Combustion synthesis of NiO-CaO-Al_2O_3 catalysts for biomass gasification of eucalyptus wood for sustainable H_2 production

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Resumo/Abstract

RESUMO - A energia do hidrogênio é a mais limpa entre as fontes alternativas, produzindo apenas água na combustão, alcançando verdadeira "emissão zero". A gaseificação da biomassa envolve oxidação parcial em altas temperaturas (700–1200°C), produzindo gases como H_2, CO, CH_4 e CO_2. O níquel é amplamente utilizado como fase ativa de catalisadores por seu baixo custo e alta seletividade de H_2, enquanto o cálcio serve como adsorvente de CO_2, aumentando indiretamente a produção de H_2. Catalisadores NiO-CaO-Al_2O_3 foram sintetizados por combustão usando ureia e nitratos metálicos. Os materiais foram caracterizados por TG e DRX. A análise termogravimétrica indicou resíduos carbonáceos em amostras contendo cálcio. Estes materiais foram calcinados a 600–800°C para remover resíduos e obter as fases desejadas. Após a calcinação, formaram-se misturas de fases espinélio (MAl_2O_4) e de óxidos segregado. Esses catalisadores foram testados na gaseificação de biomassa em altas temperaturas, com resultados promissores na produção de H_2.

Palavras-chaves: Produção de hidrogênio, gaseificação de biomassa, óxidos do tipo espinélio.

ABSTRACT - Hydrogen energy is the cleanest among alternative sources, producing only water during combustion and achieving true "zero emissions." Biomass gasification involves partial oxidation at high temperatures (700–1200°C), generating gases such as H_2, CO, CH_4, and CO_2. Nickel is widely used as the active phase in catalysts due to its low cost and high selectivity for H_2, while calcium acts as a CO_2 adsorbent, indirectly increasing H_2 production. NiO-CaO-Al_2O_3 catalysts were synthesized via combustion using urea and metal nitrates. The materials were characterized by TG and XRD. Thermogravimetric analysis indicated carbonaceous residues in samples containing calcium. These materials were calcined at 600–800°C to remove residues and obtain the desired phases. After calcination, mixtures of spinel phases (MAl_2O_4) and segregated oxides were formed. These catalysts were tested in biomass gasification at high temperatures, showing promising results in H_2 production.

Keywords: Hydrogen production, biomass gasification, spinel-like oxides

Introduction

Hydrogen energy is the cleanest among alternative energy sources, producing only water as a combustion product, which allows us to truly achieve "zero emissions" of pollutants. Gasification is a type of thermal degradation in an oxidizing atmosphere, which, in the case of biomass, involves its partial oxidation, commonly executed at higher temperatures (700-1200°C), to produce a mixture of gases containing H_2, CO, CH_4 and CO_2 (1).

Every biomass is different, being necessary to understand its composition and energy content to use it in the gasification. Biomass is made of a large number of organic compounds, moisture and inorganic compounds, which need to be known for a full understanding of the system's products.

Many are the reactions that produce H_2 when you submit the biomass to a high temperature in an oxidizing environment. The reactions which produce H_2 and, preferably, consume CO_2, such as, methane dry reforming and steam reforming are endothermic reactions requiring

elevated temperatures, but they are also catalyzed by metal supported catalysts (2).

The need of high temperatures makes oxides the best option for the catalyst support. Literature presents nickel as the current most used metal for its low cost and results in high CO and CO_2 conversion and H_2 yield, but nickel also catalyzes the methane formation, what can reduce the H_2 production, and deactivate it by coke formation or sintering. Thus, nickel needs to be stabilized in the support, and alumina seems to be adequate due to SMSI (strong metal support interaction) that favors $NiAl_2O_4$ spinel phase (3).

Other widely investigated promoter for this reaction is calcium oxide, which is not used as active phase for H_2 production reactions, but as CO_2 adsorbent in the system, indirectly favoring those reactions (4).

