

UNIVERSIDADE FEDERAL DE UBERLÂNDIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

MARIA RITA COSTA TOMAZ

**SORPTION ENHANCED STEAM REFORMING OF MODEL
COMPOUNDS OF AQUEOUS FRACTION OF BIO-OIL USING
CALCIUM-DOPED NICKEL AND OXIDE CATALYSTS AND MINERAL
RESIDUE FOR HYDROGEN PRODUCTION**

*REFORMA A VAPOR DE MOLÉCULAS MODELO DA FRAÇÃO AQUOSA DO BIO-
ÓLEO COM CAPTURA DE DIÓXIDO DE CARBONO UTILIZANDO
CATALISADORES DE NÍQUEL E ÓXIDO DOPADOS DE CÁLCIO E RESÍDUO
MINERAL PARA PRODUÇÃO DE HIDROGÊNIO*

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Orientadora: Prof^ª. Dr^ª. Carla Eponina Hori.

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Reuniu-se por meio de webconferência, a Banca Examinadora, designada pelo Colegiado do Programa de Pós-graduação em Engenharia Química, assim composta: Doutora: Karen Abreu Resende - Neste Oyj/Finlândia e Professores Doutores: Alice Medeiros de Lima - DEQUI/UFSCar, Sandra Cristina Dantas - DEQ/UFTM, Sérgio Mauro da Silva Neiro - PPGEQ/UFU e Carla Eponina Hori - PPGEQ/UFU, orientadora da candidata.

Iniciando os trabalhos a presidente da mesa, Prof^a Dr^a Carla Eponina Hori, apresentou a Comissão Examinadora e a candidata, agradeceu a presença do público, e concedeu à discente a palavra para a exposição do seu trabalho. A duração da apresentação da discente e o tempo de arguição e resposta foram conforme as normas do Programa.

A seguir, a presidente concedeu a palavra, pela ordem sucessivamente aos examinadores, que passaram a arguir a candidata. Ultimada a arguição, que se desenvolveu dentro dos termos regimentais, a Banca, em sessão secreta, atribuiu o resultado final, considerando a candidata:

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Nada mais havendo a tratar foram encerrados os trabalhos. Foi lavrada a presente ata que após lida e achada conforme foi assinada pela Banca Examinadora.



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RESUMO

A presente tese de doutorado avaliou o uso de resíduos de mineração (*MW*) como adsorvente em combinação com catalisadores Ni-Al₂O₃ e Ni-MgAl₂O₄ para a reforma a vapor com captura de CO₂ (*SESR*) de etanol. Além disso, catalisadores bifuncionais de níquel suportados em óxido de zircônio e cálcio, modificados com metais alcalinos (NiCaZr, NiCaKZr e NiCaNaZr) bem como catalisadores bifuncionais de níquel suportados em CaO e alumina (NiCaAl) e aqueles dopados com céria (NiCaAlCe), foram empregados no *SESR* de compostos modelo da fração aquosa do bio-óleo. Análises termodinâmicas usando o software Chemical Equilibrium with Applications (CEA) da NASA e simulações usando o *software* Aspen Plus foram desenvolvidas para dar suporte à otimização do processo. O uso de *MW* como adsorvente no processo *SESR* oferece um método sustentável para reduzir as emissões de CO₂ e gerenciar os resíduos dos processos. Uma análise termodinâmica levou à seleção de parâmetros operacionais. Os catalisadores Ni-Al₂O₃ e Ni-MgAl₂O₄ foram preparados usando métodos de impregnação por umidade incipiente e coprecipitação, respectivamente, e misturados com *MW* em uma razão de massa de 1:1. A caracterização das amostras envolveu difração de raios X (DRX), redução à temperatura programada (*TPR*), análise termogravimétrica (ATG). Após 10 ciclos de *SESR*, ambos os catalisadores atingiram mais de 99% de conversão de bioetanol. O catalisador Ni-Al₂O₃/*MW* produziu uma fração molar máxima de H₂ de 82,2%, e o catalisador Ni-MgAl₂O₄/*MW* atingiu 75,8%. A duração do estágio de *pre-breakthrough* (*PB*) permaneceu estável ao longo de 10 ciclos, indicando boa estabilidade do material. *SESR* de compostos modelo de fração aquosa de frações de bio-óleo também foram realizados usando duas séries de catalisadores. A primeira incluiu os catalisadores bifuncionais NiCaZr, NiCaKZr e NiCaNaZr, preparados via método sol-gel de citrato. A análise termodinâmica foi conduzida para reforma a vapor convencional (*CSR*) e *SESR*, com foco na temperatura, adição de adsorvente e razão vapor/carbono. *SESR* a 500 °C e uma razão vapor/carbono de 2,25 produziram uma alta fração molar de H₂. *TPR*, DRX, TGA, fluorescência de raios X (FRX) e fisissorção de N₂ foram realizadas. TGA revelou que o catalisador NiCaNaZr teve a menor perda de capacidade de captura de CO₂ (21%). Todos os catalisadores atingiram mais de 99% de conversão de etanol e 95% de ácido acético, com altas frações molares de H₂ (> 90 mol%) durante o estágio de *PB*. A dopagem de metais alcalinos estendeu o tempo de *PB* significativamente, com NiCaKZr e NiCaNaZr mostrando 30 e 40 min, respectivamente, em comparação com 18 minutos para o catalisador não dopado. A sinterização foi observada em catalisadores gastos, indicada pelo aumento do tamanho do cristalito de Ni⁰ e CaO. A segunda série consistiu do uso dos catalisadores NiCaAl e NiCaAlCe, os quais foram preparados usando o método do citrato. *TPR*, DRX, FRX, ATG e fisissorção de N₂ foram realizados. Fases de CaO, Ca(OH)₂ e Ni⁰ foram identificadas em ambos os catalisadores, com um pico adicional de CeO₂ em NiCaAlCe. ATG mostrou que NiCaAlCe teve uma diminuição menor na capacidade de captura de CO₂ (24%) do que o catalisador sem céria (31%) após 20 ciclos. *SESR* atingiu mais de 99% de conversão de etanol e 92% de ácido acético, com frações molares de H₂ acima de 90%. Embora a céria tenha melhorado a área de superfície, ela não impactou significativamente o rendimento de H₂ ou no tempo de *PB*. As simulações mostraram que o *SESR* superou o *CSR* com maiores rendimentos de H₂ (0,70 vs. 0,43 mol H₂/mol bio-óleo) e menores emissões de CO₂ tanto no processo de reforma a vapor (10,34 vs. 27,14 kg CO₂/kg H₂) quanto na escala geral da planta (25,12 vs. 25,73 kg CO₂/kg H₂). No entanto, *SESR* teve uma eficiência térmica menor (0,32 vs. 0,49) devido à sua maior demanda de energia, exigindo mais queima de biomassa.

Palavras-chave: reforma a vapor aprimorada por sorção, compostos modelo da fração aquosa do bio-óleo, hidrogênio de alta pureza, análise termodinâmica, simulação.

ABSTRACT

The present doctoral thesis evaluated the use of mining waste (MW) as an adsorbent in combination with Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts for the sorption enhanced steam reforming (SESR) of ethanol. Additionally, nickel catalysts supported on calcium and zirconium oxide, modified with alkali metals, as well as bifunctional nickel catalysts supported on CaO and alumina (NiCaAl) and those doped with ceria (NiCaAlCe), were employed in the SESR of model compounds of the aqueous fraction of bio-oil. Thermodynamic analysis by NASA's Chemical Equilibrium with Applications (CEA) and simulations using Aspen Plus software were developed to support the optimisation of the process. These catalysts were utilised to achieve high-purity H₂ production and enhance the efficiency of the SESR process. Using MW as an adsorbent in the SESR process offers a sustainable method for reducing CO₂ emissions and managing waste from processes. A thermodynamic analysis led to selecting operational parameters. Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts were prepared using incipient wetness impregnation and coprecipitation methods, respectively, and mixed with MW at a 1:1 mass ratio. Characterisation of the samples involved X-ray diffraction (XRD), temperature programmed reduction (TPR), thermogravimetric analysis (TGA). After 10 SESR cycles, both catalysts achieved over 99% bioethanol conversion. The Ni-Al₂O₃/MW catalyst produced a maximum H₂ molar fraction of 82.2%, and the Ni-MgAl₂O₄/MW catalyst reached 75.8%. The pre-breakthrough (PB) stage duration remained stable over 10 cycles, indicating good material stability. In addition, SESR of model compounds of aqueous fraction of bio-oil fractions were also carried out using two series of catalysts. The first series included bifunctional catalysts based on nickel supported on calcium and zirconium oxide modified with alkali metals (Na and K). Thermodynamic analysis was conducted for conventional steam reforming (CSR) and SESR, focusing on temperature, adsorbent addition, and steam/carbon ratio. The SESR at 500°C and a steam/carbon ratio of 2.25 yielded a high H₂ molar fraction. Nickel-based bifunctional catalysts on calcium and zirconium oxide, modified with alkali metals were prepared using the citrate sol-gel method. TPR, XRD, TGA, X-Ray Fluorescence (XRF), and N₂ physisorption were performed. TGA revealed that the NiCaNaZr catalyst had the lowest CO₂ capture capacity loss (21%). All catalysts achieved over 99% ethanol and 95% acetic acid conversion, with high H₂ molar fractions (> 90 mol%) during the PB stage. Alkali metal doping extended the PB time significantly, with NiCaKZr and NiCaNaZr showing 30 and 40 min, respectively, compared to 18 min for the non-doped catalyst. Sintering was observed in spent catalysts, indicated by increased crystallite size of Ni⁰ and CaO. The second series consisted of bifunctional nickel catalyst supported on CaO and alumina, as well as nickel catalyst supported on CaO and alumina doped with ceria were prepared using the citrate method. XRD, XRF, TGA and N₂-physisorption were performed. XRD identified CaO, Ca(OH)₂, and Ni⁰ in both catalysts, with an additional CeO₂ peak in NiCaAlCe. TGA showed NiCaAlCe had a smaller decrease in CO₂ capture capacity (24%) than the ceria-free catalyst (31%) after 20 cycles. SESR achieved over 99% ethanol and 92% acetic acid conversion, with hydrogen molar fractions above 90%. Although ceria improved surface area, it didn't significantly impact hydrogen yield or PB time. The simulations showed that SESR outperforms CSR with higher hydrogen yields (0.70 vs. 0.43 mol H₂/mol bio-oil) and lower CO₂ emissions in both the steam reforming process (10.34 vs. 27.14 kg CO₂/kg H₂) and overall plant scale (25.12 vs. 25.73 kg CO₂/kg H₂). However, SESR had a lower thermal efficiency (0.32 vs. 0.49) due to its higher energy demand, requiring more biomass burning.

