

Article

Conversion of Biomass-Derived Tars in a Fluidized Catalytic Post-Gasification Process

Floria Rojas Chaves ¹, Nicolas Torres Brauer ¹ , Cindy Torres ^{2,3}  and Hugo de Lasa ^{1,*} 

¹ Chemical Reactor Engineering Centre, Department of Chemical and Biochemical Engineering, University of Western Ontario, London, ON N6A 5B9, Canada; frojasch@uwo.ca (F.R.C.); ntorres5@uwo.ca (N.T.B.)

² Department of Chemical Engineering, University of Costa Rica, San Jose 11501, Costa Rica; cindy.torres@ucr.ac.cr

³ Materials Science and Engineering Research Center, University of Costa Rica, San Jose 11501, Costa Rica

* Correspondence: hdelasa@uwo.ca

Abstract: The present study deals with the development, characterization, and performance of a Ni-based catalyst over a ceria-doped alumina support as a post-gasification step, in the conversion of biomass-derived tars. The catalysts were prepared using the incipient wetness technique and characterized chemically and physically using NH₃-TPD, CO₂-TPD, H₂-TPR, XRD, Pyridine-FTIR, N₂ physisorption, and H₂-Pulse Chemisorption. It was observed that the 5 wt% CeO₂ reduced the strong and very strong acid sites of the alumina support and helped with the dispersion of nickel. It was noticed that the nickel crystallite sizes and metal dispersion remained unchanged as the nickel loading increased. The performance of the catalysts was studied in a mini-fluidized CREC Riser Simulator at different temperatures and reaction times. The selected tar surrogate was 2-methoxy-4-methylphenol, given its functional group similarities with lignin-derived tars. A H₂/CO₂ gas blend was used to emulate the syngas at post-gasification conditions. The obtained tar surrogate conversion was higher than 75%, regardless of the reaction conditions. Furthermore, the catalysts used in this research provided an enhancement in the syngas product composition when compared to that observed in the thermal experiments. The presence of hydrocarbons greater than CH₄ (C₁₊) was reduced at 525 °C, from 96 ± 3% with no catalyst, to 85 ± 2% with catalyst and steam, to 68 ± 4% with catalyst and steam-H₂/CO₂. Thus, the catalyst that we developed promoted tar cracking, tar reforming, and water-gas shift reactions, with a H₂/CO ratio higher than 3.8, providing a syngas suitable for alcohol synthesis.

Keywords: CREC Riser Simulator; nickel-ceria catalysts; water-gas shift reaction; post-gasification process



Citation: Rojas Chaves, F.; Torres Brauer, N.; Torres, C.; de Lasa, H. Conversion of Biomass-Derived Tars in a Fluidized Catalytic Post-Gasification Process. *Catalysts* **2024**, *14*, 202. <https://doi.org/10.3390/catal14030202>

Academic Editor: Gartzen Lopez

Received: 23 February 2024

Revised: 12 March 2024

Accepted: 13 March 2024

Published: 19 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Bioenergy is called on to play an important role in the global efforts to replace fossil fuels and to reach the desirable Net Zero Emission targets (NET). In this respect, the International Energy Authority (IEA) reported that there was an increase of 3% per year in the use of bioenergy between 2010 and 2020. However, the IEA noted that, in order to reach the set targets by 2023, the yearly increase should be 8% [1].

While, nowadays, the goods and services production system is based on a linear design, there is an increasing trend of shifting towards a circular economy, based on the three principles: (i) to eliminate waste and pollution, (ii) to create products and transform materials to their highest economic value, and (iii) to renew nature resources [2].

In this respect, biomass gasification is valuable for the circular economy, given that it is a process with high prospects for the production of alternative energy. It is more attractive than biological methods, given the wide variety of biomasses that can be used as feedstocks and given the much shorter reaction times required for biomass processing [3]. The use of biomass is also of interest as a renewable resource as a result of being carbon neutral:

the same number of moles of carbon are used during photosynthesis as are returned to the atmosphere when combusted [4]. Additionally, the conversion of biomass leads to low SO_x and NO_x emissions when compared to those produced from fossil fuels [5].

Syngas, biochar, and tars are all products of gasification. Syngas is predominantly composed of H_2 , CO , CO_2 , and CH_4 [4,6]. Biochar is a solid and valuable product of the gasification process [4]. However, tars are unwanted products. Tars are produced from the pyrolytic decomposition of lignocellulosic materials under gasification conditions [7]. At ambient temperatures, tars form a viscous liquid can cause operational problems, such as pipeline blockage. Moreover, the presence of tar lowers the quality of syngas and reduces the efficiency of the process [8–11].

Tars can be classified as primary, secondary, tertiary, and condensed tertiary. Primary tars are formed during the early stages of gasification. Furfural can be considered a typical example of a primary tar. Secondary tars are derived from primary tars that are further converted into phenolic and olefin species while in the presence of steam and oxygen. Tertiary tars are produced from secondary tars and are mainly composed of aromatics with methyl functional groups, such as toluene. Lastly, condensed tertiary tars are obtained from the conversion of secondary tars into polyaromatic hydrocarbons with no substituent groups, such as naphthalene [12].

Throughout the years, different methods for removing tars have been considered. These methods have been classified as *in situ* and *ex situ* [7,13]. Depending on the approach, they can be further classed as physical, chemical, or biological [14].

Catalytic tar conversion is a chemical process for tar removal. In this process, catalysts play a dual role as they assist both in promoting water-gas shift and in the cleaning of the gas that is produced. Catalysts are incorporated into this reaction to boost its rate and/or selectivity given that the tar removal reaction is kinetically limited [15]. In the design of a catalyst for “hot tar cleaning”, it is important to consider the surface species and the interactions between the metal crystallites and the catalyst support that can lead to unreactive phases, as well as to undesired crystallite agglomeration [16].

Ni-based catalysts have been acknowledged for their advantages, such as their high tar reforming efficiency, their high tar conversion, their compatibility with different supports and promoters to increase catalytic activity, their suitability as secondary catalysts, and their relative inexpensiveness [7,10]. Additionally, Ni-based catalysts facilitate the cracking of C-H and C-C bonds and perform well in steam and dry reforming reaction environments [17]. However, their activity can decay due to coke formation, sintering, or sulfur poisoning. These issues can be addressed in different ways: (i) by modifying the active metal with alloys or using other metals such as Fe, Co, Mn, and Cu [18], (ii) by adding promoters like rare earth metals, (iii) by enhancing supports, and/or iv) by improving catalyst preparation methods [19].

Rare earth metals are known for their good thermal stability and their contribution to high catalytic activity. Rare earth metals facilitate oxygen storage and oxygen mobility, which help with biochar gasification [20], and as a result, with catalyst deactivation mitigation. CeO_2 displays a fluorite face-centered cubic unit cell structure, where each Ce^{4+} is coordinated with eight oxygen atoms, and each O^{2-} in the tetrahedral space is coordinated with the four nearest Ce^{4+} s [21]. In the case of CeO_2 , oxygen capacity is associated with the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pair, which enables the ceria to release oxygen in poor-oxygen environments such as the one of the present study, and to be reoxidized in oxygen-rich environments via a Mars-van-Krevelen mechanism [22,23].

Given the above, this research aims to address the removal of gasification-derived tars by using Ni-based catalysts doped with CeO_2 . This is considered in the context of an integrated process involving biomass gasification, tar removal with the enhancement of syngas quality, and catalyst regeneration, as described in Figure 1.

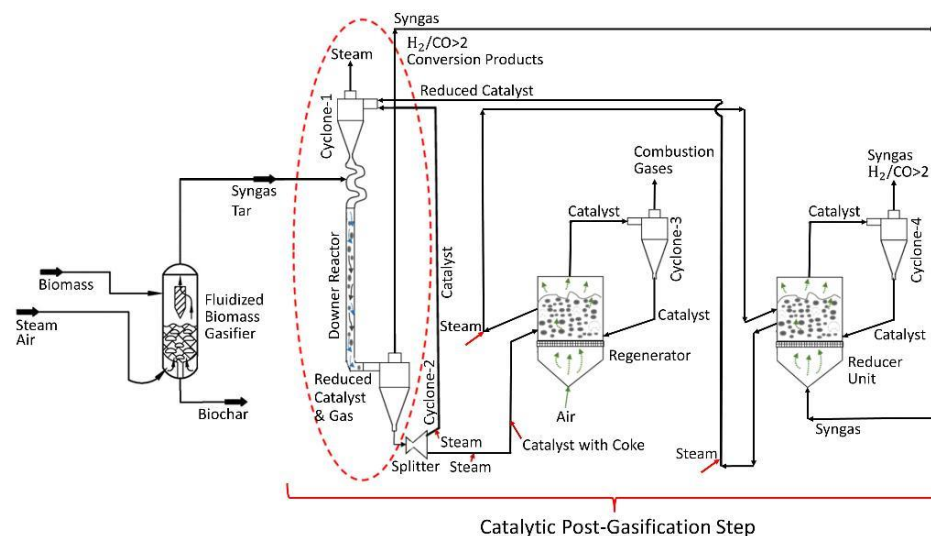


Figure 1. Tar post-biomass gasification process includes: (a) a fluidized bed biomass gasifier operated at 650 °C, (b) a downer unit providing tar conversion and syngas enrichment operated at 550 °C, (c) a catalyst regenerator and a catalyst reduction unit both operated at 615 °C, processing 1/10 of the catalyst downer flow.

The performance of the developed catalyst is shown using 2-methoxy-4-methylphenol as a tar surrogate in a mini-fluidized CREC Riser Simulator, including: (a) catalyst reduction, (b) tar post-gasification, and (c) catalyst regeneration.

2. Catalyst Characterization Results

2.1. N_2 -Physisorption

The determined structural properties of the fluidizable γ - Al_2O_3 support and the ceria-doped γ - Al_2O_3 are reported in Table 1. The obtained surface area of the γ - Al_2O_3 sample was within the 90–210 m²/g range, in agreement with that reported by the manufacturer [24]. There was no significant impact on these properties when 2 wt%CeO₂ was added. However, the 5 wt% and 10 wt% CeO₂ mildly decreased the surface area, pore volume, and pore diameter. This was attributed to the blockage of some of the micropores of the γ - Al_2O_3 . Mazumder [25] reported a similar behaviour when doping γ - Al_2O_3 with La₂O₃.

Table 1. Structural support and support-promoter parameters of the γ - Al_2O_3 support and ceria-doped γ - Al_2O_3 support established using N_2 -physisorption analysis.

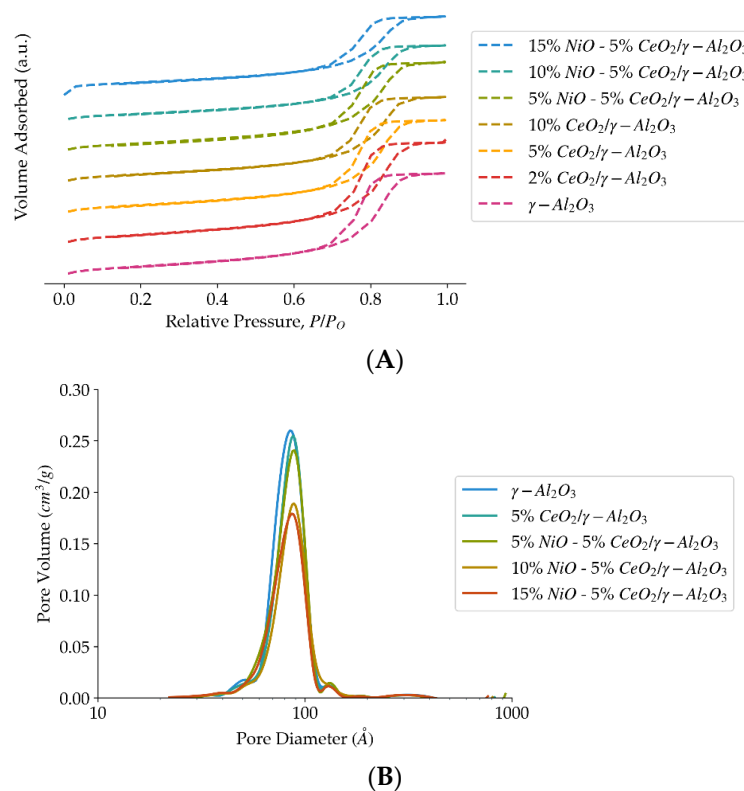
Sample	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
γ - Al_2O_3	199 ± 13	0.54 ± 0.04	109.5 ± 0.6
2 wt%CeO ₂ / γ - Al_2O_3	201 ± 3	0.54 ± 0.01	106.7 ± 0.4
5 wt%CeO ₂ / γ - Al_2O_3	183 ± 3	0.49 ± 0.01	106 ± 2
10 wt%CeO ₂ / γ - Al_2O_3	183 ± 13	0.47 ± 0.03	103.7 ± 0.1

Table 2 describes the structural parameters of the support-promoter sample obtained when it was impregnated with the active phase (NiO). The surface area, pore volume, and pore diameter all decreased mildly with the increase in nickel. This was an expected behaviour given that, as more metal was added, the smaller pores of the support were blocked. It should be noted that Mazumder [25] used nickel as the active phase over a La₂O₃-doped γ - Al_2O_3 support and reported a similar trend. Moreover, Liu et al. [26] studied different CeO₂ loadings over 15% Ni and reported a decrease in the surface area and pore volume, while the pore diameter remained almost constant. These trends were similar to the findings of the present study.

Table 2. Catalyst structural parameters established by using N₂-physisorption analysis when employing different nickel oxide loadings, over 5 wt% ceria doped on a γ -Al₂O₃ support.

Catalyst	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
5 wt%NiO-5 wt%CeO ₂ / γ -Al ₂ O ₃	164 ± 6	0.45 ± 0.02	108 ± 2
10 wt%NiO-5 wt%CeO ₂ / γ -Al ₂ O ₃	150 ± 6	0.41 ± 0.01	109 ± 1
15 wt%NiO-5 wt%CeO ₂ / γ -Al ₂ O ₃	139 ± 7	0.37 ± 0.01	103.7 ± 0.1

Figure 2a reports the adsorption-desorption isotherms for the different CeO₂ and NiO loadings that were studied. All CeO₂ and NiO loadings on fluidizable γ -Al₂O₃ consistently displayed a type IV isotherm, based on the IUPAC classification, corresponding to mesoporous materials. Additionally, the isotherms presented a H1 hysteresis loop, a consequence of the uniform narrow mesopores [27]. These results are consistent with the findings of previous studies [22,28]. Furthermore, Adamu et al. [29] indicated that the isotherms' plateau at a high relative pressure is a behaviour of a narrow pore-size distribution, which can be seen in Figure 2.

**Figure 2.** (A) Adsorption-desorption isotherms obtained from N₂-physysorption analysis, for different ceria and NiO loadings on the γ -Al₂O₃ support. (B) Adsorption-desorption isotherms obtained from N₂-physysorption analysis, for different ceria and NiO loadings on the γ -Al₂O₃ support.