Due to this, the aim of this work is to produce mixed nickel and calcium catalysts, dispersed on an alumina support, producing oxides with spinel-like structures (5) for a H_2 rich syngas from biomass gasification. For this work, Eucalyptus wood was the chosen biomass.

Experimental

Biomass characterization

Eucalyptus biomass was obtained in the form of chips and subjected to pre-treatment (grinding and sieving) for the characterization process. The biomass was characterized by proximate analysis (moisture, volatile matter, fixed carbon and ashes content according ASTM E1131-20, E871-82, E872-82, D5832-98 and E1755-01), CHNS elemental analysis, thermogravimetric analysis (TGA), elemental analysis by X-ray Fluorescence (FRX) and calorific value determination.

Elemental Analysis CHNS-O follows the standard procedures defined by ASTM standards D5373-21 (6). The analysis was performed in an elemental analyzer CHN, Perkin Elmer 2400 series II, from Central Analítica, USP.

From Thermogravimetry, it is possible to estimate the main components of the biomass (hemicellulose, cellulose and lignin) based on the degradation temperature range (7). The decomposition characteristics were analyzed by thermogravimetry in a Shimadzu DTG-60H equipment (temperature measurement accuracy: ± 2°C; microbalance sensitivity: 0.001 mg) in the range of 23–1000°C. The analyses were performed at atmospheric pressure, with 8.10 mg of sample, at a heating rate of 10 °C min^{-1}, under a flow of 50 mL min^{-1} of N_2.

The FRX analysis was performed in a S8-Tiger (Bruker) equipment, using 4.00 g of sample, 40 kV voltage and 30 mA current, according to the standard quantitative method ASTM D7085-04 (8). This technique allows us to quantify the elements which compose the ashes of the biomass.

Calorific value is the amount of heat released through the combustion of a unit of fuel, in mass (kJ kg^{-1}) or volume (kJ m^{-3}). Calorific value can be determined using the bomb calorimetric method, according to ASTM D2015 (9).

Catalyst preparation and characterization

The catalysts used in this work were synthesized by the combustion method. Ni, Ca and Al nitrates and urea were added in stoichiometrically calculated quantities and crushed in a mortar until homogenization. The mixture was then placed in a muffle furnace previously heated to 400°C, in which, after evidence of the self-ignition, the samples remained for additional 30 min to assure complete combustion. After cooling, the solid was crushed and sieved to a particle size of 80 mesh. Catalysts nominal composition and identification are shown in Table 1.

Table 1: Nominal composition of the catalysts prepared by combustion synthesis method.

Code	Mass composition (%)		
	NiO	CaO	Al_2O_3
Ca-Al	-	50	50
Ni-Al	42.3	-	57.7
Ni-Ca-Al	22.3	16.7	61.0

XRD was performed using a Shimadzu LabX XRD-6000 Diffractometer with a scanning range (2θ) of 5–80° and a goniometer speed of 2° min^{-1}. The aim of this analysis is to identify the crystallographic phases present in the structure and, with proper data treatment, quantify them.

TGA was performed using a DTG-60H equipment with a heating rate of 10°C/min under a gas flow of 50 mL min^{-1} of N_2 and 50 mL min^{-1} of synthetic air. The date generated by this analysis gives us information about the behavior of the sample in the gasification conditions.

Results e Discussion

Biomass characterization

Eucalyptus biomass elemental analysis showed 44.51% C, 6.04% H, 0.13% N, 49.36% O and the sulfur percentage was considered negligible. These results are consistent with the ones found in literature for the same type of biomass (6).

The calorimetric measurements showed a 17.331 MJ kg^{-1} calorific value, which was coherent with the predicted value obtained with the elemental analysis data (17.065 MJ kg^{-1}).

Deconvolution of DTG curve is shown in Figure 1, shows that Eucalyptus wood biomass is constituted by 40.66% of cellulose, 54.65% of hemicellulose and 3.18% of lignin.