Keywords: sorption enhanced steam reforming, model compounds of the aqueous fraction of bio-oil, high-purity hydrogen, thermodynamic analysis, simulation.

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Chapter 1 – INTRODUCTION

Climate change stands as the gravest challenge of our time, posing a significant threat to the future of planet [1]. The years between 2013 and 2021 were among the ten hottest ever documented. According to data from National Centers for Environmental Information [2], global temperatures in 2021 continued to exceed the 20th century average, marking the 45th consecutive year of this trend since 1977. Over the past 140 years, annual global temperatures have increased at an average rate of 0.08 °C per decade. However, this rate has more than doubled since 1981, rising to 0.18 °C per decade.

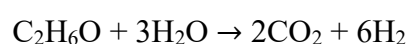
In 2018, the Intergovernmental Panel on Climate Change (IPCC) [3] released a report highlighting the need for drastic reductions in carbon dioxide (CO₂) emissions. All this effort should be carried out in order to limit the increase in global temperature to 1.5 °C by 2050. This goal requires significant changes in energy systems, land use, urban infrastructure, and industrial processes. Meeting this temperature increase target by 2050 would considerably reduce the risks of severe climate impacts and contribute to a more sustainable future. Despite the well-known environmental effects of traditional fossil fuels and their associated greenhouse gas emissions (GEE), the global industry continues to heavily rely on these sources of energy [4].

Fossil fuels primarily consist of hydrocarbons derived from coal, oil, and natural gas. However, their usage leads to significant negative consequences, primarily the production of CO₂ during combustion. This gas is closely associated with global heat retention, contributing significantly to global warming and climate change, causing serious repercussions for the planet [5]. Today, transition from fossil to renewable fuels depend on investments, highlighting the need to attract investors to the energy sector. Governments should assume a proactive role and offer clear strategic guidance, but the necessary investments far exceed public financial capacities. It is crucial to tap into the vast resources of markets and motivate private entities to contribute. Numerous financial organisations have established objectives and strategies to reduce investments in fossil fuels. There is a pressing need for greater emphasis on setting goals and plans to increase investments in clean energy transitions [6].

Unlike fossil fuels, hydrogen produces no harmful emissions when used, making it a key player in efforts to reduce GGE. In addition, it is an abundant element, which holds immense potential as an energetic vector due to its ability to store and transport energy efficiently. In 2019, during the pre-pandemic stage, global hydrogen usage reached

91 million tonnes. By 2021, this figure increased by around 3%, constituting approximately 2.5% of the world's final energy consumption. The rise in H₂ usage was primarily driven by traditional sectors like refining and industry, although new applications contributed around 40 kt, marking a 60% increase from 2020. A significant part of the increase in hydrogen demand in 2021 was supplied by H₂ generated from fossil fuels, offering no advantages in terms of climate change mitigation. Still in that year, the production of hydrogen gas with minimal GGE was less than 1 Mt. In this scenario, the majority of it comes from fossil fuels in installations that may integrate carbon capture, use, and storage technologies [7].

Various feedstocks, including methanol, ethanol, natural gas, and other can be converted into hydrogen. Unfortunately, despite their drawbacks and harmful consequences, fossil fuels currently dominate the feedstock scenario for its generation. H₂ derived from renewable biomass sources holds significant potential as a sustainable energy carrier, once appears as a carbon-neutral option and its use does not show any impact on the level of atmospheric CO₂ [8]. Its production can be accomplished through gasification and fast pyrolysis of biomass, succeeded by steam reforming of the resultant bio-oil [9]. Bio-oil is composed of a complex mixture of oxygenated compounds, including acids, alcohols, ketones, esters, ethers, aldehydes, phenols and derivatives, as well as carbohydrates and derived oligomers of lignin. It can be divided into two main fractions: the oil fraction (organic phase), with the highest commercial value, and the aqueous fraction (water-soluble phase) (AFB). The latter is generally undervalued and often discarded. In this context, its valorisation in processes such as steam reforming presents a viable alternative for utilising this material [10]. The study of the detailed reaction mechanism of AFB steam reforming is restricted due to the complex and diverse reaction pathways of the intermediates [11]. As a result, many studies use representative model molecules of AFB in their pure form, such as ethanol or acetic acid (HAc), for a simplified approach [12–14], being the overall reactions shown in Reaction 1.1 and Reaction 1.2. These compounds are often chosen for their representativeness of AFB, in addition to their characteristics such as availability, and non-toxic properties [15–17]. There are reports in the literature that also consider mixtures of model molecules applied to the conventional steam reforming process [18–20].



Reaction 1.1



Reaction 1.2

The synthesis of hydrogen from methane and methanol through steam reforming (SR) processes has been extensively studied [21–23], with established industrial procedures in place [24]. Conventional Steam Reforming (CSR) involves reacting hydrocarbons with steam in the presence of a catalyst, yielding mainly hydrogen. The conventional steam reform, although widely adopted, has significant limitations both in terms of energy efficiency and the purity of the hydrogen produced. The reforming process involves complex reactions with several intermediate by-products affecting the final hydrogen purity. Additionally, H_2 yield depends on variables such as steam to carbon ratio, temperature, and addition of adsorbent material [25]. Sorption Enhanced Steam Reforming (SESR), an alternative version, adds a sorbent material to capture and remove CO_2 , leading to increased hydrogen production and reduced greenhouse gas emissions. Zeolites, metal-based sorbents (such as calcium oxide and magnesium oxide), activated carbons and hydrotalcite-like compounds are adsorbent materials that have been employed for CO_2 capture. Among the mentioned adsorbents, calcium oxide is widely used due to its good performance and low cost, but it has some disadvantages, including poor stability and a reduction in sorption capacity after repeated carbonation and calcination cycles. Strategies have already been studied to overcome these problems, such as inserting inert materials into its structure, employing treatments like hydration, exploring new synthesis methods, and doping with metal oxides (MgO , CeO_2 , TiO_2 etc.), mixed oxides ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, Ca_2SiO_4 , $\text{Ca}_9\text{Al}_6\text{O}_{18}$) or doping with alkali metals, such as Na, K, and Li [26–29].

Oliveira and Hori [27] studied the SESR of ethanol using nickel supported on CaO , MgO , and Al_2O_3 for high-purity hydrogen production. Catalysts with 90%, 78%, and 68% CaO were prepared and characterised. 1.5 g of catalysts underwent 10 reaction cycles at 650°C with a water: ethanol molar ratio of 6:1. All achieved 100% ethanol conversion, with the 78% CaO catalyst yielding hydrogen molar fractions close to 90%. Mg and Al additions increased material stability. Vieira, Santos and Hori [30] performed a SESR of ethanol using a bifunctional Ni- CaO catalyst modified with CeO_2 and mayenite. The catalysts were characterised and tested using 2.2 g at 600°C with a steam/carbon ratio of 3 over 10 reaction cycles. Mayenite improved the active phase and support interaction, enhancing capture capacity and stability. Ceria increased the catalyst's surface area, pore size, and nickel reducibility. On the other hand, ceria-free catalyst

provided higher hydrogen molar fractions (90%). Liu et al. [31] investigated the steam reforming of a blend comprising acetone and acetic acid, chosen as model compounds of aqueous fraction of bio-oil. The authors studied the effect of various parameters such as temperature, pressure, and catalyst composition on the reaction. High conversion of the acetone and acetic acid blend into hydrogen-rich gas was achieved. About the addition of Ce, an increase in the hydrogen yields was observed. Esteban- Díez et al. [32] studied the SESR of blends of acetic acid and acetone, chosen as model compounds of aqueous phase of bio-oil. Pd/Ni-Co catalyst derived from a hydrotalcite-like material was utilised. The research focuses on understanding the impact of various operating conditions on the reforming process, and the authors highlight the importance of optimising parameters, such as temperature, pressure and feedstock composition, in order to increase efficiency in hydrogen production.

Yancheshmeh, Radfarnia and Iliuta [28] reported the use of a novel bifunctional material consisting of CeO₂-promoted Ca₉Al₆O₁₈-CaO/NiO and Ca₉Al₆O₁₈-CaO/NiO catalysts being used in the SESR of glycerol. By means of cyclic carbonation/decarbonation tests, was observed that the material with ceria in its composition achieved an excellent CaO conversion and stability. In the catalytic tests, they obtained a high H₂ purity. Hu et al. [29] investigated the impact of doping alkali metals (Li, Na, and K) into a Ni/CaO bifunctional catalyst. The aim was to assess the materials' performance in both the CO₂ capture and hydrogenation processes. The materials were prepared to have a concentration of Ni, added carbonates, and CaO at 2.5, 5, and 92.5 wt.%, respectively. The researchers discovered that the Na-Ni/CaO catalyst exhibited a notable CO₂ capture capacity (10.8 mmol/g) and a high CO₂ conversion rate (60.5%) at 650 °C. The enhancement in catalyst performance was attributed to the improvement in the catalyst surface's basicity and the formation of double salts. These factors promoted greater material stability, reducing the sintering process.