2.2. X-ray Diffraction

The crystalline structures of the different samples prepared were analyzed using X-ray Diffraction (XRD). Figure 3 shows the XRD patterns for the γ -Al₂O₃ support and the different loadings of CeO₂ that were studied, while Figure 4 presents the XRD patterns obtained for the different loadings of NiO. One should expect peaks at 37.7°, 39.4°, 45.8°, and 66.8° for the γ -Al₂O₃ support (JCPDS-79-1558) while the peaks at 28.6°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7°, 79.1°, 88.4°, and 95.4° correspond to the cubic CeO₂ crystallographic phases (JCPDS-34-0394) [30]. The XRD pattern obtained for the γ -Al₂O₃ support showed three of the peaks mentioned above (37.7°, 39.4°, and 45.8°). When analyzing the sample with the 2 wt% CeO₂ doped on the γ -Al₂O₃ support, no peaks associated to CeO₂ were observed.

This could be attributed to undetectable amounts of promoter on the surface of the support. This agrees with the results obtained from the N_2 -physorption analysis that showed that the introduction of 2 wt% CeO_2 did not lead to any significant change in the structure of the Al_2O_3 support.

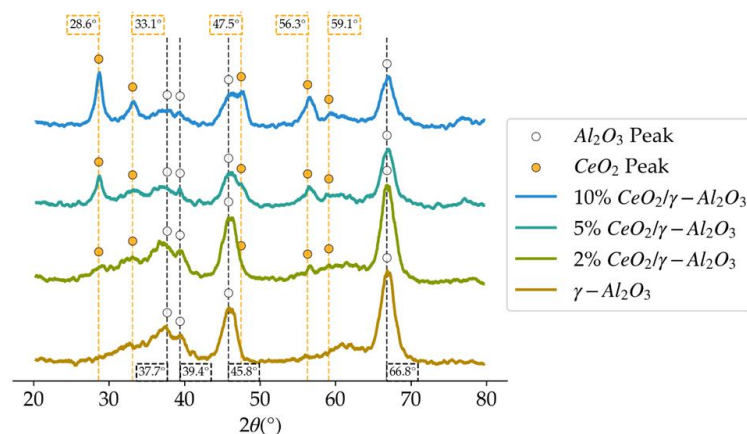


Figure 3. XRD patterns in the 2θ degrees diffractogram, for the different loadings of CeO_2 on γ - Al_2O_3 .

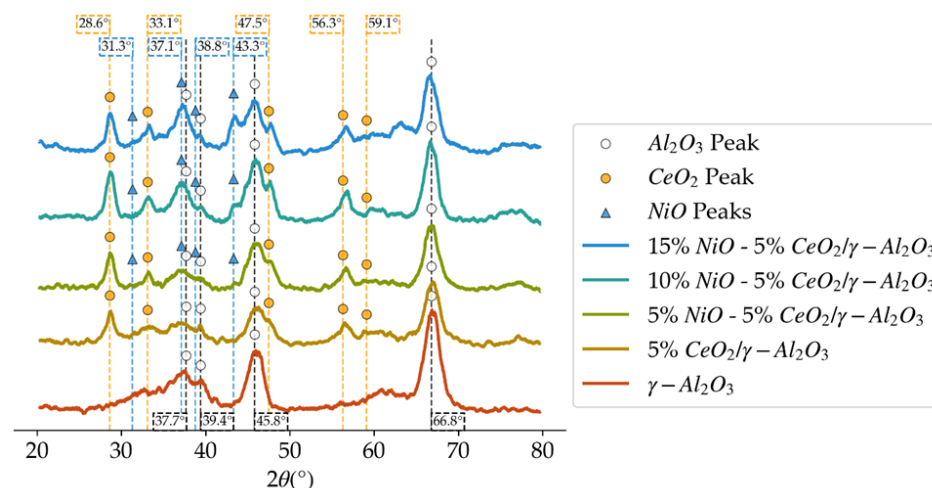


Figure 4. XRD patterns in the 2θ degrees diffractogram for the different loadings of NiO over 5% CeO_2/γ - Al_2O_3 .

However, for the 5 wt% and 10 wt% CeO_2 , two new peaks appeared: one at 28° and another at 56° . The intensity of these peaks increased when analyzing the sample with 10 wt% CeO_2 . These peaks were previously reported for CeO_2 by the JCPDS mentioned above. Furthermore, the peak at 45° became wider with the addition of ceria, given the combined interaction of the support (γ - Al_2O_3) with CeO_2 , and given that CeO_2 has a reported a characteristic peak at 47.5° [30].

The XRD pattern obtained for the 5 wt% NiO did not exhibit any additional peaks to the ones observed for the promoted support. Moreover, it should be noted that nickel and alumina may tend to strongly interact with each other, resulting in the formation of $NiAl_2O_4$. According to COD 9006011, in the XRD analysis, $NiAl_2O_4$ spinel shows characteristic peaks at 31.3° , 37.1° , 38.8° , 43.3° , 56.0° , and 65.6° [31]. However, the spinel formation could not be observed in the XRD diffractogram, given that the γ - Al_2O_3 and $NiAl_2O_4$ peaks could overlap with each other.

Furthermore, XRD analysis was performed on the catalyst with coke, after the reaction runs, preceded by catalyst regeneration and catalyst reduction. No structural changes were observed with coke being present [32].

2.3. NH_3 and CO_2 Temperature Programmed Desorption

To further understand the chemical properties of the different samples that were prepared, NH_3 -TPD and CO_2 -TPD analyses were developed to determine both the acidity and basicity, respectively. It should be mentioned that the acidity of the catalyst, and in particular the $\gamma\text{-Al}_2\text{O}_3$ strong acid sites, promote coke formation, leading to catalyst deactivation. To moderate coke formation on the prepared catalyst, CeO_2 was selected as the support promoter. Table 3 reports the influence of ceria addition on the overall $\gamma\text{-Al}_2\text{O}_3$ support acidity. It can be observed that CeO_2 had a mild influence on the “total acidity” of $\gamma\text{-Al}_2\text{O}_3$, which remained at the lowest level of $5.8 \text{ cm}^3 \text{ STP/g}$ for the 5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$. Thus, on the basis of these findings, the 5 wt% CeO_2 promoter loading was selected as the best for further catalyst development.

Table 3. Acidity and basicity of the $\gamma\text{-Al}_2\text{O}_3$ support loaded with different ceria amounts.

Sample	Acidity ($\text{cm}^3 \text{ STP/g}$) *	Basicity ($\text{cm}^3 \text{ STP/g}$) *
$\gamma\text{-Al}_2\text{O}_3$	6.4 ± 0.3	2.2 ± 0.4
2 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	6.2 ± 0.3	2.2 ± 0.4
5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	5.8 ± 0.1	2.1 ± 0.3
10 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	6.1 ± 0.1	2.8 ± 0.8

* Note: NH_3 was used to determine acidity and CO_2 was used to determine basicity.

Furthermore, the basicity of the support was also evaluated, as reported in Table 3. In agreement with Fonseca et al. [28], the basicity of the support was not altered in the range of ceria loadings that was studied. This was in contrast with the findings of Mazumder [25], who reported that La_2O_3 as an alumina promoter increased the basicity of the support.

Furthermore, the acidity and basicity of the samples with an Ni active phase were also studied. The results obtained are listed in Table 4. One can observe that the addition of the active phase led to a reintroduction of some strong acidity. This increase in acidity with the introduction of nickel was also reported by Mazumder [25] and Kuhn Bastos [33]. In addition, one can also see, in Table 4, that the nickel addition modestly increased the total basicity of the prepared catalyst.

Table 4. Total acidity and basicity observed when using different nickel loadings on the ceria-promoted $\gamma\text{-Al}_2\text{O}_3$.

Sample	Acidity ($\text{cm}^3 \text{ STP/g}$) *	Basicity ($\text{cm}^3 \text{ STP/g}$) *
5 wt%NiO-5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	7.0 ± 0.3	2.8 ± 0.3
10 wt%NiO-5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	6.8 ± 0.1	2.8 ± 0.2
15 wt%NiO-5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	6.80 ± 0.06	2.4 ± 0.5

* Note: NH_3 was used to determine acidity and CO_2 was used to determine basicity.

2.4. NH_3 -TPD Deconvolution

The NH_3 -TPD curves were deconvoluted to assess the relative influence of acid sites with different strengths on the different promoter and active phase loadings that were prepared. The model was adjusted to contain four acid sites: weak, medium, strong, and very strong. Figure 5A–C report the deconvolution of three samples: $\gamma\text{-Al}_2\text{O}_3$, 5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, and 15 wt% NiO-5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$. In the case of the undoped alumina, four types of acid sites were observed, in accordance with the findings of Torres et al. [34]. However, the introduction of CeO_2 showed three types of acid sites only, with the very strong acid type having disappeared. Further, the addition of nickel reintroduced the very strong acid site type, as evidenced by the appearance of a fourth peak. Based on these findings, the 5 wt% CeO_2 was selected as the optimum loading from the three CeO_2 loadings studied.

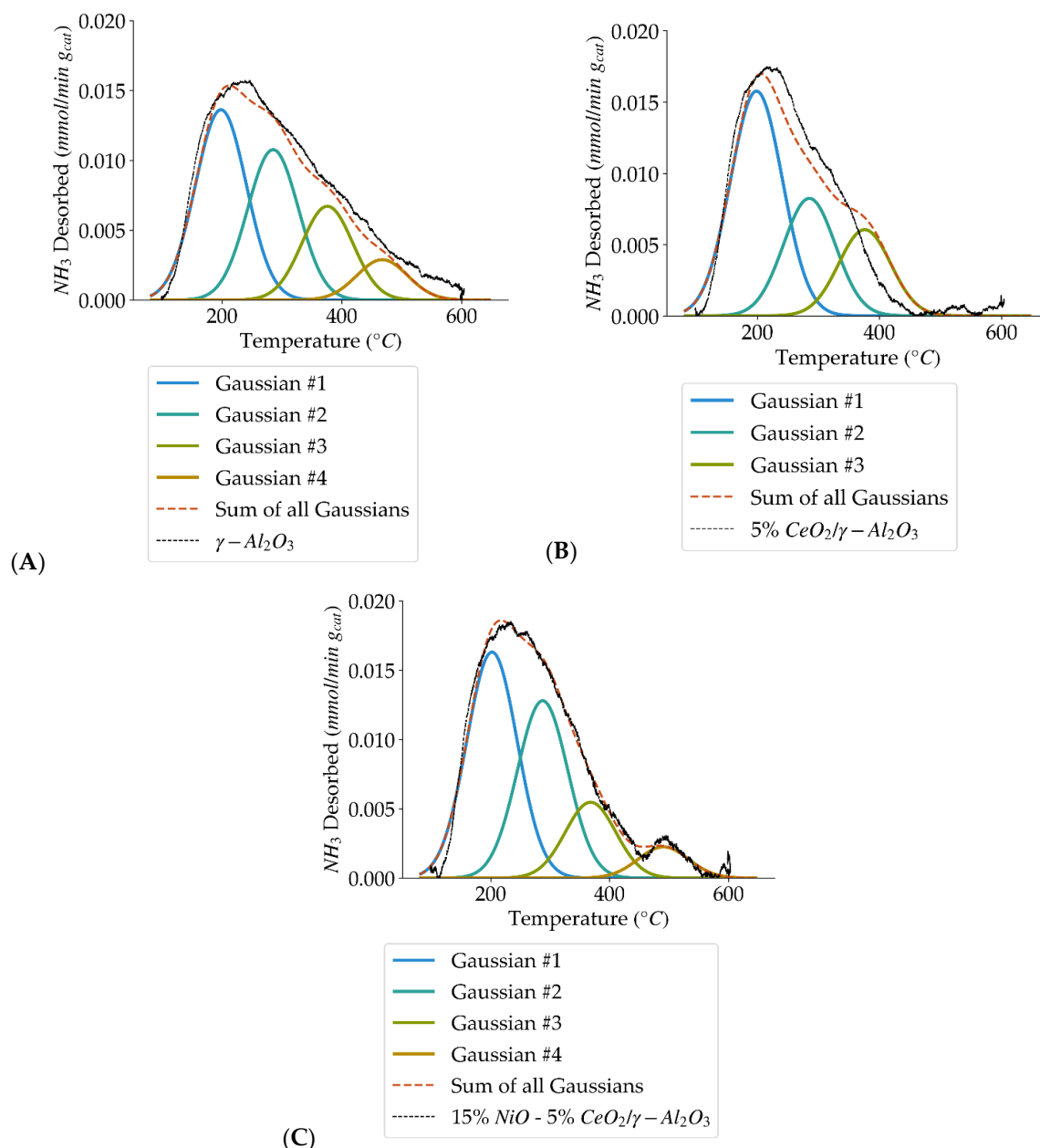


Figure 5. Deconvolution of NH_3 -TPD curves showing the four acid site types (weak, medium, strong, very strong) for: (A) $\gamma\text{-Al}_2\text{O}_3$, (B) 5% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, and (C) 15% NiO -5% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$.

Moreover, the kinetic parameters for each curve obtained from the deconvolution process were calculated using the following assumptions [35,36]:

- The ammonia desorption kinetics for the four types of acid sites were described by using the Arrhenius Law;
- There was no re-adsorption of ammonia molecules on the catalyst surface sites;
- The rate of desorption for each one of the four acid type sites was proportional to the number of sites occupied by ammonia;
- The concentration of ammonia throughout the catalyst bed remained unchanged during the ammonia desorption;
- The desorption temperature followed a linear heating ramp.

The mathematical approach used in previous studies [35,37–40] was used in the present research. The differential equation (Equation (1)) was solved using a MATLAB script involving the LSQCURVEFIT and ODE45 functions. The results obtained are listed

in Table 5. It is important to mention that, for all NH_3 -TPD curves, the coefficient of determination was 99%.

$$\left(\frac{dV_{\text{des}}}{dT}\right) = \frac{k_{\text{des},0}}{\beta'} \left(1 - \frac{V_{\text{des}}}{V_m}\right) e^{\left[-\frac{E_{\text{des}}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right]} \quad (1)$$

where V_{des} represents the volume of ammonia desorbed in $\text{mmol g}_{\text{cat}}^{-1}$, k_d stands for the desorption constant in $\text{mmol g}_{\text{cat}}^{-1} \text{min}^{-1}$, $k_{\text{des},0}$ denotes the pre-exponential factor in $\text{mmol g}_{\text{cat}}^{-1} \text{min}^{-1}$, V_m refers to the volume of ammonia adsorbed at the saturation condition in $\text{mmol g}_{\text{cat}}^{-1}$, T_m represents the centering temperature which minimizes the cross-correlation between adsorption kinetic parameters in K, and E_{des} is the activation energy of desorption in kJ mol^{-1} .

Table 5. Kinetic parameters for the desorption of ammonia, from temperature-programmed desorption analysis.

