene	$C_8H_{10}O$	-	-	3.08
25.50	1H-Inden-5-ol, 2,3-dihydro-	$C_9H_{10}O$	-	2.73	2.36
26.51	2,5-Octadiyne, 4,4-diethyl-	$C_{12}H_{18}$	-	-	2.73

The oil formed at 450 ºC and 60 min using different amounts of catalyst contained a high percentage of methyl derivatives. This indicates that some of these compounds were transformed into gases or simpler compounds, while the amount of catalyst, the reaction time and the temperature increased. For example, the disappearance of 2-methyl benzofuran and 4,7-dimethyl benzofuran corresponded to the formation of compounds with lower molecular weight (1,2-dimethyl cyclopropane, 2,3-dimethyl-2-cyclopenten-1-one,3-methyl-2-cyclopenten-1-one). According to Williams and Onwudili [42], increasing the temperature led to the hydrolysis of benzofurans into hexanediones. Thus, this compound could undergo cyclization under hydrothermal conditions to produce 3-methyl-2-cyclopenten-1-one [41,42].

In this work, the amount of alkylphenols increased with the presence of the catalyst. The highest amount of alkylphenols was obtained by adding 2 g of catalyst (76.67 %). These results indicate that the $NiFe_2O_4$ catalyst favoured the methylation and alkylation of stable compounds, such as phenols, which dominate in the organic liquid fraction.

3.3.Solid residue

The solid residue mainly consisted of char and/or recovered catalyst. Figure 6 shows the influence of the catalyst at 450 ºC on the amounts of combustible fractions (char) in the solid residue. It can be observed from the experiments that less char was produced using a higher amount of the $NiFe_2O_4$ catalyst.

Figure 6 shows that the amount of residue solid decreases with the increasing amount of catalyst and the residence time. According to the results obtained for 2 g of catalyst, increasing the residence of time from 30 min to 60 min, the solid residue decreased by 58.60 %. The small amount of solid residue formed can be also explained by the highest conversion of biomass into gaseous and liquid products.

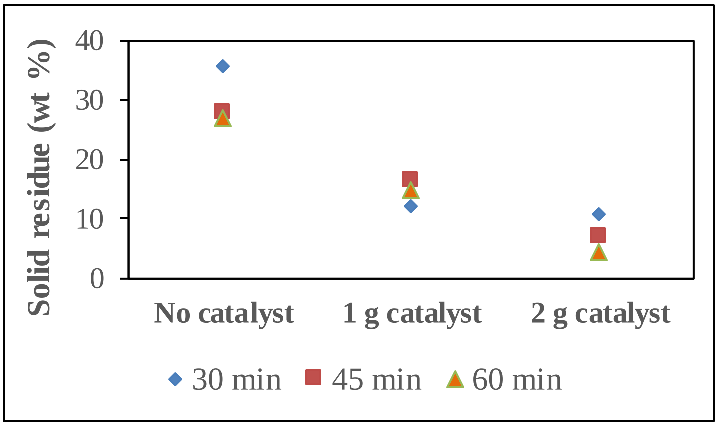

Figure 6. Influence of catalyst in the solid residue %

CONCLUSIONS

Supercritical water gasification of eucalyptus wood chips has been carried out with and without $NiFe_2O_4$ catalyst (1.0, 2.0 g) at 450 °C for reaction times of 30, 45 and 60 min. The best condition to obtain the highest H_2 mol % was at 450 °C, 2 g of $NiFe_2O_4$ catalyst and 60 min. Increasing the amount of $NiFe_2O_4$ enhanced important decomposition reactions of the eucalyptus wood chips compounds and also promoted both the water gas shift reaction, leading to higher H_2 and the methanation reaction leading to lower CO_2 production. Also, the amount of char decreased in the presence of $NiFe_2O_4$. Almost 66 % of the carbon compounds in the eucalyptus wood chips were converted to gaseous products in the presence of 2 g of $NiFe_2O_4$ catalyst at 500 °C and 60 min. However, CH_4 became the dominant gas component under this condition. The results show that the residence time had less effect to achieve higher gas yields compared to the amount of catalyst and temperature, in terms of the composition of gas products. The obtained bio-oil contained a high content of methyl derivatives in the organic phase, which may indicate the catalytic activity of $NiFe_2O_4$ in promoting methylation. These results show that eucalyptus biomass waste can be used as a renewable resource to produce hydrogen and methane by catalytic supercritical water gasification. Nevertheless, there are other variables still to be considered in a future research, including detailed understanding of the reaction mechanisms to optimize the catalytic process for enhanced methane and/or hydrogen production.

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