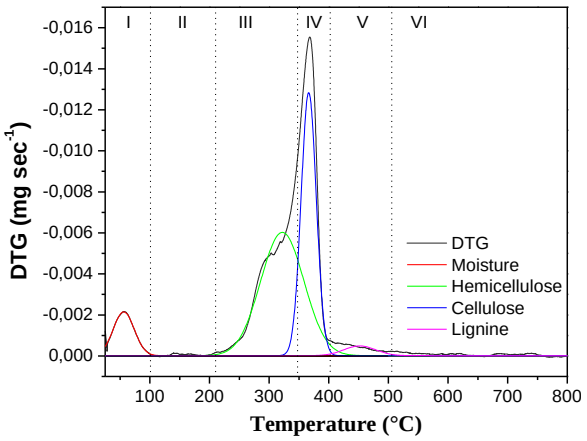

Figure 1. Deconvolution of DTG curve of Eucalyptus wood thermoanalysis.

Catalyst characterization

The TGA data was mainly used to evaluate the possible residues derived from incomplete combustion. Thermogravimetric curves in oxidant atmosphere are shown in Figure 2. For the majority of the catalyst samples, no mass loss was observed from room temperature up to 1000ºC, suggesting that no carbonaceous residues are present in the final powders. However, for the sample Ca-Al, different mass loss events can be seen in TG/DTG curves (Figure 2).

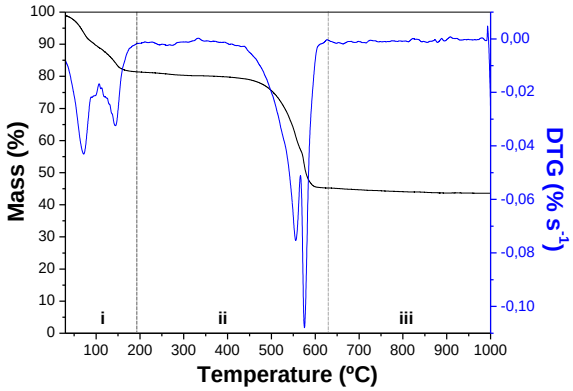

Figure 2. Thermogravimetric curve of the samples Ca-Al. Conditions: mass = 8.0 mg; heating rate β = 10°C min^{-1}, Air flow = 50 mL min^{-1}.

Figure 2 shows the TG/DTG curves for Ca-Al material, prepared containing 50% CaO and 50% Al_2O_3. For this sample, it is observed three different thermal events. The first event, between 31 and 193°C, with a mass loss of 18.6%, can be attributed to water removal. The second event, between 193 and 633°C, with a mass loss of 36.2% can be attributed to residues from the incomplete combustion of the nitrate precursors. The last event, between 633 and 1000°C, with a mass loss of only 1.7%, can be attributed to carbonaceous residues burning.

Table 2 shows a summary of the events shown by the thermogravimetric analysis.

Table 2. Quantitative analyses of TG/DTG of Ca-Al catalyst and their attribution.

T (ºC)	Mass loss (%)	Attribution
31 -193	18.6	Moisture
193 - 633	36.2	Residual nitrates
633 - 1000	1.7	Carbonaceous residues

Powder X-ray diffraction patterns of the catalyst are shown in Figure 3.