	Acid Sites	k_d (mmol K/min g_{cat})	E_{des} (kJ/mol)	T (K)
$\gamma\text{-Al}_2\text{O}_3$	Weak	1.900 ± 0.003	36.43 ± 0.07	471
	Medium	1.412 ± 0.007	59.4 ± 0.3	559
	Strong	0.843 ± 0.005	86.0 ± 0.5	651
	Very strong	0.325 ± 0.002	113.1 ± 0.6	746
5% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	Weak	2.165 ± 0.003	36.71 ± 0.07	472
	Medium	1.105 ± 0.005	59.7 ± 0.3	549
	Strong	0.703 ± 0.004	77.1 ± 0.4	617
	Very strong	-	-	-
15%NiO-5% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	Weak	2.224 ± 0.004	38.15 ± 0.09	475
	Medium	1.656 ± 0.008	62.5 ± 0.3	561
	Strong	0.672 ± 0.004	83.3 ± 0.4	641
	Very strong	0.254 ± 0.001	111.2 ± 0.6	739

It can be observed in Table 5 that there is consistency in the k_d and E_{des} values obtained for the weak, the medium, the strong, and the very strong acid sites. These findings corroborate the interpretation that the CeO_2 acted on the very strong acid sites, neutralizing them, with the nickel partially reintroducing some of this very strong acidity.

2.5. Pyridine Fourier Infrared Spectroscopy

The NH_3 -TPD helped to evaluate the total acidity of the support, and that obtained with the different loadings of CeO_2 and NiO. Furthermore, the pyridine FTIR was used to establish the nature of the acid sites of the samples. Morterra and Magnacca [41] used pyridine adsorption to study the acidity in the alumina and concluded that pyridine can interact with surface acid sites in different ways: (i) via lone nitrogen electron pairs in pyridine that bond with the hydrogen of the weak acidic-surface OH groups, (ii) via lone nitrogen electron pairs in pyridine that interact with the surface cationic centers (designated as Lewis acid sites), and (iii) via pyridinium ion species able to interact with the strong protons from the OHs on the catalyst surface (designated as Brønsted acid sites). Additionally, Parry [42] also studied the acidity of alumina and concluded that the strong acid sites on alumina were of the Lewis type.

The results obtained in the present study are in line, as shown in Figure 5A–C, with the findings reported by Parry [42], given that the FTIR bands observed for $\gamma\text{-Al}_2\text{O}_3$ are at characteristic wavenumbers assigned to Lewis acid sites. Furthermore, as was seen in the NH_3 -TPD analysis, the total acidity was not affected by the introduction of the promoter, with the CeO_2 helping, however, in the redistribution of acid sites.

In addition, the sample containing the active phase (15 wt% NiO) shows a new peak when compared to the undoped $\gamma\text{-Al}_2\text{O}_3$ with no Ni active phase, and the CeO_2 -doped $\gamma\text{-Al}_2\text{O}_3$ with no Ni active phase (Figure 6). Vázquez et al. [43] reported FTIR bands at

1612 cm^{-1} , 1622 cm^{-1} , and 1635 cm^{-1} , which corresponded to the pyridine interacting with NiO, via Lewis acid sites and pyridine bonded to Brønsted acid sites, respectively. It was also reported that the band at 1612 cm^{-1} increased proportionally with the percentage of NiO, with this FTIR band attributed to pyridine coordinatively bonded to nickel cations.

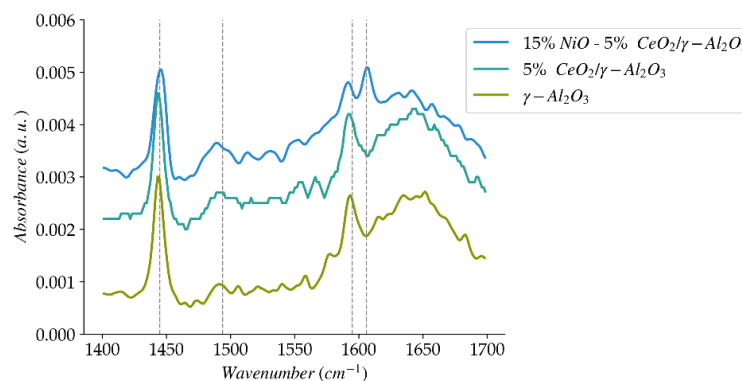


Figure 6. Pyridine FTIR spectra for the catalyst and catalyst precursors of the present study.

Within the range from 1500 cm^{-1} to 1600 cm^{-1} , no bands were identified. This was attributed to the absence of Brønsted acid sites. This behaviour was also observed by Mazumder [25] and agrees with Parry [42] and Morterra and Magnacca [41], who claimed that Lewis acidic sites on the $\gamma\text{-Al}_2\text{O}_3$ support were dominant.

2.6. H_2 Temperature Programmed Reduction and H_2 -Pulse Chemisorption

Figure 7 compares the H_2 -TPR curves obtained for the different Ni loadings (5 wt%, 10 wt%, and 15 wt%) for a fixed CeO_2 loading (5 wt%). It was observed that the TPR peaks shifted towards lower temperatures as the Ni loadings increased. This suggested that the interaction between the active Ni phase and the support was reduced at higher Ni loadings. For example, the 15 wt% Ni sample had a maximum peak at 580 $^\circ\text{C}$, while the 5 wt% Ni sample had a maximum peak at 610 $^\circ\text{C}$. It is important to mention that the 5 wt% Ni with CeO_2 -doped support and the 5 wt% Ni with an undoped support displayed similar TPR trends.

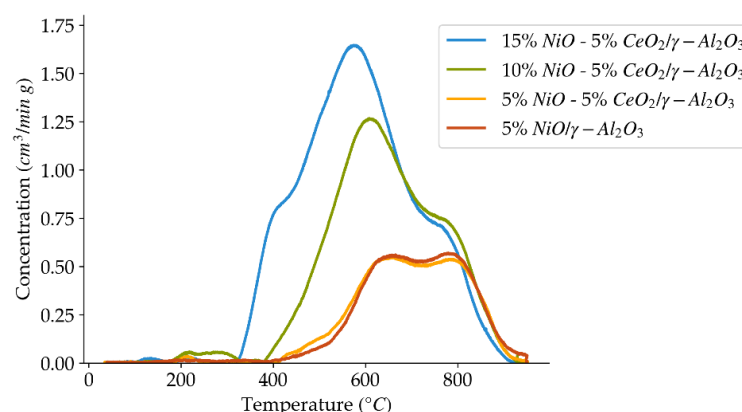


Figure 7. H_2 -TPR profiles using a 10 $^\circ\text{C}/\text{min}$ heating ramp, for the set of catalysts prepared with different nickel loadings.

Previous studies have reported that the Ce^{4+} in CeAlO_3 was reduced to Ce^{3+} at around 827 $^\circ\text{C}$ [44], while other research indicated that the reduction of Ce^{4+} in CeAlO_3 to Ce^{3+} took place at 890 $^\circ\text{C}$ [45]. However, in the present study, no reduction of the Ce^{4+} was observed, when a sample with no nickel active phase (5 wt% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$) was analyzed with H_2 -TPR. In this case, no TPR peaks were observed. This was also confirmed with XRD patterns, given that no TPR peaks attributable to CeAlO_3 were present.

Authors have categorized the different interactions between nickel and the support into three TPR signal sections [44,46] as follows:

- TPR peaks in the 300 °C < T < 400 °C range: this range corresponds to the reduction of amorphous NiO species resulting from a weak interaction between the Ni and the γ -Al₂O₃;
- TPRs in the range of 400 °C < T < 600 °C. This range corresponds to the H₂-TPR reduction of NiO species resulting from a strong interaction of the Ni with the alumina support;
- TPRs at T > 600 °C. This corresponds to the NiAl₂O₄ spinels resulting from the H₂-TPR analysis.

Table 6 reports the Ni-reducible species calculated with TPR data. In these calculations, the state of reducible nickel was fully assigned to Ni²⁺ using XPS spectra, as discussed in Appendix A. One can observe, in Table 6, that, in most cases, this reducibility reached higher than 80% of the nominal nickel loading.

Table 6. Nominal Ni loadings, Ni reduction values obtained from the H₂-TPR analysis, as well as percentage reduction of Ni species, using a heating ramp of 10 °C/min.

Catalyst	Nominal Ni (%)	Reducible Ni (%)	Percentage of Reduction (%)
5% Ni-5% CeO ₂ /γ-Al ₂ O ₃	5	4.3 ± 0.4	86
10% Ni-5% CeO ₂ /γ-Al ₂ O ₃	10	8.86 ± 0.03	87
15% Ni-5% CeO ₂ /γ-Al ₂ O ₃	15	12.5 ± 0.7	84

H₂-Pulse Chemisorption was used to study the nickel dispersion and the nickel crystallite sizes. This analysis was conducted at 615 °C, given that this was the temperature used for catalyst regeneration in the CREC Riser Simulator and in the proposed tar post-gasification process, as described in Figure 1. Table 7 reports the results obtained for this analysis. It was observed that the average Ni crystallite sizes as well as the nickel dispersion remain unchanged when increasing the nickel loading. On the other hand, the metal specific surface area increased consistently. This allowed us to conclude that the promoter (CeO₂) amount as well as the proposed multi-step catalyst preparation were adequate to provide a catalyst with stable structural properties.

Table 7. Dispersion and crystallite sizes of Ni-based catalysts obtained after H₂-Pulse Chemisorption at 615 °C.

Catalysts	Dispersion (%)	Crystallite Size (nm)	Metal Specific Surface Area (m ² /g)
5%Ni-5%CeO ₂ /γ-Al ₂ O ₃	0.74	114	0.094
10%Ni-5%CeO ₂ /γ-Al ₂ O ₃	0.81	104	0.28
15%Ni-5%CeO ₂ /γ-Al ₂ O ₃	0.79	107	0.41

3. Catalyst Performance Results for Tar Conversion

The three catalysts prepared (5 wt% Ni, 10 wt% Ni, 15 wt% Ni over ceria-doped alumina) were studied under two different atmospheres: steam, and steam and hydrogen-carbon dioxide. The reaction temperatures employed were 500 °C, 525 °C, and 550 °C, and the reaction time was set to 10 s. Furthermore, the 15 wt% Ni catalyst was also evaluated at 5 s and 7 s reaction times. Experiments in the CREC Riser Simulator reactor without the catalyst loaded were also developed and used as a reference. In the upcoming figures and tables, the 5%Ni-5%CeO₂/γ-Al₂O₃, the 10%Ni-5%CeO₂/γ-Al₂O₃, and the 15%Ni-5%CeO₂/γ-Al₂O₃ are referenced as Cat5, Cat10, and Cat15, while the results from the non-catalytic experiments are designated as NC.

3.1. Tar Surrogate Conversion under Steam Atmosphere

Figure 8 reports the 2-methoxy-4-methylphenol or 2M4MP (tar surrogate) conversion while employing Cat5, Cat10, and Cat15 at 500 °C, 525 °C, and 550 °C at 10 s under steam. One can observe that the 2M4MP catalytic conversion ranged between 75% and 92%. When these results are compared to those without a catalyst loaded in the CREC Riser Simulator, one can see that runs with and without the catalysts display similar 2M4MP overall conversions.

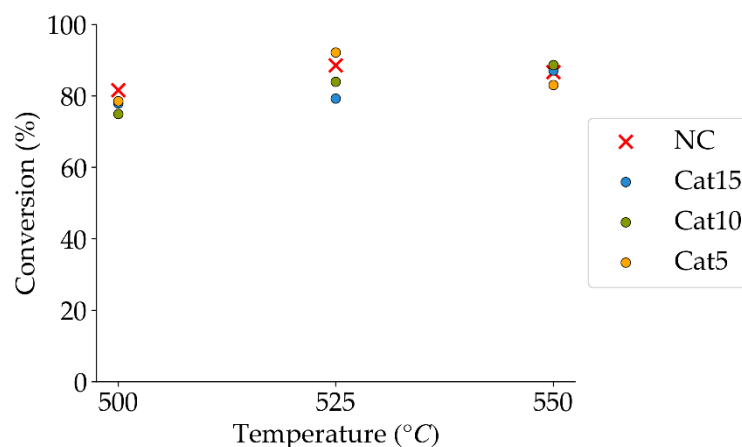
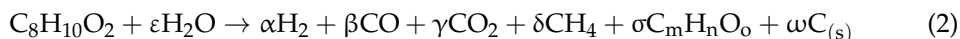
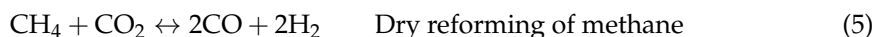
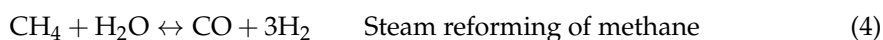


Figure 8. 2M4MP catalytic conversions under steam (mean standard deviation: $\pm 6\%$). Notes: (a) Catalysts: Cat5, Cat10, Cat15, (b) catalyst weight: 0.30 g, (c) reaction time: 10 s, (d) non-catalytic (NC) runs' conversions are reported as a reference.

To assess the 2M4MP conversion, it is important to consider tar “primary reactions” such as tar steam cracking (Equation (2)), as well as subsequent “secondary reactions” such as the water-gas shift and steam and dry reforming reactions, which are represented by Equations (3)–(5) [34,47].



where α , β , γ , ε , δ , σ , and ω are the stoichiometric coefficients, $\text{C}_m\text{H}_n\text{O}_o$ represents the hydrocarbon product formula, from tar cracking and tar reforming, and $\text{C}_{(s)}$ denotes the carbonaceous solid, designated as coke.



The extent of the secondary reactions is strongly affected by the temperature, the reaction environment (e.g., partial pressures of H_2O , H_2 , and CO_2), the reaction time, and the type of catalyst used.

Figure 9A,B report the selectivities towards CO and CO_2 for the Cat5, Cat10, and Cat15 catalysts. The CO and CO_2 selectivities obtained for the runs without a catalyst are also provided, as a reference.

Figure 9A,B show that CO and CO_2 selectivities augment with increasing temperature, from 0.007 to 0.027 for CO, and from 0.09 to 0.13 for CO_2 when using Cat5, Cat10, and Cat15. Another interesting observation is that the CO_2 selectivities improved considerably when comparing the catalytic runs with the non-catalytic ones.