As it is trivial to insert the CO₂ adsorbent material into the SESR process, alongside the commercial CaO-based materials cited in literature [33,34], the utilisation of waste-derived CaO stands out as another practical choice. This approach not only helps to reduce waste but also allows to utilise resources that would otherwise be discarded [35]. Many of these materials are industrial waste or by-products from manufacturing processes, which can be recycled and reused for CO₂ capture [36]. This makes the process more economical and sustainable. Among the industrial wastes that can be used are lime mud, carbide slag, and waste marble powder. Natural sorbents can include limestone,

dolomite, calcite, and calcium residues from biogenesis (such as eggshells, crab shells, and scallop shells) [37]. In this sense, Barbosa, Damasceno and Hori [38] applied high limestone content mining waste in the CO₂ capture process. The material was sourced from Vale Fertilizantes, generated during an apatite concentration process. Using thermogravimetric analysis (TGA), the authors studied the influence of calcination conditions on the CO₂ capture capacity, conducting 5 cycles of calcination-hydration-carbonation reactions. The results indicate that the maximum CO₂ capture capacity decreases throughout the reaction cycles due to the sintering of the sorbent. However, the authors suggested the possibility of using the studied residue in the separation of CO₂ from combustion gases.

Despite numerous studies on the SESR process and its demonstrated advantages over conventional steam reforming (SR), a direct comparison between SR and SESR systems is still necessary, particularly in the context of energy utilisation [39]. The use of simulation of process makes possible this type of approach, and has significant importance in the field of engineering and process industries for several reasons, as it allows the design and optimisation of processes, thermodynamic modelling, thermal and material balances, environmental impact assessment, solution process problems etc [40]. Furthermore, a thermodynamic analysis is essential for optimising conditions to maximise hydrogen yield and minimise undesirable products.

This present study aims to fill a gap in the literature regarding the sorption enhanced steam reforming of mixture of model compounds of aqueous fraction of bio-oil. For this, the selected model molecules were acetic acid and ethanol. While steam reforming for hydrogen production has been extensively studied, the thermodynamic and catalytic behaviours of AFB model compounds in SESR remain underexplored. This investigation was conducted using three series of catalysts. The first, nickel on alumina and nickel on magnesium aluminate catalysts physically mixed with a mineral waste used as CO₂ sorbent. The second, bifunctional catalysts based on nickel and calcium oxide doped with aluminium and cerium. And the third, bifunctional catalysts based on nickel and calcium oxide doped with zirconium, potassium and sodium. The objectives of this study focus on investigating the Sorption Enhanced Steam Reforming (SESR) process applied to the aqueous fraction of bio-oil, primarily composed of ethanol and acetic acid, with the aim of producing high-purity hydrogen. This research seeks to advance technological developments in the field of renewable energy by proposing more efficient and sustainable solutions for hydrogen production. The innovation of this work lies in the

fact that, while numerous studies have explored conventional steam reforming of model mixtures representing the aqueous fraction of bio-oil, only a limited number have investigated the integration of sorption within the process. Notably, this study employs simulations conducted using Aspen Plus, offering a detailed exploration of the novel aspects of the proposed methodology. To achieve these objectives, the study involves the synthesis and characterisation of bifunctional catalysts based on nickel (Ni) and calcium oxide (CaO), whose properties and performance will be evaluated under various reaction conditions. Furthermore, the research includes the quantification of products across 10 reaction cycles, enabling an assessment of the stability and efficiency of the developed catalysts. Additionally, a comparative analysis of the SESR and conventional Steam Reforming (CSR) processes will be conducted through simulations, highlighting the advantages and limitations of each approach. By doing so, the study aims not only to refine steam reforming technology but also to gain an in-depth understanding of the chemical interactions underlying the SESR process, ensuring the production of high-purity hydrogen.

1.1. Outline of this thesis

Chapter 1 – General Introduction

Chapter 2 presents a sample of the literature, covering topics such as hydrogen production, the methodologies used, as well as the feedstocks used (specifically, the biomass and range of bio-oil compositions derived from it). Additionally, the chapter explores conventional and enhanced reforming processes, showing the materials that are used in this process. Another significant topic discussed is process simulation, highlighting its importance and applications.

Chapter 3 presents the methodology applied in this thesis.

Chapter 4 presents the results of the thermodynamic analysis conducted, considering the operational conditions employed in the experimental tests of this study. For this purpose, the NASA's CEA (Chemical Equilibrium with Applications) software was utilised. Through this analysis, the ideal temperature conditions and reagent compositions were determined to maximize the process efficiency.

Chapter 5 presents the study of steam reforming of ethanol using mining waste (MW) with a high limestone content as a CO₂ adsorbent material. In this study, the reaction mixture was simplified because the MW itself has a complex composition that can affect the SESR process. Therefore, this system was chosen to provide a better understanding of the material in this type of process. The fresh and spent materials were characterised by X-ray fluorescence (XRF), X-ray diffraction (XRD), temperature-programmed reduction (TPR), and thermogravimetric analysis (TGA).

Chapter 6 involves the use of bifunctional catalysts based on nickel and calcium oxide doped with aluminium and cerium in the SESR of ethanol and acetic acid blend, utilised as model compounds of aqueous fraction of bio-oil. The fresh and spent materials were characterised by XRF, XRD, TPR, TGA, and N₂-physisorption.

Chapter 7 involves the study of sorption enhanced steam reforming of bio-oil model compounds (ethanol and acetic acid blend) using bifunctional catalysts based on nickel and calcium oxide doped with zirconium, potassium and sodium. Various characterisation techniques, including XRF, XRD, TPR, TGA, and N₂-physisorption, were employed to analyse both the fresh and spent materials.

Chapter 8 comprises the results obtained from the simulation of two steam reforming plants: one conventional and the other with enhanced CO₂ capture. The study considered the same reaction mixture used in the catalytic tests. The results include the energy efficiency of the plant, hydrogen yield, and CO₂ emissions per unit mass of hydrogen produced.

Chapter 9 summarizes the recommendations of approaches for future work.

Chapter 10 lists the references of works cited in this thesis.

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Chapter 2 – STATE OF THE ART

2.1. Hydrogen

Hydrogen stands as the most abundant element in the Universe, existing in water and organic compounds. While it is also present in various combinations with other elements, its occurrence in pure gaseous form is uncommon. In contrast to other carbon-based fuels like petroleum, graphite, or paraffin, hydrogen exhibits a higher energy during combustion. To put it in perspective, the amount of energy per unit of mass released in combustion is 2.4 and 2.8 times greater than that of burning methane and gasoline, respectively [41].

The primary pathways for hydrogen production fall into four main categories: thermochemical, electrolytic, biological processes, and direct water solar splitting. In the thermochemical process, fossil fuels feedstock is utilised to generate hydrogen. At present, steam methane reforming (SMR) remains the foremost and economically optimal technique for generating hydrogen [41]. This process depends on natural gas and coal gasification, predominantly from methane gas mixed with other hydrocarbons. The steam reforming of methane typically involves several steps: desulphurisation, steam reforming, water-gas shift reaction and purification [42]. Alternative thermochemical routes include partial oxidation, thermal reforming, coal gasification, pyrolysis, and supercritical water gasification [41]. In general, in order to make the process more sustainable, the use of carbon capture and storage (CCS) is essential, once it directly addresses the issue of CO₂ emissions, which are a significant driver of climate change [41].

There are nine color-codes used to designate hydrogen, which correspond to the source or the method employed for its production. The codes include: green, blue, grey, brown or black, turquoise, purple, pink, red, and white [43]. In the Figure 2.1, the hydrogen colour-based classification is shown, relating it to the fuel, process and showing the products generated in the process.

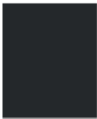
	Colour	Fuel	Process	Products
	Brown/Black	Coal	Steam reforming or gasification	$H_2 + CO_2$ (released)
	White	N/A	Naturally occurring	H_2
	Grey	Natural Gas	Steam reforming	$H_2 + CO_2$ (released)
	Blue	Natural Gas	Steam reforming	$H_2 + CO_2$ (% captured and stored)
	Turquoise	Natural Gas	Pyrolysis	$H_2 + C$ (solid)
	Red	Nuclear Power	Catalytic splitting	$H_2 + O_2$
	Purple/Pink	Nuclear Power	Electrolysis	$H_2 + O_2$
	Yellow	Solar Power	Electrolysis	$H_2 + O_2$
	Green	Renewable Electricity	Electrolysis	$H_2 + O_2$

Figure 2.1. Hydrogen colour-based classification [44].

While the majority of H_2 is currently derived from hydrocarbons, there is a growing interest in utilising renewable resources to produce green hydrogen. Hydrogen with a low-carbon footprint has the potential to significantly reduce energy-related CO_2 emissions and play a role in limiting the global temperature rise to $2^\circ C$. In this context, green hydrogen can be produced from water or biomass-derived compounds [45].

Water splitting uses an electrical current (electrolysis) passing through two electrodes to break water into hydrogen and oxygen. But others sources of energy can be applied in the splitting process, such as thermal energy (thermolysis), photonic energy (photo-electrolysis) and biophotolysis, by using microorganisms [45]. In Table 2.1 is summarised the hydrogen production technologies from water.

Table 2.1. Hydrogen Production Technologies from water [45].

Technology	Energy Source	Operating conditions	Maturity
Electrolysis	Electricity	> 30 bar 50 – 900 °C	Commercial
Thermolysis	Heat	2500 < °C < 1000 °C	Research and development
Photoelectrolysis	Solar	Ambient conditions	Research and development
Biophotolysis	Microorganism metabolism	Ambient conditions	Research and development

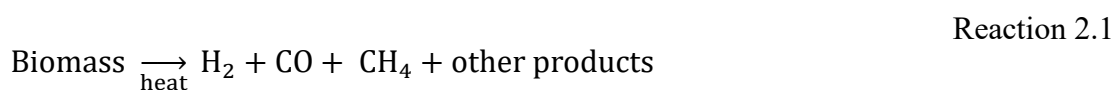
Biomass is a renewable source of primary energy derived from plants and animal materials, which are considered potential resources for fuels and chemical feedstock [46]. There are two approaches to convert biomass into hydrogen: the biological method and the thermochemical method. The thermochemical method is faster and yields more hydrogen. Table 2.2 outlines the key technologies for both processes, the energy source type, operational conditions, and the process development stage [45].