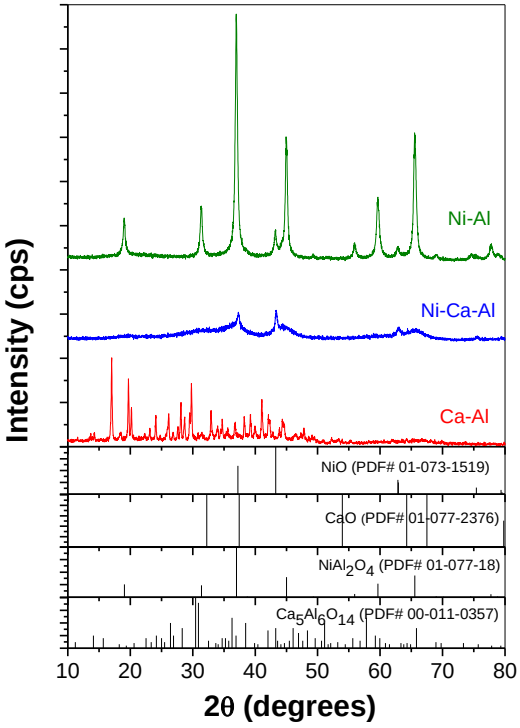

Figure 3. X-ray diffractograms of the synthesized materials after calcination

For Ni-Al, prepared containing the proportions for $NiAl_2O_4$ formation, which are 42.3% NiO and 57.7% Al_2O_3. The diffractogram presented the $NiAl_2O_4$ (PDF# 01-077-18) phases, but also some residual NiO (PDF# 01-073-1519), noticed by smaller intensity peaks.

For Ni-Ca-Al, prepared containing the proportions for formation of the $Ni_{0.5}Ca_{0.5}Al_2O_4$, which are 22.3% NiO, 16.7% CaO and 61.0% Al_2O_3. For this sample, the diffractogram showed a not very crystalline sample, with peaks indicating the presence of NiO phases and a vast amorphous halo throughout the graph. Calcination of these samples in 800°C did not alter this condition.

For Ca-Al, prepared containing 50% CaO and 50% Al_2O_3, a more detailed study was made. The sample was calcined in different temperatures aiming to obtain the mixed oxide phases. The powder X-ray diffractograms are shown in Figure 4.

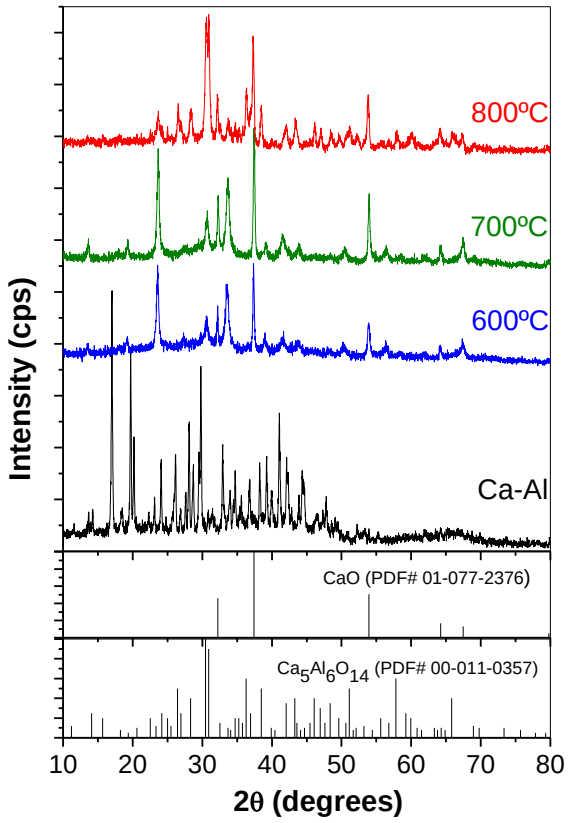

Figure 4. Powder X-ray diffraction patterns of sample Ca-Al before and after calcination in different temperatures.

Analyzing the diffractogram of the sample Ca-Al without treatment, it shows at least two phases, in which only two could be identified. The identified phases were calcium nitrate ($Ca_4N_8O_{24}$; COD# 96-591-0046) and calcium carbonate ($CaCO_3$; PDF# 01-072-1651). Many other peaks could not be characterized, being most likely by-product phases resulting from the incomplete combustion of nitrates and urea.