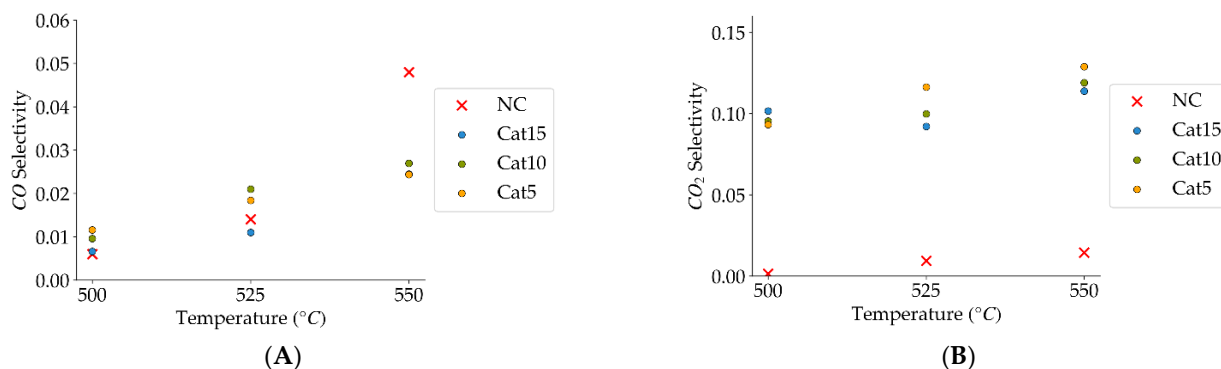


Figure 9. (A) Catalyst selectivity towards carbon monoxide (the mean standard deviation is ± 0.007), (B) catalyst selectivity towards carbon dioxide (the mean standard deviation is ± 0.01). Notes: (a) Tar surrogate: 2M4MP, (b) reaction time: 10 s, (c) steam atmosphere, (d) catalysts: Cat5, Cat10, Cat15, (e) catalyst weight: 0.30 g, (f) non-catalytic (NC) runs' conversions are reported as a reference.

Furthermore, Table 8 reports the CO₂/CO ratios. In the case of the catalytic runs, the CO₂/CO ratios were consistently higher than 4. Furthermore, a decrease in the CO₂/CO ratios with the rise in temperature was observed. This reduction in the CO₂/CO ratios agrees with the product changes expected with increasing temperature for exothermic reactions such as the water-gas shift reaction (Equation (3)), at chemical equilibrium.

Table 8. CO₂/CO ratios obtained at the different reaction temperatures, with the three catalysts of the present study, at 10 s reaction time, and under a steam atmosphere.

Catalyst	Temperature (°C)		
	500	525	550
5%Ni-5%CeO ₂ /γ-Al ₂ O ₃ (Cat5)	8.1	6.3	5.3
10%Ni-5% CeO ₂ /γ-Al ₂ O ₃ (Cat10)	10.0	4.8	4.3
15%Ni-5% CeO ₂ /γ-Al ₂ O ₃ (Cat15)	15	8.4	4.7

Figure 10A,B report the selectivities towards CH₄ and C₁⁺ (hydrocarbons with more than one carbon in their molecular formula).

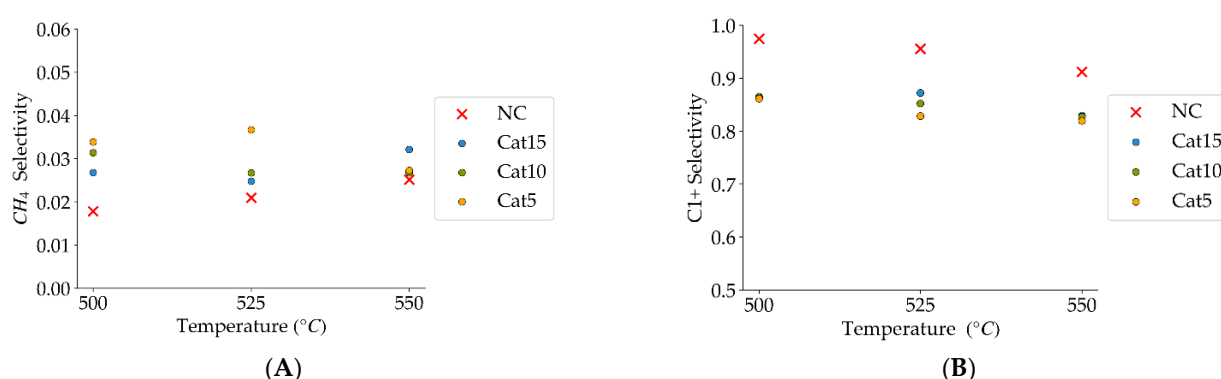
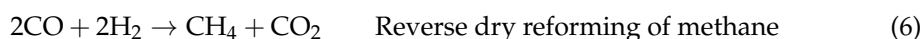


Figure 10. (A) Methane selectivities (mean standard deviation is ± 0.004), (B) c₁⁺ hydrocarbon selectivities (more than one carbon in their molecular formula) (the mean standard deviation is ± 0.02). Notes: (a) Tar surrogate: 2M4MP, (b) reaction time: 10 s, (c) steam atmosphere, (d) catalysts: Cat5, Cat10, Cat15, (e) catalyst weight: 0.30 g, (f) non-catalytic runs' selectivities are reported, as a reference.

Figure 10A shows that there is no important change in methane selectivity when employing Cat5, Cat10, and Cat15. Furthermore, when comparing the CH₄ selectivities obtained in the catalytic runs with the ones from the non-catalytic ones, one can observe that

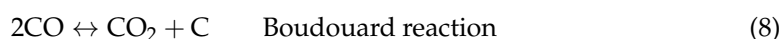
the CH₄ selectivities are always significantly higher in the catalytic runs, while displaying closer values at 550 °C.

Thus, on this basis, one can conclude that there is a mild enhancement of CH₄ formation when using Cat5, Cat10, and Cat15. This is consistent with an increased influence of the reverse methane dry reforming reaction (Equation (6)).

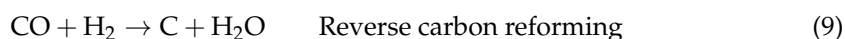


In accordance with this, Figure 10B shows a significant decrease in C₁⁺ hydrocarbon selectivities in the catalytic runs versus those obtained in the non-catalytic experiments: 0.82–0.87 versus 0.91–0.97, respectively. These valuable findings can be attributed to the intensified tar steam cracking activity that occurs as per Equation (2), in the catalytic runs.

Another important issue in the 2M4MP conversion is the coke formation. Coke is a carbonaceous solid product that deposits on the catalyst surface. Coke can reduce catalytic activity, leading to catalyst deactivation. Two competing reactions, namely methane pyrolysis and the Boudouard reaction, can contribute to coke formation, as shown in Equations (7) and (8) [44,48].



Methane pyrolysis is an endothermic reaction, while the Boudouard reaction is exothermic. Furthermore, reverse carbon reforming (Equation (9)), which is an exothermic reaction, can also yield coke.



Thus, temperature can have, in principle, a complex influence on coke yield, and coke formation must be established experimentally, as attempted in the present study.

Figure 11 reports the coke as determined, with TOC (total organic carbon) analysis. One can observe that, under a steam atmosphere, the temperature did not have a significant influence on coke formation, with Cat5 showing a slight coke reduction at 550 °C and Cat15 displaying the lowest coke value at all temperatures studied.

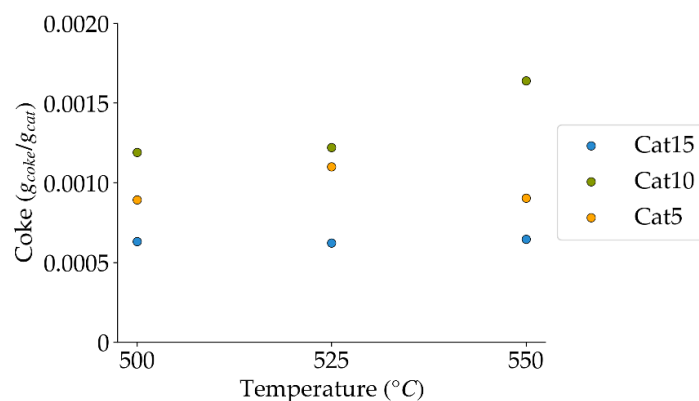


Figure 11. Coke formation at 10 s reaction time, under a steam atmosphere (mean standard deviation is: ± 0.0003). Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) catalysts: Cat5, Cat10, Cat15, (d) reported coke amounts were obtained after two consecutive injections of 2M4MP.

Given that the lowest 0.0005 coke yield per injection was obtained with Cat15, as reported in Figure 11, further studies were developed with this catalyst, using 5 s, 7 s, and 10 s at 500 °C, 525 °C, and 550 °C, under a steam atmosphere.

3.2. Effect of Reaction Time under Steam Atmosphere

Figure 12 reports the 2M4MP catalytic conversion at 5 s, 7 s, and 10 s at 500 °C, 525 °C, and 550 °C, while using the Cat15 catalyst. One can observe that the 2M4MP catalytic conversions fall within a band of values. This shows a slightly changed 2M4MP conversion with increasing reaction times, while it is positively influenced by temperature, with the highest (83–87%) tar conversions being obtained at 550 °C. These are valuable findings, as they show that the reaction time required can be set to 5 s in order to achieve desirable tar conversions, a most convenient reaction time for a downer unit operation.

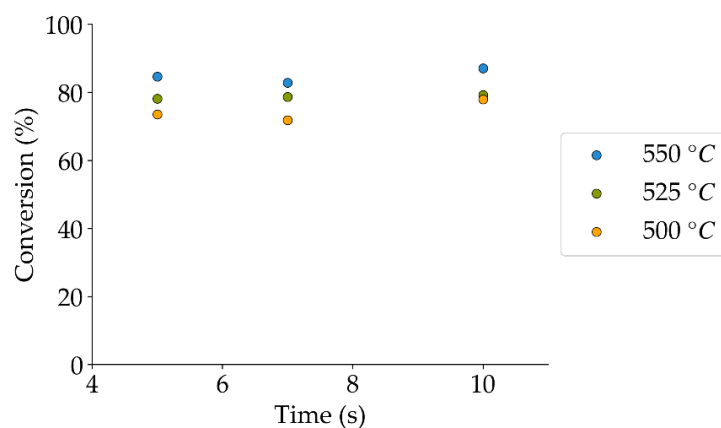


Figure 12. 2M4MP catalytic conversion at various reaction times and temperatures, and under a steam atmosphere (the mean standard deviation is: $\pm 5\%$). Notes: (a) Catalyst: Cat15, (b) catalyst weight: 0.30 g.

Table 9 shows the similar tar conversions obtained during non-catalytic experiments.

Table 9. Tar surrogate conversion obtained during the non-catalytic experiments.

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	84	74	91
7	78	86	88
10	82	89	87

Table 10 reports the CO₂/CO ratios obtained with Cat15 at 5 s, 7 s, and 10 s under a steam atmosphere. Overall, the CO₂ selectivities were much higher (around five times higher) than the CO selectivities. Furthermore, the CO₂/CO ratios decreased with an increasing temperature, with the smallest 2.5 CO₂/CO ratio being obtained at 550 °C and 5 s. One can notice, in Table 10, that all CO₂/CO ratios obtained were larger than 1, suggesting a dominant influence of the exothermic water-gas shift reaction.

Table 10. CO₂/CO ratios at various temperatures, reaction times, under a steam atmosphere, and using a Cat15 catalyst.

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	9.7	3.8	2.5
7	10.8	10.8	3.1
10	15.4	8.4	4.7

The methane selectivity is reported in Table 11. It can be observed that both increasing temperatures and reaction times modestly enhanced the methane selectivity.

Table 11. Methane selectivities at various temperatures and reaction times, under a steam atmosphere, and using the Cat15 catalyst. Note: the mean standard deviation is: ± 0.004 .

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	0.024	0.032	0.033
7	0.026	0.033	0.029
10	0.027	0.025	0.032

Furthermore, Table 12 describes the C_{1+} hydrocarbons' selectivity at various reaction times and temperatures. One can see that the C_{1+} selectivities fell within a band of values, with a desirable mild decreasing trend, towards lower C_{1+} selectivities, being observed at 550 °C and 10 s.

Table 12. Selectivities towards C_{1+} hydrocarbons at the different temperatures and reaction times under a steam atmosphere and using the Cat15 catalyst. Note: the mean standard deviation is: ± 0.03 .

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	0.91	0.90	0.86
7	0.90	0.84	0.86
10	0.87	0.87	0.83

Figure 13 reports the effect of the reaction time on coke formation when using the Cat15. At 10 s, in the 500–550 °C range, one can see no significant change in the formed coke. In contrast, at the 5 s reaction time, higher coke formation values were observed at 550 °C. This can be explained by assuming that, at shorter contact times and higher temperatures, there is a marked influence of the steam cracking of the 2M4MP, leading to higher coke levels. In addition, it appears that, at 7 s and 10 s, the carbon gasification reaction (Equation (10)) diminishes the already-formed coke [22,49].

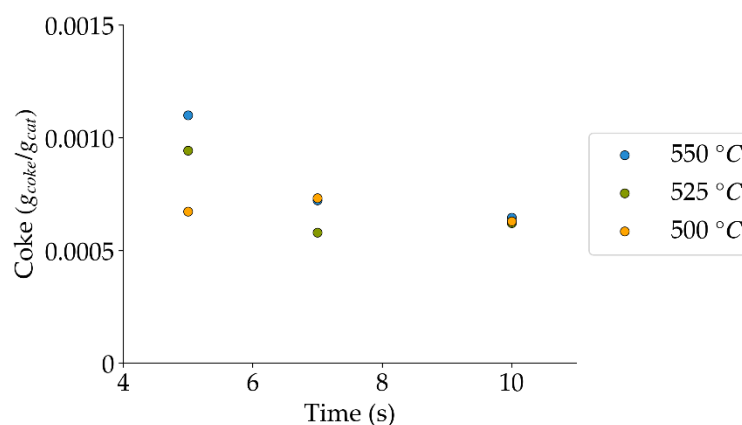


Figure 13. Coke formation under a steam atmosphere at the different reaction times and temperatures (mean standard deviation is: ± 0.0002). Notes: (a) Tar surrogate: 2M4MP, (b) catalyst: Cat15, (c) catalyst weight: 0.30 g, (d) reported coke corresponds to that formed after two consecutive injections of 2M4MP.

3.3. Mechanistic Insights from Tar Surrogate Conversion Runs under Steam Atmosphere

On the basis of the data reported in Section 3.2, one can see that the 2M4MP conversion is not affected by the catalyst type or the reaction time in the 5–10 s range. Gas chromatograms in Appendix C (Figures A2 and A3) show the dominant products including

methane, $C1^+$ species (mostly $C7$), and alkylated 2M4MP ($C9$). This points to a very first thermal reaction step where a methyl or methoxydealkylation formation takes place simultaneously with 2M4MP re-alkylation during reaction times smaller than 5 s. Following this first step, the gas phase, which is either inert or composed of a steam atmosphere, determines, together with the catalyst type, the $C1$ – $C6$ product species fractions, the CO_2/CO ratio, and the coke formed.

3.4. Tar Surrogate Conversion under Steam- H_2/CO_2 Atmosphere

As stated previously, the objective of the present study was to investigate the application of a $Ni-CeO_2/\gamma-Al_2O_3$ catalyst in a post-gasification process. To evaluate this, an atmosphere composed of combined steam and a 50%v H_2 /50 v% CO_2 was used to emulate the outlet stream of a catalytic biomass gasifier.