Table 2.2. Hydrogen Production Technologies from biomass [45].

Technology	Principle	Energy source	Operating conditions	Maturity
Dark fermentation	Biological	Carbohydrate-rich substrates	Anoxic conditions	Research and development
Photofermentative	Biological	Small organic molecules	Anaerobic conditions	Research and development
Pyrolysis	Thermochemical	Dried biomass	300 – 1000 °C absence of O ₂	Commercial
Gasification	Thermochemical	Dried biomass	800 – 900 °C	Commercial
Hydrothermal liquefaction*	Thermochemical	Wet biomass	250 – 370 °C 4 – 22 MPa	Research and development
Steam reforming	Thermochemical	Biomass-derived liquids	800 – 1000 °C	Commercial

Hydrogen generation from biomass is technically viable and has economic potential, especially in developed countries with the infrastructure and resources to manage the process efficiently [48]. However, economic viability can depend on factors such as biomass availability, processing costs, and regional policy support.[47]. It is expected that by 2050, approximately 25% of energy demand will be fulfilled through

biomass utilisation [48]. This is advantageous as biomass aids in reducing CO₂ emissions and sequesters CO₂ from the environment, presenting a carbon-neutral emission scenario. Thermochemical processes for producing hydrogen from biomass include pyrolysis, gasification, liquefaction and hydrothermolysis. Pyrolysis refers to the burning of biomass without oxygen. Biomass is heated to extremely high temperatures leading to the generation of gases, liquids and charcoal. While the majority of pyrolysis-related research has concentrated on the generation of liquid biofuels, it is noteworthy that hydrogen can be generated directly under conditions of elevated residence time and temperature, following the Reaction 2.1.



Following gasification, the gases from pyrolysis can be reformed again to obtain hydrogen. Gasification involves the transformation of biomass into a combustible gas, known as synthesis gas, by using a gasifying agent such as water vapor or CO₂. Synthesis gas has H₂, CO, and other components where hydrogen is recovered in additional steps. Liquefaction is a process that involves heating solid biomass products and other materials under specific pressures to form oils. This hydrogen may be further extracted from the bio-oil. Hydrothermolysis is an autohydrolysis process whereby water at elevated pressures and temperatures acts on biomass. As a result, hydrogen is produced through this process. Having exposed the concepts, it is clear that all processes are characterised by unique features, advantages, challenges. The choice from amongst them is dependent on several factors like the composition of the biomass, the desired operating conditions, and the objective for producing hydrogen [49–52].

2.2. Biomass

2.2.1 Structural composition

Typically, biomass is composed of three majority groups of polymers: cellulose, hemicellulose and lignin. The combinations of these polymers is called “lignocellulose”, constituting approximately half of the plant material generated through photosynthesis, standing as the most abundant renewable organic resource on Earth [53,54]. Small amounts of lipids, proteins, simple sugars and starches are also present in the structure, as well inorganic constituents and a fraction of water. The analysis of the structure of biomass is crucial in the advancement of processes to produce other fuels and chemical

products, as well as in the study of the combustion phenomenon. Furthermore, it plays a significant role in estimating the highest calorific value of biomass [54].

2.2.2 Feedstock analysis

The assessment of biomass is a crucial step in determining its value as a raw material for pyrolysis, also for other process, e.g. liquefaction, gasification etc. This involves analysing reaction conditions and predicting the behaviour of the resulting product. Several types of analysis are carried out, such as proximate analysis, ultimate analysis, fibre analysis, inorganic metals in feedstock, thermal and kinetic analysis. Proximate and ultimate analysis are the simplest and most common, and the data obtained from them are of great use in understanding the composition of biomass [53].

Proximate analysis is conducted to identify the four fundamental fractions of feedstock: (a) moisture, (b) fixed carbon (the non-volatile fraction of biomass), (c) volatile matter (constituting the components of biomass, excluding water, released as gases and vapours at high temperatures in the absence of oxygen), and (d) ash (the inorganic residue that remains after combustion). Biomass with a high amount of volatile matter demonstrates more efficient conversion compared to that with a high fixed carbon content. In theoretical terms, biomass containing a higher volatile fraction may be more suitable for bio-oil production, while that with a higher fixed carbon content may be more suitable for bio-char production [55].

Ultimate analysis provides more sensitive data than the results obtained by proximate analysis. In this technique, the elements carbon, hydrogen, sulphur, oxygen and nitrogen in the material are determined. The proportion of these elements allows for a more accurate comparison between raw materials, and the results can be used to calculate the calorific value of the raw material [55].

2.2.3 Future of biomass

The prospect of using biomass as an energy source in the near future is increasingly clear, and it is necessary that the demand for this raw material be supplied in a sustainable way. For example, a raw material extracted from sensitive environmental areas, where there may be a risk of loss of diversity and natural habitat, as well as degradation of river basins, would be of little use. Therefore, the use of sustainable biomass is essential [54]. The future of biomass heating relies on the evolution of fossil fuel markets and policy decisions related to the heating sector. The European Biomass

Association (AEBIOM) estimates for 2030 a 300 Mt of biomass being used in European market, which is 80 Mtoe higher than predicted for 2020 decade. In this scenario, around two thirds will be used for heat, 15% for electricity, mainly for cogeneration units and the rest for biofuels [56]. According to AEBIOM, the guiding principle for future biomass strategy should be efficiency. The primary objective is to optimize the contribution of biomass to overall energy consumption while keeping costs low for consumers. The future priorities for the deployment of biomass are focused on bioheat, followed by transportation fuels, and electricity generated through heat-driven cogeneration units.

2.2.4 Bio-oil

Bio-oils are obtained through some processes, such as from liquefaction of ligno biomass and pyrolysis, which is the thermal decomposition of organic materials from biomass in the absence of oxygen [57]. It comprises a blend of organic compounds, primarily consisting of acids, alcohols, aldehydes, esters, ketones, and phenols. The liquid generally has a dark brown hue, a free-flowing consistency, and is characterised by a unique smoky aroma. The organic acids cause bio-oil to be acidic, with a pH of about 2.3 to 3.0 [58,59].

This material typically undergoes separation into aqueous and organic phases. The aqueous phase contains water-soluble compounds, such as acids and phenols. Acetic acid is present in this composition, and the content of this carboxylic acid is significantly high, regardless of the nature of the initial biomass. The organic phase comprises a mixture of hydrocarbons, oxygenated compounds, and other organic substances. The composition can vary depending on the feedstock and the specific conditions of the pyrolysis process [52,60]. Diebold [59] published a review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. The author very clearly and succinctly presents a table of compounds identified in bio-oils and similar pyrolysis products. The described process is schematized in the Figure 2.2, with an indication of how hydrogen is obtained from biomass.

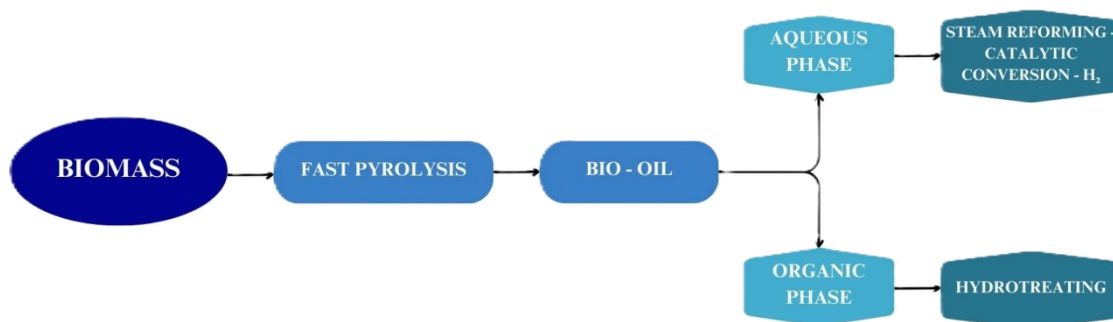


Figure 2.2. H₂ production from bio-oil. Adapted from Mukarakate et al. [60].

Among the advantages of using bio-oil, it has a higher energy density than biomass, and can be easily stored and transported. Furthermore, this product can be used as a renewable liquid fuel or in chemical production. The aqueous phase of bio-oil contains mainly carbohydrate-derived compounds, consisting of 20% organics and 80% water. Steam reforming the aqueous phase of bio-oil presents challenges, due to the thermal instability of oxygenated compounds and their extremely heterogeneous composition [9]. This characteristic is related to factors that influence the pyrolysis of biomass and the storage of bio-oil, contributing to this variation in its compositions. A summary of the literature relating to the composition of fast pyrolysis oils is presented in Table 2.3.

In this study, acetic acid and ethanol were considered as representative molecules of the aqueous fraction of bio-oil. Despite existing in smaller quantities (0.6-1.4 wt.%), ethanol was chosen as a representative of alcohols because it has a longer carbon chain (2C) compared to methanol (1C). Furthermore, for being a less toxic compound and considered a clean fuel.

Table 2.3. Compounds identified in bio-oils. Adapted from Diebold [59].