When calcined in 600°C and 700°C, the XRD data show similar patterns and the same phases. CaO (PDF# 01-077-2376) is present between those phases, but also calcium aluminates, such as $Ca_5Al_6O_{14}$ (PDF# 00-011-0357)

Calcination of the same sample in 800°C presented the same samples shown in 600°C and 700°C. However, some other peaks, which were not very evident in the other diffractograms, came to light. Those peaks were highlighted in the 800°C diffractogram due to the higher temperature effect. This fact also suggests a higher degree of crystallinity.

Catalytic evaluation

Gasification experiments were performed with eucalyptus wood as shown in Table 3. For the experiments, two different gasification agents were used, pure O_2 and synthetic air. For pure O_2 eucalyptus gasification, a negligible amount of solid residue was achieved and the products were mainly liquid. Changing the gasification agent, the liquid phase percentage of products decreased, the solid residue was no longer negligible and there was also an increase in the gaseous products percentage, which continued to appear in different experiments with the same gasification agent.

Table 3. Gasification tests with eucalyptus biomass

Test	Gasification Agent	Solid (%)	Liquid (%)	Gas (%)
Eucalyptus	O_2	-	84	16
Eucalyptus	Synth. air	9	46	45
Eucal. + Ni-Al	Synth. air	8	36	56
Eucal. + Ca-Al	Synth. air	10	42	48
Eucal. + Ni-Ca-Al	Synth. air	10	42	48

The use of catalysts had some effect of increase in the gas percentage, which were more pronounced for the catalysts containing only Ni and Al. As show in the Figure 5, although Eucalyptus + Ni-Al result looks the most favorable for H_2 content in syngas, the CG analysis showed this test had the lowest H_2 concentration, only 1.3 % of the gas products.

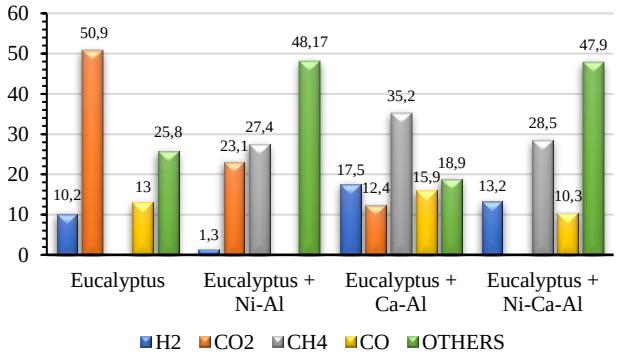

Figure 5. Molar fraction of light gases produced during eucalyptus biomass gasification in the presence of different catalysts. Conditions: 5 g of biomass, 0.5 g of catalyst, air flow= 100 mL min^{-1}, T= 800 ºC, t= 30 min

The highest H_2 was showed in the Eucalyptus + Ca-Al test, with 17.5% of the gas product. Most studies on catalytic gasification using calcium-based catalysts attribute the increased H_2 production to the interaction between CaO and

the synthesis products, as it acts as an effective CO_2 adsorbent, a factor that promotes hydrogen-producing reactions occurring in the reaction medium, such as water-gas shift reaction (11).

Conclusion

The combustion method was successfully used for spinel-like oxide (MAl_2O_4) synthesis from nitrates precursors of the desired metals. Ca and Ni aluminates were prepared, characterized and tested for biomass gasification aiming H_2 production.

In the presence of catalysts prepared by the combustion method synthesis it was observed that there was an increase in the production of phase, a decrease in the formation of tar, but no significant change in the amount of solid residue. The catalysts prepared with Ca and Al resulted in a greater H_2 content in the gas phase. On the other hand, the presence of Ni seems to increase the contribution of the methanation reaction.

Acknowledgements

Wilson S. Mercês Neto thanks to FAPESB for the scholarship and Supergasbras for financial support. The authors thank to the projects INCITERE (FAPESB, Process n.0008/2022), CATSUS-H2 (CNPq, Process n.405869/2022-3), USINA (FINEP Process n.0057/21) and FGTL (FINEP Process n. 2435/22)

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