Figure 14 further reports the 2M4MP conversions obtained under combined steam and H_2/CO_2 for Cat5, Cat10, and Cat15 at 500 °C, 525 °C, and 550 °C at a 10 s reaction time, reaching values as high as 90%.

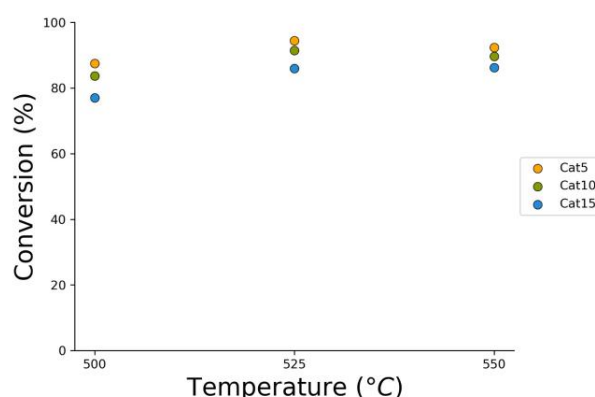


Figure 14. 2M4MP catalytic conversions under a steam- H_2/CO_2 atmosphere (mean standard deviation: $\pm 6\%$). Notes: (a) Catalysts: Cat5, Cat10, Cat15, (b) catalyst weight: 0.30 g, (c) reaction time: 10 s.

Figure 15A displays the CO selectivities under steam- H_2/CO_2 in the 500 °C–550 °C range. At 550 °C, one can notice higher 0.068–0.077 CO selectivities than the 0.024–0.027 CO selectivities obtained under steam-only conditions (refer to Figure 9A). These results agree with those of Kuhn Bastos [33], who showed a similar increasing trend in CO selectivity when CO_2 was introduced in the feed.

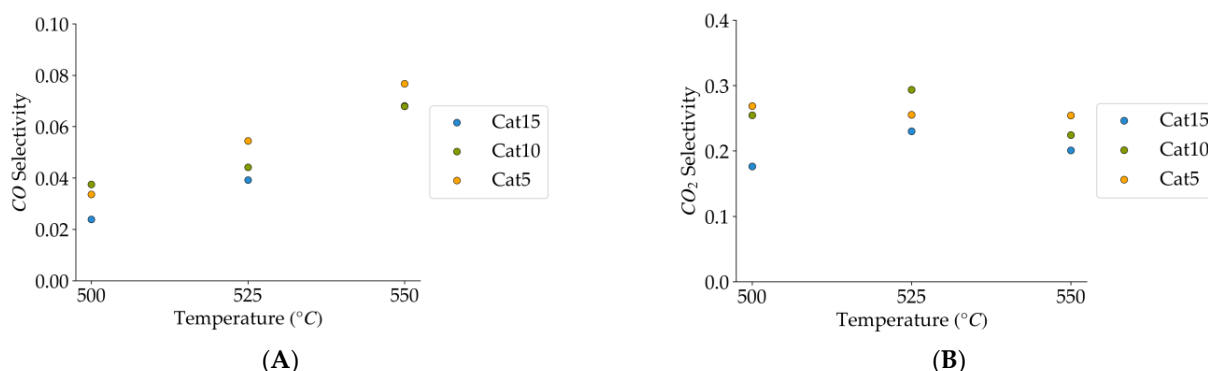


Figure 15. (A) CO selectivity (mean standard deviation is: ± 0.01). (B) CO_2 selectivity (mean standard deviation is: ± 0.04). Notes: (a) Tar surrogate: 2M4MP, (b) reaction time: 10 s, (c) steam- H_2/CO_2 atmosphere, (d) Catalysts: Cat5, Cat10, Cat15, (e) catalyst weight: 0.30 g.

Figure 15B reports the CO_2 selectivities at 500 °C, 525 °C, and 550 °C. At 550 °C, one can also notice higher 0.2–0.25 CO_2 selectivities with steam- H_2/CO_2 than the 0.11–0.13 CO_2 selectivities obtained with steam only (refer to Figure 9B).

Furthermore, the CO_2/CO ratios under combined steam and H_2/CO_2 are reported in Table 13. Although these CO_2/CO ratios are lower than the ones reported in Table 8, under steam, they are all higher than 3, and show a CO_2/CO ratio decreasing with an increasing temperature, which can be attribute, to the catalyst's promotion of the water-gas shift reaction.

Table 13. CO_2/CO ratios at the various temperatures and for three catalysts of the present study. Notes: (a) reaction time: 10 s, (b) catalyst weight: 0.30 g, and (c) a steam- H_2/CO_2 atmosphere.

Catalyst	Temperature (°C)		
	500	525	550
5%Ni-5%CeO ₂ /γ-Al ₂ O ₃	8.0	4.7	3.3
10%Ni-5%CeO ₂ /γ-Al ₂ O ₃	6.8	6.6	3.3
15%Ni-5%CeO ₂ /γ-Al ₂ O ₃	7.4	5.9	3.0

Furthermore, Figure 16A reports the methane selectivities, under steam- H_2/CO_2 , at three different temperatures. At 500 °C, these values fall in the 0.045–0.058 range. These methane selectivities can be compared with the 0.027–0.032 selectivities obtained under steam only and reported in Figure 10A. Thus, one can conclude that the cofeeding of steam and H_2/CO_2 enhances CH_4 formation. In brief, one can consider that the catalysts developed in the present study favour the hydrogenation of methyl groups, resulting from the steam cracking of 2M4MP and the reverse dry reforming reaction.

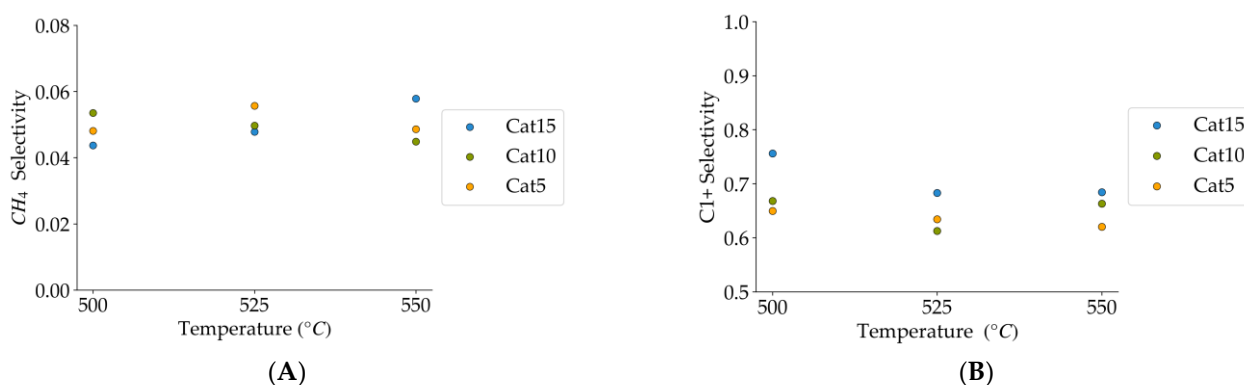


Figure 16. (A) Methane selectivities (mean standard deviation is: ± 0.005). (B) C_{1+} hydrocarbon selectivities (more than one carbon in their molecular formula) (the mean standard deviation is: ± 0.04). Notes: (a) Tar surrogate: 2M4MP, (b) reaction time: 10 s, (c) steam- H_2/CO_2 atmosphere, (d) Catalysts: Cat5, Cat10, Cat15, (e) catalyst weight: 0.30 g.

Furthermore, when the CH_4 selectivities obtained for the different catalysts under steam- H_2/CO_2 are compared, one can observe the following, at 550 °C (a) Cat5 and Cat10 show 0.049 and 0.045 CH_4 selectivities, respectively, and (b) Cat15 exhibits an increased CH_4 selectivity of up to 0.058. Therefore, one can conclude that Cat15 is a better choice for methane formation. Figure 16B reports C_{1+} selectivities under steam- H_2/CO_2 . These values fall in the range of 0.61–0.76, comparing favourably with the 0.82–0.87 C_{1+} selectivity values obtained under steam only (refer to Figure 10B).

Figure 17 reports the coke yield obtained with Cat5, Cat10, and Cat15 at 10 s under the steam- H_2/CO_2 atmosphere.

Regarding the coke yield, one can note that a higher coke formed at 500 °C than at 525 °C and 550 °C when using Cat5. This behaviour can be assigned to the increased influence of coke gasification at the higher temperatures. One should note, however, that when the Cat15 was employed under a combined steam- H_2/CO_2 , the coke formed stabilized at 550 °C, remaining in the $0.0006\text{--}0.00067 \text{ g}_{\text{coke}}\text{g}_{\text{cat}}^{-1}$ range. This coke level stabilization is similar to the one observed in experiments under steam (refer to Figure 11), with these stabilization values being in a similar range.

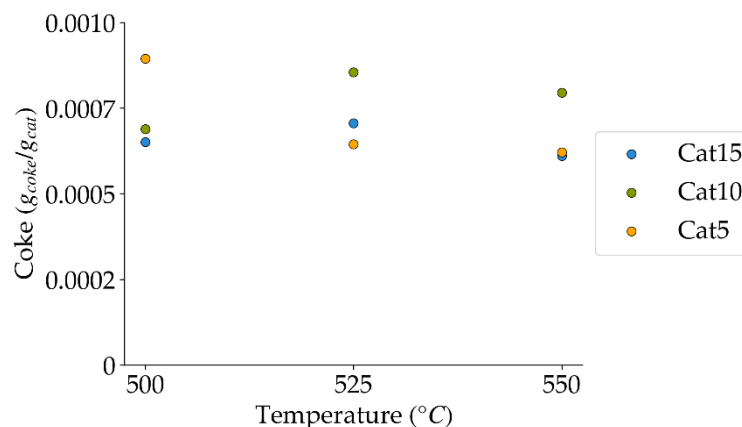


Figure 17. Coke formed under a steam-H₂/CO₂ atmosphere, at the three temperatures of the present study (mean standard deviation is: ± 0.0001). Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) catalysts: Cat5, Cat10, Cat15, (d) reaction time: 10 s, (e) reported coke corresponds to that formed after two consecutive injections of 2M4MP.

3.5. Effect of Reaction Time under Steam-H₂/CO₂ Atmosphere

Figure 18 describes the effect of the reaction time on the 2M4MP catalytic conversion, under steam and H₂/CO₂, while using the Cat15 catalyst. As in the cases formerly discussed, the overall 2M4MP conversion was not significantly influenced by the reaction time. For instance, at the various reaction times studied, the tar conversion remained in the high 86–91% range at 550 °C.

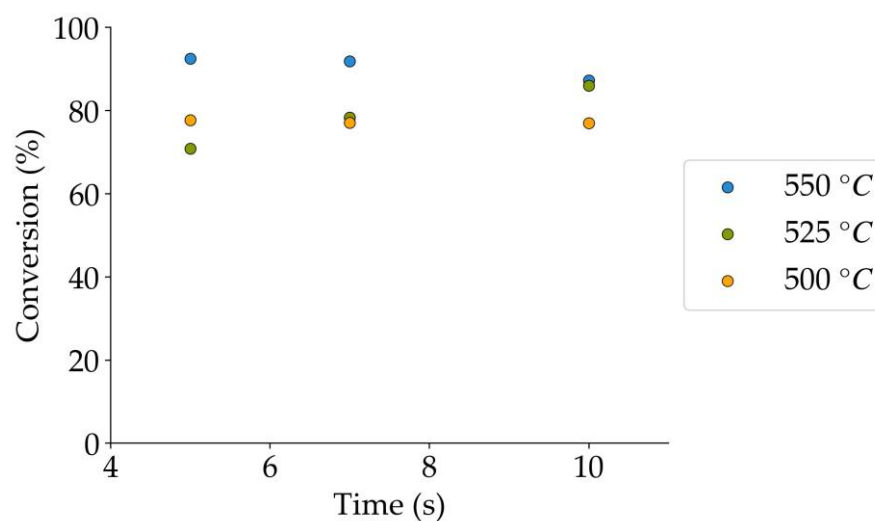


Figure 18. 2M4MP catalytic conversion at various reaction times and temperatures and under a steam-H₂/CO₂ atmosphere (the mean standard deviation is: $\pm 8\%$). Notes: (a) Catalyst: Cat15, (b) catalyst weight: 0.30 g.

Furthermore, the CO₂/CO ratios can be calculated with the CO and CO₂ selectivities reported by Rojas Chaves [32]. Trends observed in Table 14 are similar to the ones obtained for the runs under steam (refer to Table 10), where all the CO₂/CO ratios were greater than 2.5. This suggests that there is a significant influence of the water-gas shift reaction, with CO₂/CO ratios decreasing with increasing temperatures. This agrees with the expected trend of the exothermic water-gas shift reaction, which is strongly influenced by chemical equilibrium.

Table 14. CO₂/CO ratios at the different temperatures and reaction times of the present study. Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) catalyst: Cat15, (d) steam-H₂/CO₂ atmosphere.

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	9.7	3.8	2.5
7	8.0	8.6	3.9
10	7.4	5.9	3.0

Table 15 reports the methane selectivities at the various reaction times and temperatures of the present study, using Cat15 under steam-H₂/CO₂. It is apparent that the methane selectivities remain in a band of values, providing a best 0.058 methane selectivity at the 10 s reaction time and at 550 °C.

Table 15. Methane selectivities at the different reaction temperatures and reaction times of the present study. Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) catalyst: Cat15, (d) steam-H₂/CO₂ atmosphere. The mean standard deviation is ± 0.010 .

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	0.045	0.040	0.042
7	0.048	0.041	0.045
10	0.044	0.048	0.058

Table 16 describes the C₁⁺ hydrocarbon selectivities using Cat15 under steam-H₂/CO₂ atmosphere. This table shows similar results to those reported in Table 12, where a steam atmosphere was used. Similarly to the results reported in Table 12, the C₁⁺ selectivities in Table 16 display a consistent and desirable reduction, caused by the extra cracking and promoted by the combined steam and H₂/CO₂ feed.

Table 16. Selectivities towards C₁⁺ hydrocarbons at the different temperatures and reaction times of the present study. Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) catalyst: Cat15, (d) steam-H₂/CO₂ atmosphere. The mean standard deviation is ± 0.09 .

Reaction Time (s)	Temperature (°C)		
	500	525	550
5	0.70	0.74	0.71
7	0.70	0.71	0.67
10	0.76	0.68	0.68

Figure 19 reports the coke obtained for Cat15 under a steam-H₂/CO₂ atmosphere. One can see that, at the 10 s reaction time, the coke stabilized close to $0.0007 \text{ g}_{\text{coke}} \text{g}_{\text{cat}}^{-1}$, which is equivalent to a 0.58 wt% coke yield per injection. This coke amount was similar to the coke levels observed under steam.