Ketones	wt%	Phenols	wt%	Acids	wt%
Acetone	2.8	Phenol	0.1-3.8	Formic (methanoic)	0.3-9.1
2-Butenone	-	2-Methyl phenol	0.1-0.6	Acetic (ethanoic)	0.5-12
2-Butanone	0.3-0.9	3-Methyl phenol	0.1-0.4	Propanoic	0.1-1.8
2,3 Butandione	-	4-Methyl phenol	0.1-0.5	Hydroxyacetic	0.1-0.9
Cyclo pentanone	-	2,3 Dimethyl phenol	0.1-0.5	2-Butenic(crotonic)	-
2-Pentanone	-	2,4 Dimethyl phenol	0.1-0.3	Butanoic	0.1-0.5
3-Pentanone	-	2,5 Dimethyl phenol	0.2-0.4	Pentanoic (valeric)	0.1-0.8
2-Cyclopentenone	-	2,6 Dimethyl phenol	0.1-0.4	2-Me butenoic	-
2,3 Pentenedione	0.2-0.4	3,5 Dimethyl phenol	---	4-Oxypentanoic	0.1-0.4
3Me2cyclopenten2ol1one	0.1-0.6	2-Ethylphenol	0.1-1.3	4-Hydroxypentanoic	-
Me-cyclopentanone	-	2,4,6 TriMe phenol	0.3	Hexanoic (caproic)	0.1-0.3
2-Hexanone	-	1,2 DiOH benzene	0.1-0.7	Benzoic	0.2-0.3
Cyclo hexanone	trace	1,3 DiOH benzene	0.1-0.3	Heptanoic	0.3
Methylcyclohexanone	-	1,4 DiOH benzene	0.1-1.9		
2-Et-cyclopentanone	0.2-0.3	4-Methoxy catechol	0.6		
Dimethylcyclopentanone	0.3	1,2,3 Tri-OH-benzene	0.6		
Trimethylcyclopentenone	0.1-0.5				
Trimethylcyclopentanone	0.2-0.4				

Misc. Oxygenates	wt%	Furans	wt%	Esters	wt%
Hydroxyacetaldehyde	0.9-13	Furan	0.1-0.3	Methyl formate	0.1-0.9
Acetol (hydroxyacetone)	0.7-7.4	2-Methyl furan	0.1-0.2	Methyl acetate	-
Methylal	-	2-Furanone	0.1-1.1	Methyl propionate	-
Dimethyl acetal	-	Furfural	0.1-1.1	Butyrolactone	0.1-0.9
Acetal	0.1-0.2	3-Methyl-2(3h)furanone	0.1	Methyl Crotonate	-
Acetyloxy-2-propanone	0.8	Furfural alcohol	0.1-5.2	Methyl n-butyrate	-
2-OH-3-Me-2-cyclopentene-1-	0.1-0.5	Furoic acid	0.4	Valerolactone	0.2
Methyl cyclopentenolone	0.1-1.9	Methyl furoate	-	Angelicalactone	0.1-1.2
1-Acetyloxy-2-propanone	0.1	5-Methylfurfural	0.1-0.6	Methyl valerate	-
2-Methyl-3-hydroxy-2-pyrone	0.2-0.4	5-OH-methyl-2-furfural	0.3-2.2		
2-Methoxy-4-methylanisole	0.1-0.4	Dimethyl furan	-		
4-OH-3-methoxybenzaldehyde	0.1-1.1				
Maltol	-				

Guaiacols	wt%	Aldehyde	wt%	Syringols	wt%
2-Methoxy phenol	0.1-1.1	Formaldehyde	0.1-3.3	2,6-DiOMe phenol	0.7-4.8
4-Methyl guaiacol	0.1-1.9	Acetaldehyde	0.1-8.5	Methyl syringol	0.1-0.3
Ethyl guaiacol	0.1-0.6	2-Propenal (acrolein)	0.6-0.9	4-Ethyl syringol	0.2
Eugenol	0.1-2.3	2-Butenal	trace	Propyl syringol	0.1-1.5
Isoeugenol	0.1-7.2	2-Methyl-2-butenal	0.1-0.5	Syringaldehyde	0.1-1.5
4-Propylguaiacol	0.1-0.4	Pentanal	0.5	4-Propenylsyringol	0.1-0.3
Acetoguaiacone	0.8	Ethanedial	0.9-4.6	4-OH-3,5-diOMe phenyl ethanone	0.1-0.3
Propioguaiacone	0.8				

Sugars	wt%	Alcohols	wt%	Alkenes	wt%
Levogluconan	0.4-1.4	Methanol	0.4-2.4	Dimethylcyclopentene	0.7
Glucose	0.4-1.3	Ethanol	0.6-1.4		
Fructose	0.7-2.9	2-Propene-1-ol	-		
D-xylose	0.1-1.4	Isobutanol	-		
D-Arabinose	0.1	3-Methyl-1-butanol	-		
Cellobiosan	0.6-3.2	Ethylene glycol	0.7-2.0	Aromatic and Nitrogen compounds	0 wt%
1,6 Anhydroglucofuranose	3.1				

2.3. Steam Reforming process

2.3.1 Conventional steam reforming process (CSR)

The conventional steam reforming process is usually conducted at high temperatures, being the most common method of producing H_2 in chemical industries, providing products with high concentrations of H_2 (more than 70% in dry volume) [61]. The endothermic reaction takes place in a reformer loaded with catalyst. The typical steam-to-carbon molar ratio ranges from 2 to 6, and the reformer is heated by external gas burners. To enhance both hydrogen yield and purity, the incorporation of water gas shift reactors (at high and low temperatures) and purification units are necessary [62]. Industrially, this chemical process occurs in four stages as illustrated in Figure 2.3.

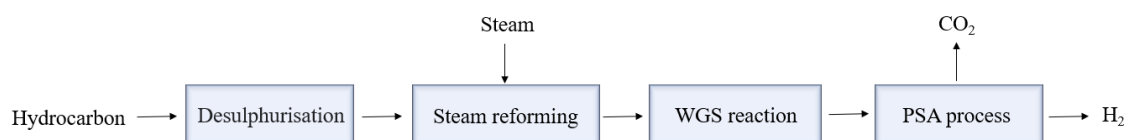
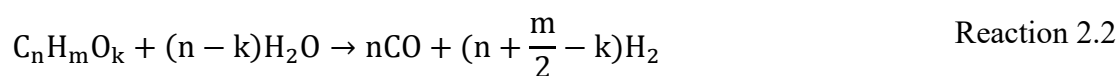


Figure 2.3. Block diagram: stages of steam reforming of an adapted industrial-scale hydrocarbon. Adapted from Cheng, Dupont and Twigg [63].

In the initial stage, the hydrocarbon undergoes purification to eliminate sulfur-containing compounds, preventing catalytic deactivation. In the second phase, an endothermic reaction takes place between the hydrocarbon and water vapor at high temperatures and pressure. A solid catalyst is employed, leading to the production of primarily H_2 , CO , CO_2 , and CH_4 [64]. The overall steam reforming reaction of hydrocarbons can be represented by Reaction 2.2.



In the third step, the water gas shift reaction (Reaction 2.3) takes place, the CO produced reacts with the vapour water, producing CO_2 and hydrogen. In the fourth phase, the WGS reaction by-products undergo a process of carbon dioxide removal using pressure swing adsorption (PSA), resulting in hydrogen with a high purity [64].



The catalysts used in the reform process vary significantly depending on the feedstock used. Nickel-based catalysts have demonstrated great suitability in the steam

reforming reaction of hydrocarbons. Its attractiveness lies in its considerably lower cost, combined with a catalytic activity that is comparable to catalysts based on noble metals, such as platinum (Pt), rhodium (Rh) and palladium (Pd) [65]. In the reforming process, nickel-alumina catalysts are often used, however, an associated disadvantage is the propensity for coke formation on their surface. For nickel-based catalysts to be considered viable, it is essential that the nickel particles are small and highly dispersed on the surface of the support, with high surface areas and porosity. These characteristics guarantee effective contact of the reactants with the active sites of the catalyst. Commonly used supports include mixtures of oxides of aluminium, silicon, magnesium, lanthanum, cerium, calcium, among others [66].

The literature contains a variety of studies on the steam reforming with the aim of generating hydrogen. Mathure et al. [67] conducted an investigation into ethanol steam reforming employing a commercial nickel-alumina-magnesium oxide catalyst. The material was characterised via X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) specific surface area (SSA) analysis, and energy-dispersive spectroscopy (EDS). The catalytic tests were performed in a fixed bed reactor at ambient pressure, addressing the effects of several parameters. Among them, the influence of temperature (400-600 °C), the molar ratio of steam to ethanol in the feed ($S/E = 3:1 - 18:1$), the feed flow rate ($W/F_{EtOH} = 46.2-555.25 \text{ g}_{cat}min/mol$), catalyst particle size (0.75 - 2.25 mm) and flow time analysis were considered. The best S/E and W/F_{EtOH} conditions ($g_{cat}min/mol$) were 12:1 and >185 to obtain the highest conversion (>95%), and 12:1 and >110 to obtain the highest hydrogen yield (3 mol H_2 /mol ethanol), at a temperature of 600 °C. Regarding the performance of the catalyst, the authors highlighted the feasibility of using this material in the process. The formation of coke on the surface of the catalyst was observed, but not enough to compromise the activity of the material. The data obtained from the tests was adjusted to kinetic models in the form of power law and the Eley-Rideal mechanism, and as a result the authors calculated the activation energy (23 kJ/mol). However, it was emphasised the need to obtain a more elaborate reaction scheme to describe the complex reactions that occur during the reform process.

Kumar, Singh and Sinha [68] carried out a study on catalyst modification strategies to increase catalyst activity and stability. The authors highlighted that in the acetic acid reforming process, the deposition of coke on the surface of the catalyst is a recurring problem. Therefore, the work suggests the use of catalysts based on Rh and Pt, since both exhibit excellent activity, long-term stability and less coke formation.

However, they point out that the high cost prevents the use of these materials on an industrial scale. In this sense, the work suggests the use of lower-cost catalysts, such as those based on nickel. The use of this pure material is discussed, since the formation of coke on its surface is an obstacle. The authors indicate that this problem can be overcome by supporting this type of catalyst on $\text{ZrO}_2/\text{CeO}_2/\text{LaO}_2$. The addition of alkaline and alkaline earth metals, such as Mg and K, over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst is also proposed, once oxide supports used for steam reforming reactions (such as Al_2O_3 , CaO and MgO) suffer deactivation problems. Some other suggestions emerge throughout the study, such as the incorporation of small amounts of oxygen during the reaction, aiming to gasify the deposited C during the process.