In addition to the carbon-based products quantified during the various catalytic runs using Ni-CeO₂/γ-Al₂O₃ catalysts, hydrogen measurements were taken during the runs under steam-H₂/CO₂ atmospheres at 550 °C, and at various reaction times (5 s, 7 s, 10 s). Table 17 reports the H₂/CO ratios obtained at 550 °C for Cat15. This table shows, in all cases, H₂/CO ratios greater than 3.8. Thus, it can be postulated that the water-gas shift reaction is key in obtaining the high CO₂/CO ratios shown in Tables 8, 10, 13 and 14. These high H₂/CO ratios also demonstrate the value of a catalytic post-gasification step, such as the one considered here, where tar species are converted into lighter hydrocarbons, providing, at the same time, a H₂/CO ratio larger than 2, which is required for the synthesis of alcohols such as methanol.

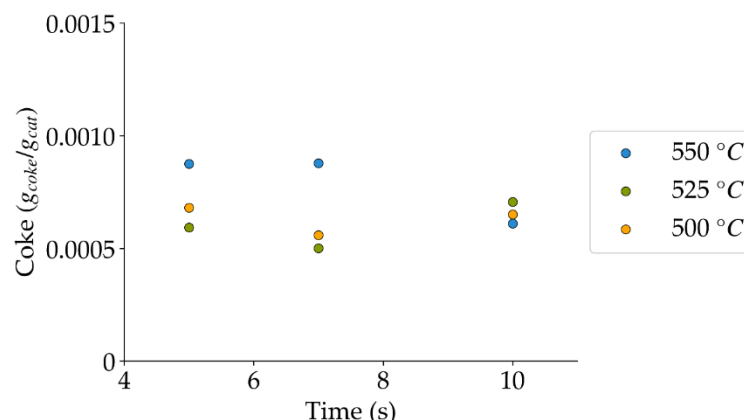


Figure 19. Coke formation under a steam-H₂/CO₂ atmosphere at the different reaction times and temperatures (mean standard deviation is: ± 0.0001). Notes: (a) Tar surrogate: 2M4MP, (b) catalyst: Cat15, (c) catalyst weight: 0.30 g, (d) reported coke corresponds to that formed after two consecutive injections of 2M4MP.

Table 17. H₂/CO ratios obtained at 550 °C using the different nickel-loaded catalysts and the various reaction times of the present study. Notes: (a) Tar surrogate: 2M4MP, (b) catalyst weight: 0.30 g, (c) steam-H₂/CO₂ atmosphere.

Catalyst	Reaction Time (s)	H ₂ /CO Ratio
Cat5	10	3.8
Cat10	10	4.0
Cat15	10	3.8
Cat15	7	3.8
Cat15	5	3.9

3.6. Mechanistic Insights from Tar Surrogate Conversion Runs under Steam-H₂/CO₂ Atmosphere

Data reported in Section 3.4, consistent with results of Section 3.2, show that the 2M4MP conversion is not affected significantly by the catalyst type or the reaction time (from 5 s to 10 s). It is shown, however, that a steam-H₂/CO₂ atmosphere promotes 2M4MP conversions with the formation of higher levels of lighter hydrocarbon product fractions, such as methane, as shown in Figure A4 (Appendix C). Thus, following this first thermal dealkylation step, the radicals formed are more prone, under steam-H₂/CO₂, to be hydrogenated via secondary reactions, enhancing, as a result, methane formation and catalyst water-gas shift activity, leading to H₂/CO ratios that are adequate for alcohol synthesis.

4. Future Perspectives for Tar Catalytic Post-Gasification

While tar reforming in the CREC Riser Simulator under steam and CO₂ was already shown by others [29,33,50,51], these authors did not address the important issue of the performance of these catalysts under syngas compositions as observed at the outlet of a gasifier unit. To address this important issue, the present study establishes, with the developed catalysts, the valuable basis of a tar post-gasification step, where both tar removal and a desirable H₂/CO ratio are achieved, yielding a syngas with a H₂/CO ratio larger than 2. This syngas is suitable for alcohol synthesis. One can notice, however, that at 525 °C, the catalysts developed in the CREC Riser Simulator yielded hydrocarbons with a carbon number greater than CH₄ (C₁⁺), as follows: (a) $96 \pm 2\%$ without catalyst loaded, under steam, (b) $85 \pm 2\%$ with catalyst loaded, under steam, and (c) $68 \pm 4\%$ with catalyst loaded, under steam-H₂/CO₂. All this was achieved with H₂/CO ratios higher than 3.8. These results are encouraging, given that they were obtained using 0.6 v% catalyst volumetric concentrations in the CREC Riser Simulator. These catalyst volumetric concentrations are considered to be low when employed both in riser and downers, given that these

reactors are typically operated by using higher catalyst volumetric concentrations in the 2–5 v% range.

Thus, and on this basis, one can see that, while catalytic tar post-gasification was demonstrated to be valuable, at the conceptual stage in the resent study, there is still significant room to improve tar adsorption processes, and as a result, catalytic tar conversion performance, using the Ni-CeO₂/γ-Al₂O₃ catalysts of the present study. In our view, this should be achieved with higher catalyst volumetric concentrations, reaching in this manner, levels of complete tar removal.

5. Materials and Methods

5.1. Catalyst Synthesis

Fluidizable catalysts were prepared using the incipient wetness technique under vacuum conditions. To accomplish this, a 53–106 μm sieved Sasol Catalox SCCa[®] γ-Al₂O₃ particle fraction was used as the support. Cerium oxide was employed as the promoter, and nickel as the active phase. Specifically, Ce(NO₃)₃·6H₂O (Sigma Aldrich CAS N^o: 10294-41-4, St. Louis, MO, USA) and Ni(NO₃)₂·6H₂O (Sigma Aldrich CAS N^o: 13478-00-7) were selected as the promoter and the active phase precursors, respectively. The amount of precursor solution added at every impregnation step was based on the available support pore volume, as calculated from the N₂-physisorption analysis. Impregnation steps were always followed by calcination, under airflow, at a maximum of 500 °C for 4 h. By using this approach, supports loaded with different cerium levels were prepared (2 wt%, 5 wt%, and 10 wt%). However, and for the more extensive runs, a 5%wt CeO₂ was selected, with three different loadings of the nickel being evaluated (5 wt%, 10 wt%, and 15 wt%).

5.2. Catalyst Characterization

The surface area, pore volume, and average pore diameter were analyzed using N₂-physisorption at 77 K. This was done using a Micromeritics ASAP 2920 Analyzer (Norcross, GA, USA). First, the sample was degassed at 250 °C for 3 h. Then, the surface area was calculated using the Brunauer, Emmett, and Teller (BET) method. The Barret, Joyner, and Halenda (BJH) method was employed to determine the pore-size distribution and pore diameter.

Temperature Programmed analyses, such as NH₃-TPD, CO₂-TPD, H₂-TPR, and H₂-Pulse Chemisorption, were conducted in a Micromeritics AutoChem II Analyzer (Norcross, GA, USA). For these analyses, a 0.10–0.20 g sample was placed in the U-shape tube, over quartz wool.

NH₃-TPD was used to determine the total acidity of the catalysts, as well as the kinetic desorption parameters. First, the sample was pretreated by heating it up from room temperature to 600 °C, and later cooling it down to 100 °C. The sample was then saturated with 5% NH₃ (balance He) for 1 h. Finally, the sample was purged with a He flow, raising the temperature progressively from 100 °C to 600 °C, at a rate of 15 °C/min. The desorbed ammonia was measured using a thermal conductivity detector (TCD). The NH₃-TPD curves were deconvoluted by employing a Gaussian function to classify the acidity as weak, medium, strong, and very strong.

CO₂-TPD was also used to analyze the basicity of each sample. This was done by heating each sample up to 600 °C under a helium flow. It was then cooled down to 45 °C while the sample was saturated with a 10% CO₂ (balance He) flow. Following this, it was purged with helium, while increasing the temperature from 45 °C to 600 °C, at a rate of 15 °C/min. The desorbed carbon dioxide was measured using a thermal conductivity detector (TCD).

The active metal surface area, the metal dispersion, and the average active metal crystallite size were studied using the H₂-Pulse Chemisorption technique. First, the sample was reduced with a flow of 10% H₂ (balance Ar) at 615 °C. Following this, hydrogen was injected in consecutive pulses of 1.0 mL until two consecutive outlet peaks had the same area.

H₂-TPR was employed to determine the reducibility of the catalyst. The sample was treated under a flow of 10% H₂ (balance Ar) while being heated from room temperature up to 950 °C at a rate of 10 °C/min. A water trap using liquid nitrogen and isopropanol was placed in the unit to condense the water produced from the reduction reaction. Then, the hydrogen consumption was measured using a thermal conductivity detector (TCD). The amount of reducible nickel was calculated from the reduction reaction of nickel oxide to metallic nickel.

FTIR analyses were employed to study the nature of the acid sites. These analyses were conducted in a Bruker Hyperion 2000 microscope, attached to a Tensor II (Etlingen, Germany). Prior to the analyses, the samples were pretreated using pyridine. Then, the samples were first heated up to 550 °C for 2 h under an N₂ flow. Then, they were cooled down to 100 °C. At that temperature, the samples were saturated with pyridine for 1 h. Finally, the samples were purged with an N₂ flow at 100 °C for 1.5 h.

The crystalline structure of the prepared catalysts was analyzed using the X-ray Diffraction technique. The analyses were conducted in a Rigaku MiniFlex Diffractometer (Woodlands, TX, USA) with a U4 fixed monochrome, and at a scan range from 20° to 80°, with a rate of 2.0°/min, and using CuKα ($\lambda = 0.15406$ nm) radiation.

The X-ray photoelectron spectroscopic analysis of nickel transition metal and the analysis of their oxides were carried out with a Kratos AXIS Supra Spectrometer (Manchester, UK) using a monochromatic Al K (alpha) source (10 mA, 15 kV). High resolution analyses were carried out with an analysis area of 300 × 700 microns and a pass energy of 20 eV. Spectra have been charging-corrected to the main line of the carbon 1 s spectrum (adventitious carbon), set to 284.8 eV. Spectra were analysed using CasaXPS software (version 2.3.26). The XPS spectra analysis was valuable for assessing the extent of nickel reducibility on the Ni-Ce- γ -Al₂O₃ catalyst developed.

5.3. Catalyst Performance

The performance of the prepared catalysts was assessed in the CREC Riser Simulator. This is a bench-scale mini-fluidized batch unit that allows for changing of reactant partial pressures, reaction times, temperatures, and C/O (catalyst/reactant) ratios in a range of conditions compatible with expected industrial rise/downer operation [52]. Additionally, the CREC Riser Simulator is set with a configuration allowing online analysis of the gas produced, in a gas chromatograph, as well as in situ regeneration of the catalysts, as seen in Figure 20. Likewise, the reactor and the vacuum box of the CREC Riser Simulator have pressure transducers that monitor the pressure during the reaction (Appendix B shows an example of a pressure profile obtained during one of the experiments).

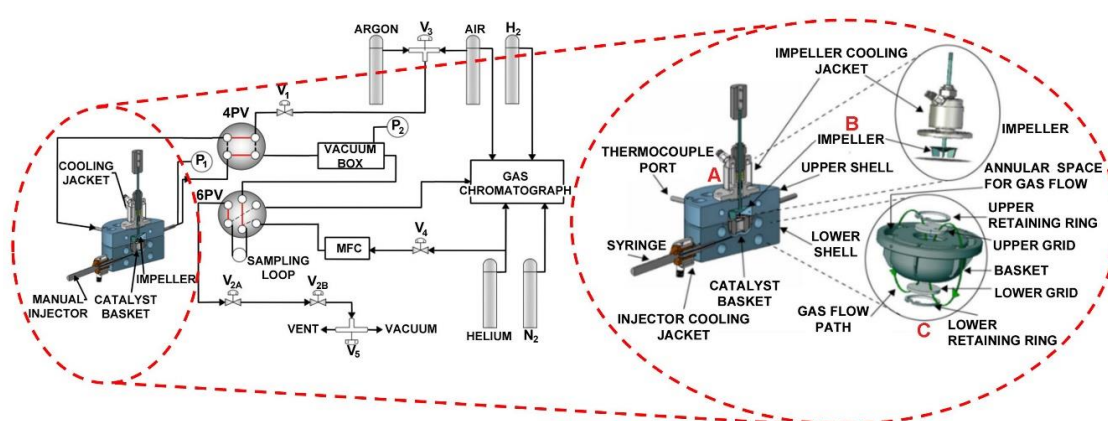


Figure 20. Schematic diagram of the CREC Riser Simulator and its accessories. Adapted from [52–54].

The 2-methoxy-4-methylphenol (Sigma Aldrich CAS N°: 93-51-6) was selected as tar surrogate for the experimental runs given its elemental composition (weight basis) of 69.5% C, 23.1% O, and 7.24% H, and its functionalities of one aromatic group, one OH group,

one methoxy group, and one methyl group. This composition makes this tar surrogate similar to lignin. Moreover, given its high solubility in water, 0.036 g of 2M4MP-water solution (50 wt% water, 50 wt% 2M4MP) can be injected into the reactor with high accuracy.

Approximately 0.30 g of catalyst was placed in the Riser Simulator reactor basket. Then, the reactor was sealed and leak tested. Before the reaction, the catalyst was activated in situ, at 615 °C, by flowing air through it for 15 min, and then by flowing hydrogen through it for 15 min. Then, the reaction temperature was set. It is worth mentioning that helium was flown through the reactor during its heating or cooling steps.

Cat5, Cat10, and Cat 15 were tested using 0.018 g of 2M4MP at three reaction temperatures (500 °C, 525 °C, and 550 °C) and at a fixed reaction time of 10 s. Additionally, the 15 wt% Ni-5 wt%CeO₂/γ-Al₂O₃ performance was assessed at 5 s and 7 s. This temperature range prevents Ni-carbonyl-formation, which can be neglected above 180 °C [55]. All experiments were done twice to corroborate the results' reproducibility.

The Cat5, Cat10, and Cat15 catalysts developed were evaluated under two different atmospheres: steam and a mix of steam, hydrogen, and carbon dioxide. The second atmosphere was considered to closely emulate post-gasification conditions in a downer reactor when converting biomass-derived tars. For the experiments under steam and H₂/CO₂, the injection was performed in two steps: first, by using a defined volume of a 50 v%H₂/50 v%CO₂ (10–11 cm³), and secondly, by employing a 0.036 g mix of water and tar surrogate species (with a water/tar weight ratio of approximately 1).

The quantification of the various reactants and products was conducted in a Shimadzu GC/MS-2010 (Kyoto, Japan), equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) in a parallel configuration arrangement. The TCD was connected to a packed HayeSep D column, with a film thickness of 2 µm, a length of 9.1 m, and an inner diameter of 2 mm. The FID was connected to a capillary BPX5 column, with a film thickness of 0.25 µm, a length of 30 m, and an inner diameter of 0.25 mm (See Appendix C for examples of the FID chromatograms obtained).

Moreover, coke formation over the catalyst was quantified using a Shimadzu TOC-V Analyzer (Kyoto, Japan), following two consecutive repeat 2-methoxy-4-methylphenol injection runs.