Reeve et al. [69] carried out a kinetic study of the steam reforming of acetic acid (HAc) using an 18 wt.% NiO /calcium aluminate catalyst. The reaction took place at atmospheric pressure, at temperatures of 550, 620 and 650 °C, with S/C ratios of 3, 3.5 and 4. The molar fraction of HAc: H_2O feed ranged from 0.048-0.342 to 0.058-0.473. The feed volumetric flow rate in STP (cm^3/min) of HAc solution and water varied from 0.109 to 0.921, with nitrogen flow varying from 150 to 800 mL/min. As a result, the authors observed that the conversion of acetic acid was related directly with the temperature and the ratio of weight of catalyst to molar flow rate of ethanol. For example, for S/C of 3, in a W/F range of 0 to 12, the conversion of HAc at 550, 620 and 650°C varied from 90-100, 70-98 and 75-90%, respectively. Regarding the rate of carbon deposition in the catalysts, a low level was observed (average of 1% of the feed), this result being correlated to operation at high temperature and with excess water. The experimental data were fitted using gPROMS, a process modelling and simulation software. Four kinetic models were proposed, with the model consisting of steam reforming of HAc, decomposition of HAc in synthesis gas and WGS, being considered the most accurate. For process design and optimisation purposes, the importance of this study was the possibility of grouping the data obtained with other models already published, in order to enable the study of Ni-catalyst in the steam reforming of more complex mixtures representing bio-oils. or organic waste streams, under conditions of excess steam and temperatures above 550 °C, and where the WGS reaction would be an essential common step.

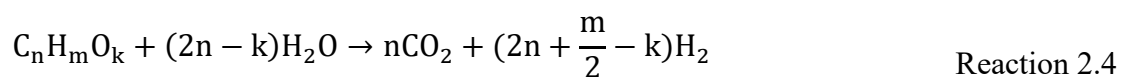
Sabokmalek et al. [70] presented a study of the effect of Ni loading on the $\text{Ni}/\text{CaO}-\text{Al}_2\text{O}_3$ catalyst in the glycerol reforming process. The nickel loads tested were 2.5, 5, 10, 15 and 20%. The $\text{CaO}-\text{Al}_2\text{O}_3$ support was synthesized by mechanochemical method, and

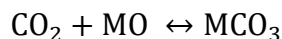
in order to have a catalyst with an active phase, different amounts of Ni were impregnated into the support via the wet impregnation method. The material was then characterised via X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), temperature programmed oxidation (TPO), temperature programmed desorption (TPD), temperature programmed reduction (TPR), Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). The catalytic tests were carried out by coupling 0.1 g of catalyst in a quartz microreactor with a fixed bed. The material was reduced under a pure hydrogen atmosphere (30 mL/min), at 700 °C for 2 h. The operating conditions for the reaction were temperatures ranging from 500 to 700 °C, atmospheric pressure, stream of water-glycerol mixture (WGMR = 9), total inlet feed (50 ml/min), with liquid mixture and N₂. The reactions were carried out by keeping the catalyst reacting for 5h at each temperature (500, 550, 600, 650 and 700 °C). The 15%Ni/CaO–Al₂O₃ catalyst showed better catalytic performance, with glycerol conversion of 99.4% at 700 °C. The results obtained in the characterisations showed that this catalyst presented high reducibility, proper BET area (96.6 m²/g), and suitable basicity. In general, all catalysts were stable over the reaction time, and the conversion of glycerol decreased with increasing gas hourly space velocity and calcination temperature.

Extensive information is available in the literature on the effectiveness of Ni catalysts in the conventional steam reforming process. Likewise, several works are reported using different raw materials in this process [23,71–74]. Although CSR is a well-established and widely used method for producing hydrogen, it has some disadvantages such as CO₂ emissions. However, research and development are currently underway with the aim of investigating alternative and more sustainable methods of hydrogen production, aiming to minimize environmental impact, such as sorption enhanced steam reforming [75,76].

2.3.2 Sorption Enhanced Steam Reforming (SESR)

Compared to the conventional process, the sorption enhanced steam reforming can lead to a higher fuel conversion and purity hydrogen. In this type of operation, CO₂ is captured in situ, causing a shift in equilibrium towards hydrogen production, as shown in Reaction 2.4 and Reaction 2.5 [77].





Reaction 2.5

Where M can be, for example, Mg, Ca, Sr and Ba.

In this sense, the reforming reaction, CO₂ capture and WGS will take place in a single reactor. The carbon dioxide will be removed from the gas phase by the adsorbent material, causing the reaction shift towards hydrogen production. The reaction products will be mainly H₂, H₂O and, in smaller quantities, CO, CO₂ and CH₄ [75,78]. Figure 2.4 illustrates how Le Chatelier's principle works in the CSR and SESR processes.

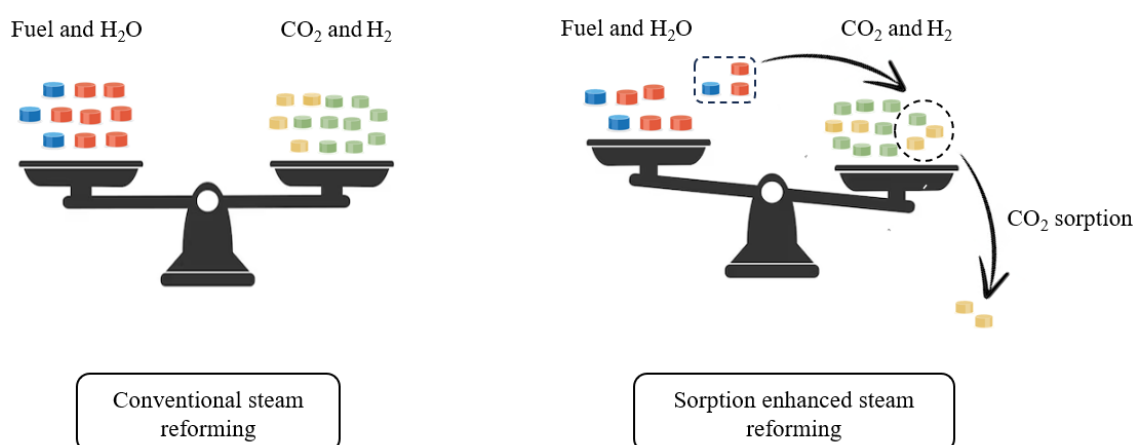


Figure 2.4. Representation of the CSR and SESR utilising Le Chatelier's principle.

Adapted from Oliveira [78].

This method facilitates the production of hydrogen at relatively low temperatures ranging from 550 to 700 °C [27]. Among its benefits are cost savings in high-purity hydrogen production and improved overall thermal efficiency [30]. Additionally, this process involves simultaneous endothermic reforming and exothermic water-gas shift reactions, reducing the need for complex purification steps and lowering reaction temperatures [79]. It is also reported that there is a decrease in carbon formation in the catalysts [80,81]. Key factors influencing successful outcomes include identifying efficient catalysts and adsorbent materials capable of functioning effectively under challenging conditions [28,64].

Some works categorise the evolution of gas composition in SESR into three stages, i.e., pre-breakthrough, breakthrough and post-breakthrough [26,27,30,79]. In the first stage (identified as I in Figure 2.5), CO₂ is quickly captured by the sorbent material, through the CaO carbonation reaction, resulting in a high concentration of H₂. When the sorbent material begins to saturate, the kinetically controlled phase of the carbonation

reaction concludes, leading to a gradual rise in CO₂ during the breakthrough stage. Thus, there is a transition from the steam reforming operation with CO₂ capture to conventional steam reforming (breakthrough stage, identified as II in Figure 2.5). In the post-breakthrough stage (III), the absorbent is practically saturated, resulting only in the steam reforming and WGS reactions, that is, conventional steam reforming.

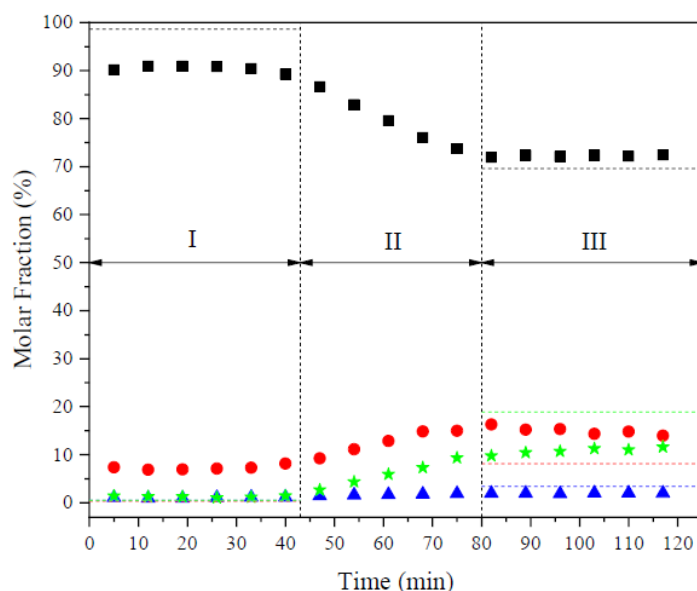


Figure 2.5. Product distribution found on the second cycle of SESR of ethanol bounded by the three typical stages (I, II, III: pre-breakthrough, breakthrough and post-breakthrough stages, respectively). Operational conditions: Steam/ethanol ratio = 6, $T_{\text{reaction}} = 600\text{ }^{\circ}\text{C}$, 1 atm, 1.5 g of catalyst, $W/F = 11.41\text{ min.mg}_{\text{cat.mL}}^{-1}$. Legend: ■ H₂; ● CO; ▲ CH₄; ★ CO₂. Dashed line: thermodynamic equilibrium. Oliveira and Hori [27].

In addition to the SESR process, others advanced reforming processes are known, as the chemical looping steam reforming (CLSR) and the sorption enhanced chemical looping steam reforming (SE-CLSR). In the first, the oxygen transfer material (OTM), also known as an oxygen carrier, is a solid material that is fed together with steam and the raw material to be reformed. OTM plays the role of supplying oxygen, inducing oxidation of the reforming material. During the process, the oxygen carrier undergoes reduction and is subsequently regenerated in a separate reactor through oxidation, resulting in notable heat generation. One of the advantages of this process lies in the energy gain in the plant. Several materials, such as Cu, Ce, Ni, among others, have been studied as oxygen transporters. The addition of these materials during catalytic tests contributed to the increase in H₂ selectivity, as well as to the conversion of the raw

material. Furthermore, this addition resulted in greater stability of the catalyst and a reduction in the formation of coke on its surface. In this context, nickel-based OTMs stand out, not only for their superior regeneration capacity, but also for acting as catalysts in reforming reactions when they are in their reduced form. The combination of SESR processes with CLSR appears as an option that maximizes the benefits that both processes present. For example, hydrogen can be obtained with high yield and purity, operating in an autothermal mode. In addition to energy gains in the plant and the need for separation processes is minimized, as purer products are obtained, almost free from the presence of CO₂ [75,82].

Several studies have been carried out regarding sorption enhanced steam reforming, for different feedstocks, such as glycerol, ethanol, propane, methane, among others [83–86]. Some of these works will be cited here in order to expand the panorama of this field of research. SESR of ethanol was studied by Menendez, Gracinsky and Amadeo [87]. In their study, the authors used NiMgAl hydrotalcite as the catalyst precursor and calcium oxide as the sorbent material. The material was subjected to 20 carbonation and regeneration cycles to analyse its capture capacity. The catalytic tests were carried out in a fixed-bed reactor using a total mass of 650 mg of catalyst mixed with 880 mg of CaO, with 4 different layer configurations of these two materials. The authors found that when the catalyst was mixed with the sorbent, greater purity of hydrogen was obtained in the pre-breakthrough stage. The highest hydrogen yields were obtained at 500 °C, with H₂ purity greater than 95%. This work shows that the use of a catalyst physically mixed with a sorbent material has its relevance, being an option to bifunctional catalysts in reforming processes.

Liu et al. [88] studied the SESR of ethanol using a bifunctional Ni-CaO-Al₂O₃ catalyst, prepared via the citrate sol-gel synthetic route. The prepared catalysts were labelled as Ni/Al/Ca-x, with x indicating the mass percentage of CaO in the bi-functional materials (0, 95% and 100%). After reduction, the weight fraction of Ni in each catalytic material was maintained at 10 wt.%. The characterisations performed were X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), N₂-physisorption, Temperature programmed reduction (TPR) and Scanning Electron Microscopy (SEM). Catalytic tests were carried out in a fixed bed quartz reactor, loaded with 50 mg of catalyst. The reduction process occurred at 850 °C for 1 h, under an atmosphere of 10% H₂/N₂ (100 ml/min). 10 reaction cycles were conducted at 600 °C lasting 30 minutes each, under conditions of steam/ethanol = 4, reaction liquid space velocity (RLSV) = 0.05

ml/min, and calcination temperature = 900 °C (10% H₂/N₂, 15min). The Ni/Al/Ca-85.5 catalyst showed a long pre-breakthrough stage even after 10 reaction cycles (18 min), and this behaviour was related to the incorporation of Al stabilizer. The characterisations showed that this catalyst presented a large surface area, abundant porosity with "fluffy" morphology. Furthermore, the best results from CO₂ sorption capacity tests (20 carbonation/calcination cycles) were obtained with this material. The highest concentration of hydrogen (96%) was obtained using this catalyst. Even after 10 cycles, the material demonstrated superior performance, exhibiting hydrogen purity of approximately 90%, indicating its potential for the reforming process.

The SESR of ethanol using MgO-modified Ni/CaO catalysts was studied by Sang et al. [16]. The catalysts were prepared via coprecipitation method, and named as 5Ni/xMgO-CaO (5Ni/xM-C, x= 10, 20, 30) and 5Ni/CaO. The characterisations conducted were XRD, field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), N₂ adsorption-desorption, inductively coupled plasma optical emission spectroscopy (ICP-OES), H₂-TPR, O₂-TPO, thermogravimetric analysis (TGA), Raman technology, In-situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFTS), and C₂H₅OH-TPD. SESRE tests were conducted in a quartz fixed-bed tubular reactor, loaded with 0.5 g of catalyst. The reaction conditions were steam-to-carbon molar ratio (S/C) of 4, reaction duration of 1h. The material was regenerated at 700 °C for 1 hr in a flow of 20 vol% H₂/N₂ (50 ml/min). From the characterisations, the authors noted that Ni and MgO were uniformly dispersed on the CaO particles, and MgO contributed to reducing the sintering of calcium oxide particles. 10 cycles of catalytic tests were carried out, and in all of them a conversion of 100% of ethanol and a production of hydrogen with purity greater than 96% were obtained for the catalyst containing 20% MgO. The pre-breakthrough stage started at 50 minutes, decreasing 15 minutes in the 10th cycle. This behaviour was related to the loss of catalyst capture capacity throughout the process. The work proved to be important in demonstrating that magnesium oxide works as a dopant, increasing the catalytic stability of the catalyst, contributing to obtaining high purity hydrogen.

Materials used in the SESR

Various adsorbent materials have been used to capture CO₂, such as zeolites, mesoporous silica, porous carbons and organic polymers (POPs), metal-organic frameworks (MOFs), hydrotalcite, organic-inorganic polymers, and metal oxides [89].

Figure 2.6 illustrates a summary of the commonly employed sorbents for CO₂ capture, along with their typical operational temperature ranges, at 1 atm. No adsorbent material is universally optimal for all CO₂ sorption conditions. Instead, the appropriateness of a specific type of sorbent is influenced by its integration with processes and infrastructure, among other factors [90]. MOFs, supported solid amines, carbon-based sorbents, zeolites, alkali carbonate-based sorbent and hydrotalcite-like compounds operate at a low temperature. While the MgO, CaO and SrO-based sorbents react at medium and high temperatures. Understanding the physicochemical characteristics that contribute to solid adsorption is a prerequisite for enhancing both gravimetric and volumetric CO₂ uptake [89]. Table 2.4 lists some adsorbent materials used in the SESR process.

Table 2.4. Different sorbents used in the sorption enhanced steam reforming process. Adapted from Aniruddha et al. [91].

	Feed	Sorbent	Ref.
1	Methane	CaO	[35]
2	Methane	Na ₂ CO ₃ -CaO	[92]
3	Glycerol	Ni-CaO-Ca ₁₂ Al ₁₄ O ₃₃	[93]
4	Methane	CaO-NiO/CaZrO ₃	[94]
5	Methanol	MgO	[95]
6	Glycerol	CaO	[96]
7	Coke Oven gas	CaO	[97]
8	Glycerol	CaO	[98]
9	Black liquor	CaO	[99]
10	Biomass air	CaO	[100]
11	Methanol	CaO	[101]
12	Phenol	MgO	[102]
13	Glycerol	CaO	[103]
14	Glycerol	CaO on γ -Al ₂ O ₃	[104]
15	Bio-oil	CeO ₂ -modified CaO/Ca ₁₂ Al ₁₄ O ₃₃	[105]
16	Organic waste	Ni/CeO ₂ -ZrO ₂ -CaO	[106]
17	Glycerol	CaO	[96]

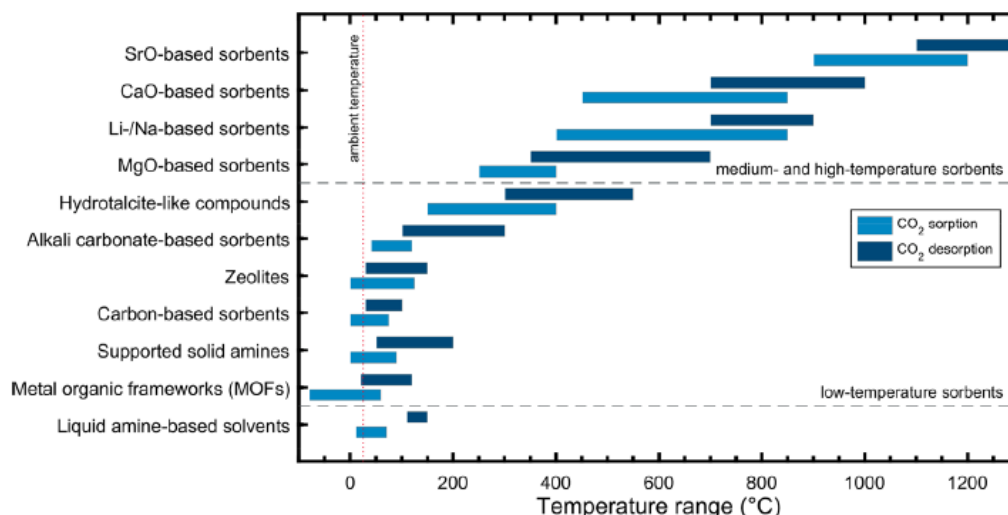


Figure 2.6. Frequently employed solid sorbents for CO₂ capture and the temperature ranges typically associated with their applications [90].

Calcium oxide for CO₂ capture

Porous metal oxides (MOs) are materials frequently used in the CO₂ capture, due properties as promising thermal stability, high availability, adsorption capacity, structural and textural properties. Compounds like alkali and alkaline-earth metal oxides (CaO and MgO) blends with CO₂ in the flue gas, leading to production of carbonates that are thermodynamically stable [89].

Calcium minerals are frequently encountered in the form of carbonates like limestone or dolomite. When subjected to elevated temperatures, leads to the release of CO₂ and the formation of calcium oxides. Consequently, calcium oxides serve as easily accessible CO₂ adsorbents [107]. The carbonation and calcination are described in Reaction 2.6 and Reaction 2.7, respectively.



CaO shows different conversion profiles depending on the pore size distributions, and this particle size is intrinsically related to the phenomena that occur on the surface of the sorbent. Dunstan et al. [90] carried out a study that explores the fundamental aspects, mechanistic insights, and recent advances in CO₂ capture at medium to high temperatures utilizing solid oxide-based sorbents. Regarding the carbonation process in the CaO-CaCO₃ system, the surface of CaO serves as the site for the nucleation of calcite (CaCO₃),

with the lateral spreading of CO_3^{2-} groups occurring layer by layer. About the kinetics, the initial surface reaction is fast and measuring it requires precise control of the reaction conditions. Nucleus formation and growth have rarely been observed at increasing rates of carbonation. The intrinsic constant rate for the reaction between CaO and CO_2 was reported as first order, in most cases, and the authors highlighted that different kinetic model have been used to describe the carbonation reaction, such as shrinking core, pore, and grain models.