Finally, product selectivity and tar surrogate conversion were calculated by using Equations (11) and (12), respectively:

$$y_i = \frac{n_i}{n_T} \quad (11)$$

$$X = \left(1 - \frac{n_{c,MC}}{n_T}\right) \times 100 \quad (12)$$

where y_i represents the selectivity towards the i species, n_i denotes the moles of carbon in the i species, n_T refers to the total moles of carbon in mol, $n_{c,MC}$ stands for the moles of carbon of the unconverted model compound in mol, and X stands for the conversion of carbon-containing species in %. Appendix D reports the closure of the carbon balance for all the experiments.

6. Conclusions

- The Sasol γ-Al₂O₃ support of the present study displays favourable structural properties for a fluidizable catalyst that can be used in a post-gasification step to convert tars;
- The CeO₂ promoter addition does not significantly affect the γ-Al₂O₃ support structural properties (specific surface area, pore volume, pore diameter). It, however, reduces as desired the strong Lewis site acidity of the γ-Al₂O₃ while its basicity remains unchanged;
- The addition of the Ni to the CeO₂-γ-Al₂O₃, as evaluated with H₂-TPR analysis, shows that the H₂-consumption peaks shift towards lower temperatures, pointing to a decreasing interaction of the nickel active phase with the CeO₂-γ-Al₂O₃ at higher nickel loadings;

- The prepared fluidizable Ni-CeO₂-γ-Al₂O₃ catalysts displayed 0.74–0.81% Ni dispersion and 104–114 nm Ni crystallite sizes, as demonstrated using H₂-Pulse Chemisorption;
- The runs developed in the CREC Riser Simulator, using the 2M4MP tar surrogate, established that nickel loading did not have an important effect on the overall surrogate tar conversion. Furthermore, the influence of the reaction time and temperature on the tar conversion were very modest. These observations were considered significant given the possible application of the developed catalyst in short contact downers or risers, in the 500–550 °C targeted range;
- The catalytic runs in the CREC Riser Simulator with 2M4MP were also valuable in determining the important impact of both the catalyst type and steam-H₂/CO₂ on the CO₂/CO and on the H₂/CO ratios, with these ratios being higher than 2 and 3, respectively. The amount of coke remained very low. This makes the proposed post-gasification step, in principle, a valuable process for producing a syngas blend for alcohol synthesis, following the required water and light hydrocarbon removal and syngas (H₂-CO) compression.

Author Contributions: F.R.C. contributed with the development of the experimental studies for catalyst synthesis, characterization, and experimental runs in the CREC Riser Simulator, and preparation of this manuscript. N.T.B. contributed with data analysis. C.T. contributed with the development of the catalysts and technical assistance. H.d.L. participated in the development of the catalyst, data interpretation, discussion, and review of this manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from the Organization of American States (OAS) with a postgraduate scholarship awarded to Floria Rojas Chaves, and from the Natural Science and Engineering Research Council of Canada (NSERC) via Hugo de Lasa’s Discovery Grant.

Data Availability Statement: Additional information and clarification of the data reported can be found in [32].

Acknowledgments: The authors are thankful to Florencia de Lasa for her assistance with the editing of the present manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Nomenclature

E_{des}	Activation energy of desorption in kJ mol ^{−1}
k_d	Desorption constant in mmol g _{cat} ^{−1} min ^{−1}
$k_{\text{des},0}$	Pre-exponential factor in mmol g _{cat} ^{−1} min ^{−1}
$n_{\text{C},\text{MC}}$	Moles of carbon of the model compound injected in mol
n_i	Moles of carbon in the i species in mol
n_T	Total moles of carbon in mol
R	Gas constant in cm ³ atm K ^{−1} mol ^{−1}
T_m	Centering temperature minimizing the cross-correlation between adsorption kinetic parameters in K
V_{des}	Volume of ammonia desorbed in mmol g _{cat} ^{−1}
V_m	Volume of ammonia adsorbed at saturation condition in mmol g _{cat} ^{−1}
X	Conversion of the carbon containing species in %
y_i	Selectivity towards the i species in mol
β'	Heating rate in °C/min

Abbreviations

2M4MP	2-Methoxy-4-Methylphenol
BET	Brunauer-Emmet-Teller Surface Area Method
Cat5	5%Ni-5%CeO ₂ /γ-Al ₂ O ₃
Cat10	10%Ni-5%CeO ₂ /γ-Al ₂ O ₃
Cat15	15%Ni-5%CeO ₂ /γ-Al ₂ O ₃
CREC	Chemical and Reaction Engineering Centre

FID	Flame Ionization Detector
FTIR	Fourier Transformed Infrared Spectroscopy
GC	Gas Chromatograph
NC	Non-Catalytic Experiments
STP	Standard Pressure and Temperature
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
XRD	X-ray Diffraction

Appendix A. State of Reducible Nickel

XPS spectrum results showed that, when employing the catalysts of the present study, only Ni (II) was present. In fact, quantification of Ni(III), based on expected bands for Ni(III) species peaks [56], returns results showing no significant amounts of Ni(III) present.

Appendix B. CREC Riser Simulator Pressure Profile

This appendix reports the four typical and distinctive pressure profile conditions in the CREC-Riser Simulator operation, as shown in Figure A1: (a) a first pressure jump that corresponds to the H_2/CO_2 addition, designated as “A”, (b) a second pressure jump that represents the water-tar surrogate injection, designated as “B” or the initiation of the tar conversion, (c) a third and progressive increase of pressure which shows the tar surrogate and syngas conversion, ending in “C”, and (d) a fourth sudden pressure reduction that signals the reactor content evacuation towards the vacuum box, designated as “D”. One should note that the time difference between “C” and “B” is used to define the reaction time.

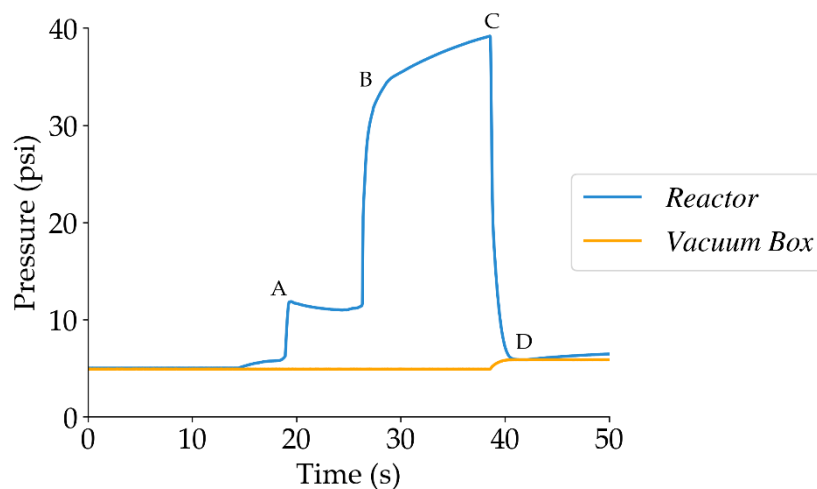


Figure A1. Typical pressure profiles in the CREC-Riser Simulator: (a) the first pressure jump designated as “A”, corresponds to the addition of H_2/CO_2 , (b) the second pressure jump designated as “B”, represents the water-tar surrogate injection (50% wt water, 50 wt 2M4MP, or 7.22 pH₂O/pMC ratio equivalent), (c) the third progressive pressure increase ending in “C”, indicates the tar surrogate conversion and the syngas conversion reaction period, (d) the fourth sudden pressure decrease period designated as “D” shows the CREC Riser Simulator product evacuation period.

Appendix C. Typical FID Chromatograms

Figures A2–A4 show the evolution of methane and illustrate its importance for the conversion of the tar surrogate (2M4MP) in the following three cases: (a) Non-catalytic run (Figure A2), (b) catalytic run under steam atmosphere (Figure A3), (c) catalytic run under steam- H_2/CO_2 atmosphere (Figure A4).

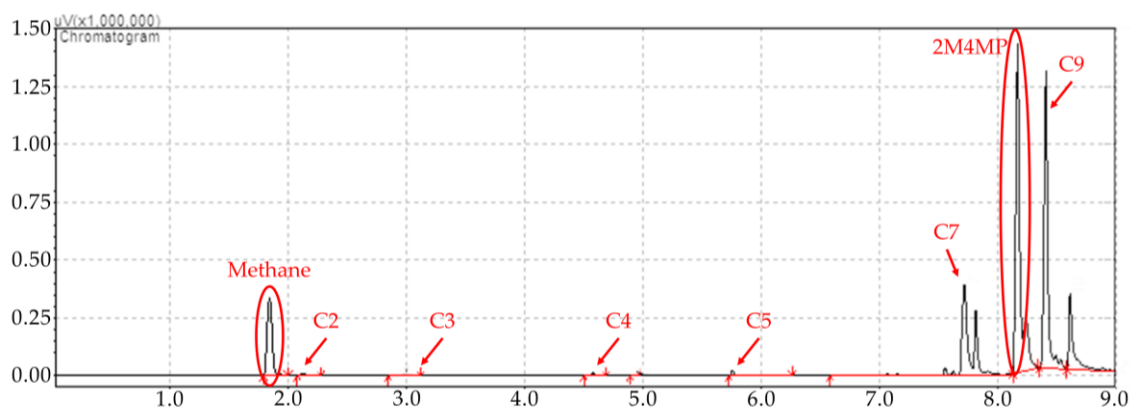


Figure A2. Example of an FID chromatogram obtained from a non-catalytic experiment under a steam atmosphere, 10 s of reaction time, and 500 °C of reaction temperature.

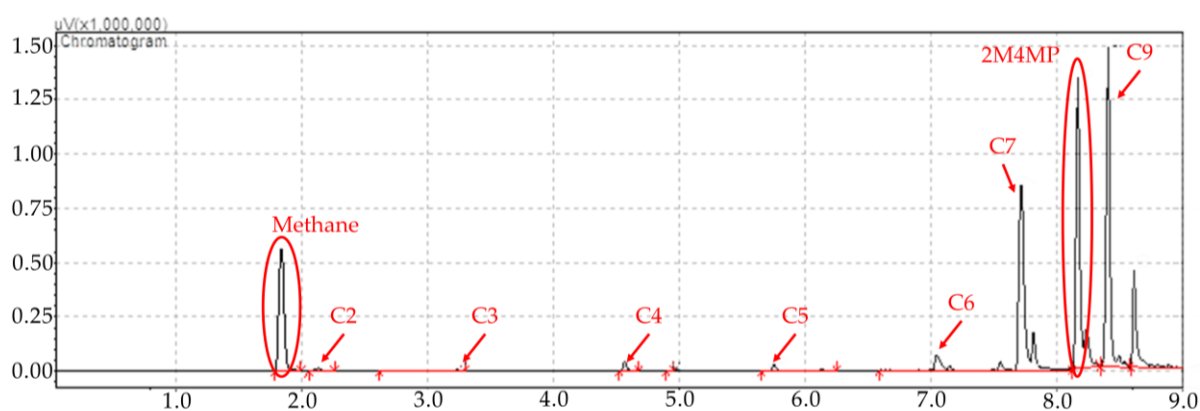


Figure A3. Example of an FID Chromatogram obtained from an experiment under a steam atmosphere, 10 s of reaction time, 500 °C of reaction temperature, and using a Cat5 catalyst (5%Ni-5%CeO₂/γ-Al₂O₃).

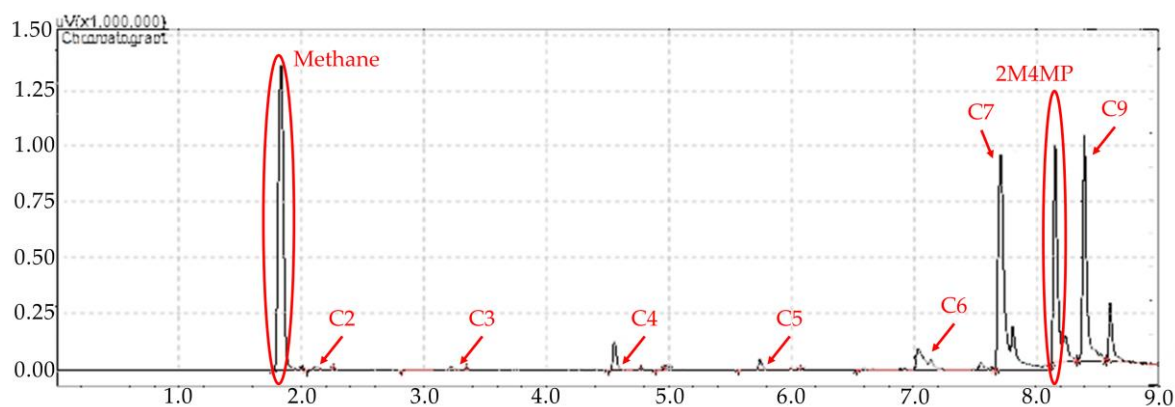


Figure A4. Example of an FID chromatogram obtained from an experiment under a steam-H₂/CO₂ atmosphere, 10 s of reaction time, 500 °C of reaction temperature and using Cat5 catalyst (5%Ni-5%CeO₂/γ-Al₂O₃).

Appendix D. Carbon Balance

Figure A5 reports the carbon balance closure for all the experiments performed, including the thermal non-catalytic runs as well as the catalytic runs. These balances yielded an average value of 92%, with a standard deviation of 11%. Additional information regarding carbon balances is reported in [32].

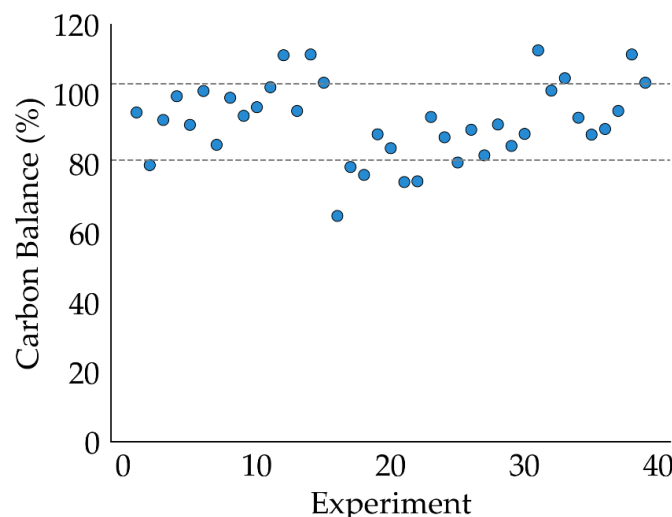


Figure A5. Carbon balance closures for all the experiments, including the catalytic experiments performed under steam and steam-H₂/CO₂ atmospheres, and the thermal non-catalytic experiments.

References

- Bioenergy. Available online: <https://www.iea.org/energy-system/renewables/bioenergy> (accessed on 21 September 2023).
- The Circular Economy Glossary. Available online: <https://ellenmacarthurfoundation.org/topics/circular-economy-introduction/glossary> (accessed on 21 September 2023).
- Guan, G.; Kaewpanha, M.; Hao, X.; Abudula, A. Catalytic Steam Reforming of Biomass Tar: Prospects and Challenges. *Renew. Sustain. Energy Rev.* **2016**, *58*, 450–461. [\[CrossRef\]](#)
- Chandraratne, M.R.; Daful, A.G. Recent Advances in Thermochemical Conversion of Biomass. In *Recent Perspectives in Pyrolysis Research*; IntechOpen: London, UK, 2021; ISBN 978-1-83969-915-3.
- Emissions Advantages of Gasification. Available online: <https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/low-emissions> (accessed on 21 September 2023).
- Luo, X.; Wu, T.; Shi, K.; Song, M.; Rao, Y. Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact. In *Gasification for Low-Grade Feedstock*; IntechOpen: London, UK, 2018; ISBN 978-1-78923-289-9.
- Narnaware, S.L.; Panwar, N.L. Catalysts and Their Role in Biomass Gasification and Tar Abatement: A Review. *Biomass Conv. Bioref.* **2021**, *7*, 1–31. [\[CrossRef\]](#)
- Puig-Gamero, M.; Pio, D.T.; Tarelho, L.A.C.; Sánchez, P.; Sanchez-Silva, L. Simulation of Biomass Gasification in Bubbling Fluidized Bed Reactor Using Aspen Plus®. *Energy Convers. Manag.* **2021**, *235*, 113981. [\[CrossRef\]](#)
- Cortazar, M.; Santamaria, L.; Lopez, G.; Alvarez, J.; Zhang, L.; Wang, R.; Bi, X.; Olazar, M. A Comprehensive Review of Primary Strategies for Tar Removal in Biomass Gasification. *Energy Convers. Manag.* **2023**, *276*, 116496. [\[CrossRef\]](#)
- Lotfi, S. Technologies for Tar Removal from Biomass-Derived Syngas. *PPEJ* **2021**, *5*, 1–35. [\[CrossRef\]](#)
- Feng, D.; Zhang, Y.; Zhao, Y.; Sun, S. Mechanism of In-Situ Catalytic Cracking of Biomass Tar over Biochar with Multiple Active Sites. In *Applications of Biochar for Environmental Safety*; IntechOpen: London, UK, 2020; ISBN 978-1-78985-896-9.
- Milne, T.A.; Evans, R.J.; Abatzoglou, N. Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion; Technical Report p. NREL/TP-570-25357, ON: DE00003726; National Renewable Energy Laboratory: Golden, CO, USA, 1998.
- Gao, N.; Salisu, J.; Quan, C.; Williams, P. Modified Nickel-Based Catalysts for Improved Steam Reforming of Biomass Tar: A Critical Review. *Renew. Sustain. Energy Rev.* **2021**, *145*, 111023. [\[CrossRef\]](#)
- Zeng, X.; Ueki, Y.; Yoshiie, R.; Naruse, I.; Wang, F.; Han, Z.; Xu, G. Recent Progress in Tar Removal by Char and the Applications: A Comprehensive Analysis. *Carbon Resour. Convers.* **2020**, *3*, 1–18. [\[CrossRef\]](#)
- Shen, Y.; Yoshikawa, K. Recent Progresses in Catalytic Tar Elimination during Biomass Gasification or Pyrolysis—A Review. *Renew. Sustain. Energy Rev.* **2013**, *21*, 371–392. [\[CrossRef\]](#)
- Jang, W.-J.; Shim, J.-O.; Kim, H.-M.; Yoo, S.-Y.; Roh, H.-S. A Review on Dry Reforming of Methane in Aspect of Catalytic Properties. *Catal. Today* **2019**, *324*, 15–26. [\[CrossRef\]](#)
- Ngo, T.N.L.T.; Chiang, K.-Y.; Liu, C.-F.; Chang, Y.-H.; Wan, H.-P. Hydrogen Production Enhancement Using Hot Gas Cleaning System Combined with Prepared Ni-Based Catalyst in Biomass Gasification. *Int. J. Hydrogen Energy* **2021**, *46*, 11269–11283. [\[CrossRef\]](#)
- Ren, J.; Cao, J.-P.; Zhao, X.-Y. Fabrication Strategies of Ni-Based Catalysts in Reforming of Biomass Tar/Tar Model Compounds. *Appl. Energy Combust. Sci.* **2022**, *9*, 100053. [\[CrossRef\]](#)
- Zhang, Z.; Liu, L.; Shen, B.; Wu, C. Preparation, Modification and Development of Ni-Based Catalysts for Catalytic Reforming of Tar Produced from Biomass Gasification. *Renew. Sustain. Energy Rev.* **2018**, *94*, 1086–1109. [\[CrossRef\]](#)

20. Ekeoma, B.C.; Yusuf, M.; Johari, K.; Abdullah, B. Mesoporous Silica Supported Ni-Based Catalysts for Methane Dry Reforming: A Review of Recent Studies. *Int. J. Hydrogen Energy* **2022**, *47*, 41596–41620. [CrossRef]
21. Yang, C.; Lu, Y.; Zhang, L.; Kong, Z.; Yang, T.; Tao, L.; Zou, Y.; Wang, S. Defect Engineering on CeO₂-Based Catalysts for Heterogeneous Catalytic Applications. *Small Struct.* **2021**, *2*, 2100058. [CrossRef]
22. Marinho, A.L.A.; Toniolo, F.S.; Noronha, F.B.; Epron, F.; Duprez, D.; Bion, N. Highly Active and Stable Ni Dispersed on Mesoporous CeO₂-Al₂O₃ Catalysts for Production of Syngas by Dry Reforming of Methane. *Appl. Catal. B Environ.* **2021**, *281*, 119459. [CrossRef]
23. Papadopoulou, C.; Matralis, H.; Verykios, X. Utilization of Biogas as a Renewable Carbon Source: Dry Reforming of Methane. In *Catalysis for Alternative Energy Generation*; Guczi, L., Erdöhelyi, A., Eds.; Springer: New York, NY, USA, 2012; pp. 57–127, ISBN 978-1-4614-0344-9.
24. PURALOX and CATALOX. Available online: <https://products.sasol.com/pic/products/home/grades/ZA/5puralox-and-catalox/index.html> (accessed on 22 September 2023).
25. Mazumder, A.S.M.J. Steam Gasification of Biomass Surrogates: Catalyst Development and Kinetic Modelling. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2014.
26. Liu, H.; Zou, X.; Wang, X.; Lu, X.; Ding, W. Effect of CeO₂ Addition on Ni/Al₂O₃ Catalysts for Methanation of Carbon Dioxide with Hydrogen. *J. Nat. Gas Chem.* **2012**, *21*, 703–707. [CrossRef]
27. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [CrossRef]
28. Fonseca, J.; Bion, N.; Licea, Y.E.; Morais, C.M.; do Carmo Rangel, M.; Duprez, D.; Epron, F. Unexpected Redox Behaviour of Large Surface Alumina Containing Highly Dispersed Ceria Nanoclusters. *Nanoscale* **2019**, *11*, 1273–1285. [CrossRef] [PubMed]
29. Adamu, S.; Xiong, Q.; Bakare, I.A.; Hossain, M.M. Ni/CeAl₂O₃ for Optimum Hydrogen Production from Biomass/Tar Model Compounds: Role of Support Type and Ceria Modification on Desorption Kinetics. *Int. J. Hydrogen Energy* **2019**, *44*, 15811–15822. [CrossRef]
30. Kamonsuangkasem, K.; Therdthianwong, S.; Therdthianwong, A.; Thammajak, N. Remarkable Activity and Stability of Ni Catalyst Supported on CeO₂-Al₂O₃ via CeAlO₃ Perovskite towards Glycerol Steam Reforming for Hydrogen Production. *Appl. Catal. B Environ.* **2017**, *218*, 650–663. [CrossRef]
31. Zurita-Mendez, N.N.; Carbajal-De la Torre, G.; Cadenas, E.; Liu, H.; Espinosa-Medina, M.A. Synthesis and Characterization of Nickel Aluminate Nanoparticles. *Mater. Res. Express* **2018**, *6*, 015036. [CrossRef]
32. Rojas Chaves, F. Conversion of Biomass Derived Tar in a Catalytic Post-Gasification Process. Master's Thesis, Western University, London, ON, Canada, 2023.
33. Kuhn Bastos, A. CO₂ Biomass Fluidized Gasification. Thermodynamic and Reactivity Studies. Master's Thesis, The University of Western Ontario, London, ON, Canada, 2018.
34. Torres, C.; Rostom, S.; de Lasa, H. An Eco-Friendly Fluidizable Fe_xO_y/CaO-γ-Al₂O₃ Catalyst for Tar Cracking during Biomass Gasification. *Catalysts* **2020**, *10*, 806. [CrossRef]
35. Rostom, S. Propane Oxidative Dehydrogenation Under Oxygen-Free Conditions Using Novel Fluidizable Catalysts: Reactivity, Kinetic Modeling and Simulation Study. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2018.
36. Adamu, S.; Khan, M.Y.; Razzak, S.A.; Hossain, M.M. Ceria-Stabilized Meso-Al₂O₃: Synthesis, Characterization and Desorption Kinetics. *J. Porous Mater.* **2017**, *24*, 1343–1352. [CrossRef]
37. Tonetto, G.; Atlas, J.; de Lasa, H. FCC Catalysts with Different Zeolite Crystallite Sizes: Acidity, Structural Properties and Reactivity. *Appl. Catal. A Gen.* **2004**, *270*, 9–25. [CrossRef]
38. Adnan, M.A.; Muraza, O.; Razzak, S.A.; Hossain, M.M.; de Lasa, H.I. Iron Oxide over Silica-Doped Alumina Catalyst for Catalytic Steam Reforming of Toluene as a Surrogate Tar Biomass Species. *Energy Fuels* **2017**, *31*, 7471–7481. [CrossRef]
39. Adnan, M.A.; Adamu, S.; Muraza, O.; Hossain, M.M. Fluidizable NiO-Fe₂O₃/SiO₂-γ-Al₂O₃ for Tar (Toluene) Conversion in Biomass Gasification. *Process Saf. Environ. Prot.* **2018**, *116*, 754–762. [CrossRef]
40. Al-Ghamdi, S.; Volpe, M.; Hossain, M.M.; de Lasa, H. VO_x/c-Al₂O₃ Catalyst for Oxidative Dehydrogenation of Ethane to Ethylene: Desorption Kinetics and Catalytic Activity. *Appl. Catal. A Gen.* **2013**, *450*, 120–130. [CrossRef]
41. Morterra, C.; Magnacca, G. A Case Study: Surface Chemistry and Surface Structure of Catalytic Aluminas, as Studied by Vibrational Spectroscopy of Adsorbed Species. *Catal. Today* **1996**, *27*, 497–532. [CrossRef]
42. Parry, E.P. An Infrared Study of Pyridine Adsorbed on Acidic Solids. Characterization of Surface Acidity. *J. Catal.* **1963**, *2*, 371–379. [CrossRef]
43. Vázquez, M.I.; Corma, A.; Fornés, V. Characterization of NiO Supported on Zeolite Y, by Pyridine Adsorption. *Zeolites* **1986**, *6*, 271–274. [CrossRef]
44. Luisetto, I.; Tuti, S.; Battocchio, C.; Lo Mastro, S.; Sodo, A. Ni/CeO₂-Al₂O₃ Catalysts for the Dry Reforming of Methane: The Effect of CeAlO₃ Content and Nickel Crystallite Size on Catalytic Activity and Coke Resistance. *Appl. Catal. A Gen.* **2015**, *500*, 12–22. [CrossRef]
45. Sepehri, S.; Rezaei, M. Ce Promoting Effect on the Activity and Coke Formation of Ni Catalysts Supported on Mesoporous Nanocrystalline γ-Al₂O₃ in Autothermal Reforming of Methane. *Int. J. Hydrogen Energy* **2017**, *42*, 11130–11138. [CrossRef]

46. Fu, L.; Li, Y.; Cui, H.; Ba, W.; Liu, Y. Highly Stable and Selective Catalytic Deoxygenation of Renewable Bio-Lipids over Ni/CeO₂-Al₂O₃ for N-Alkanes. *Appl. Catal. A Gen.* **2021**, *623*, 118258. [CrossRef]
47. Calzada Hernandez, A.R.; Serrano Rosales, B.; de Lasa, H. Kinetic Model of Catalytic Steam Gasification of 2-Methoxy-4-Methylphenol Using 5% Ni–0.25% Ru/ γ -Al₂O₃ in a CREC-Riser Simulator. *Catalysts* **2022**, *12*, 282. [CrossRef]
48. Zhou, L.; Li, L.; Wei, N.; Li, J.; Basset, J.-M. Effect of NiAl₂O₄ Formation on Ni/Al₂O₃ Stability during Dry Reforming of Methane. *ChemCatChem* **2015**, *7*, 2508–2516. [CrossRef]
49. Bereketidou, O.A.; Goula, M.A. Biogas Reforming for Syngas Production over Nickel Supported on Ceria–Alumina Catalysts. *Catal. Today* **2012**, *195*, 93–100. [CrossRef]
50. Mazumder, J.; De Lasa, H.I. Steam Gasification of a Cellulosic Biomass Surrogate Using a Ni/La₂O₃- γ -Al₂O₃ Catalyst in a CREC Fluidized Riser Simulator. Kinetics and Model Validation. *Fuel* **2018**, *216*, 101–109. [CrossRef]
51. Adamu, S.; Hossain, M.M. Kinetics of Steam Gasification of Glucose as a Biomass Surrogate over Ni/Ce–Mesoporous Al₂O₃ in a Fluidized Bed Reactor. *Ind. Eng. Chem. Res.* **2018**, *57*, 3128–3137. [CrossRef]
52. de Lasa, H.I. Riser Simulator. U.S. Patent 5102628, 7 April 1992. Available online: <https://patents.google.com/patent/US5102628A/en> (accessed on 12 March 2024).
53. de Lasa, H. Reactor and Multifunctional Riser and Downer Simulator Incorporating the Same. U.S. Patent 10220363, 5 March 2019. Available online: <https://patents.google.com/patent/US10220363B2/en> (accessed on 12 March 2024).
54. Quddus, M. A Novel Mixed Metallic Oxygen Carrier for Chemical Looping Combustion: Preparation, Characterization and Kinetic Modeling. Ph.D. Thesis, The University of Western Ontario, London, ON, Canada, 2013.
55. Tasylov, B.A. Heterogeneous and Homogenous Decomposition of Nickel carbonyl. *Sov. Powder Metall. Met. Ceram.* **1971**, *10*, 362–366. [CrossRef]
56. Biesinger, M.; Payne, B.; Grosvenor, A.; Lau, L.; Gerson, A.; Smart, R. Resolving surface chemical states in XPS analysis of first row transition metals oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **2011**, *257*, 2717–2730. [CrossRef]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.