Dunstan et al. [90] highlighted that the carbonation rate decreases as the available surface of CaO is covered by a layer of CaCO_3 generated, since the calcium carbonate has almost twice the volume molar compared to calcium oxide. In general, when studying the stability of the sorbent in carbonation and calcination cycles, a transition from the kinetically controlled process (fast carbonation) to the diffusion-controlled process (slow regime) is verified. Trying to explain this behaviour, the concept of a critical product layer thickness (ranging from 20 to 90 nm) was raised by the authors. Based on published works [108–110], some points of the process were summarized: the increase in CaCO_3 crystallite size is related to this fast-slow regime transition in the carbonation process, since the CaO surface is not uniformly covered by CaCO_3 . Grain boundary diffusion dominates the initial product layer diffusion when the average CaCO_3 crystallite size is small, whereas lattice diffusion becomes more dominant as the product layer diffusion continues. In summary, the transition phase between surface kinetic control and product layer diffusion is marked by a combination of pore diffusion and the gradual obstruction of small pores by the formed CaCO_3 product.

Figure 2.7 illustrates four representative scenarios depicting the evolution of the carbonation reaction. In the first case (a), an ideal scenario is showed, where almost all CaO is converted to CaCO_3 . The sharp transition from a fast to a slow carbonation regime suggests a rapid change in the rate-limiting step (from kinetic control to diffusion control). In the second scenario (b), a similar behaviour is noted, but the observed conversion values are much lower than in case (a), indicating that part of the CaO is no longer accessible to CO_2 , since some pores are blocked with CaCO_3 . In case (c), only a small fraction of CaO is converted under kinetic control. Carbonation occurs at a slower rate due to diffusion restrictions and the movement of CO_2 through a network of narrow pores, but reaches near completion in a reasonable amount of time. In the last case (d), initially, a substantial quantity of CaO is available for CO_2 under kinetic control, leading to a gradual decline in the carbonation rate. This could be assigned to the rising diffusional

transport resistance within the pore network. Ultimately, CaCO_3 blocks the smallest pores, leaving some unconverted CaO inaccessible to CO_2 .

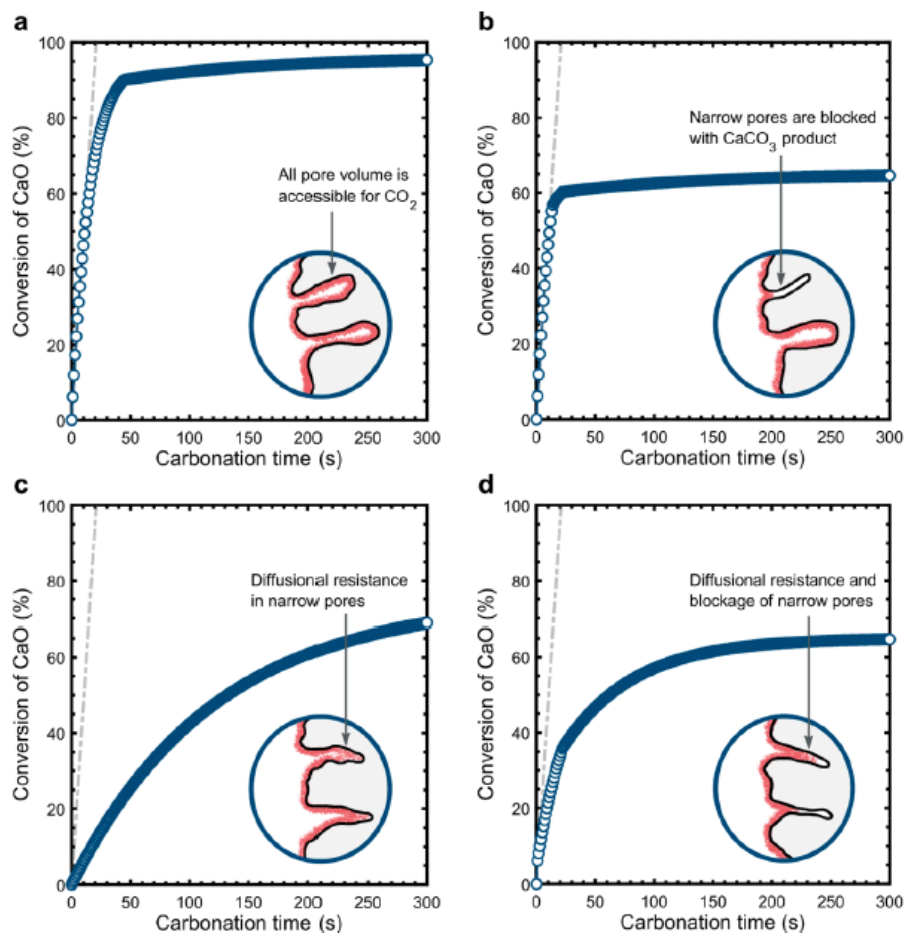


Figure 2.7. Conversion profiles of CaO typically observed for different pore size distributions [90].

In this case, the conversion rate is dictated by the diffusion of the product layer. This is a scenario commonly observed with natural CaO -based sorbents.

Regarding the calcination process in the CaO - CaCO_3 system, Dunstan et al. also made considerations about the functioning of the process mechanism. By the authors' definition, the calcination is characterised by the loss of CO_2 on the surface of the calcite. In this process, due to the strain accumulation, a mesoporous structure is formed. The remaining CO_2 is expelled from the structure, diffusing outwards, inducing porosity in the material. Further aggregation and sintering of the material lead to a reduction in surface area and porosity, leading to the closure of mesopores and the development of micrometre-sized pores. The morphological and structural properties, such as crystallite size, surface area and porosity, are influenced by the reaction conditions during calcination, as well as by the impurities present in the sorbents. These characteristics play a crucial role in determining the material's CO_2 capture capacity. On an industrial scale,

this process, due to its highly endothermic nature, requires the combustion of a fuel to provide energy to the system.

Waste for CO₂ capture

Waste statistics report from the European Commission indicates that the main generators of solid waste in 2020 were the coal industry, which encompasses mining and energy, followed by the agricultural sector, water treatment processes and the domestic sector [111]. Figure 2.8 illustrates how different sectors and households contributed to the total waste generated.

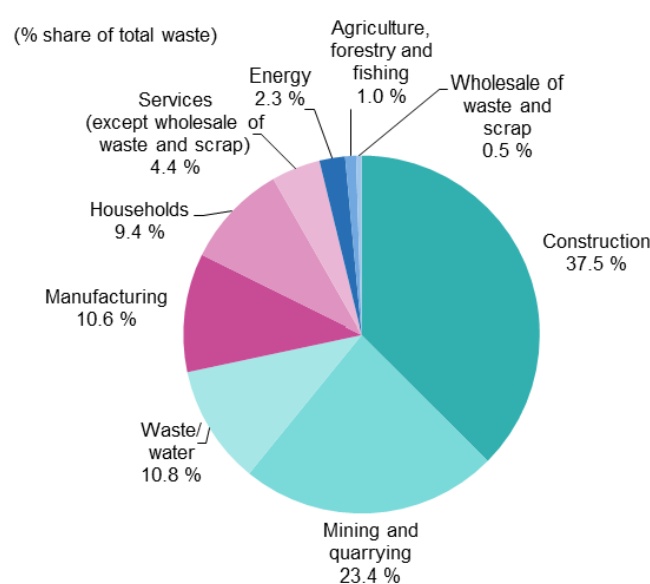


Figure 2.8. Total waste generated in 2020 [111].

The use of different waste material as CO₂ adsorbents is a strategy of great environmental, economic and technological importance. This approach offers an innovative solution to two of the biggest global challenges: sustainable waste management and climate change mitigation [112]. Table 2.5 shows a brief survey of the literature of works that test different materials as CO₂ adsorbents at high temperatures (from 100 to 850 °C). In this context, the use of mining waste as adsorbent materials for CO₂ capture is a promising strategy that simultaneously addresses waste management and climate change mitigation. In some cases, these materials demonstrate CO₂ capture capacities comparable to pure CaO, highlighting their potential in sustainable applications. This method offers significant environmental benefits, economic advantages and promotes sustainability and technological innovation.

Table 2.5. Adsorbents derived from waste for CO₂ capture.

Source	Raw material	CO ₂ capture capacity (gCO ₂ /g _{sorb})	Ref.
Pure CaO	-	0.635 at 600 °C	[92]
Coal by-products	Coal fly ashes	> 0.107 at 600 °C	[113]
	High Carbon fly ashes	> 0.02 at 120 °C	[114]
Biomass by-products	Bagasse used	> 0.06 at 150 °C	[115]
	Rice husk	> 0.32 at 150 °C	[116]
Biogenesis	Eggshell	0.5 – 0.63 at 650 °C	[117]
Natural sorbents	High limestone content from mining activity	0.4 – 0.15 at 723 – 850 °C	[38]

As shown in Table 2.4 (pg. 42) and Table 2.5, many published works have used CaO and wastes as adsorbent materials in the steam reforming process. In the study conducted by Wang et al. [118], the pros and cons of different types of sorbents are analysed, including those based on CaO, sorbents derived from hydrotalcite, bifunctional materials, sorbents containing alkali metals and sorbents made from waste. Furthermore, the strategies and techniques used to improve the sorption properties of these materials are discussed.

SESR of bio-oil

As previously showed in Table 2.3, bio-oil is rich in a variety of compounds, making the study of its reaction processes highly complex. During the reforming process, cracking, hydrogenation, deoxygenation and other transformations occur to modify the composition of the bio-oil, making the study of this process complex. Studies on steam reforming of bio-oil or bio-oil model compounds have been reported on literature. Zhao et al. [119] investigated the use of Ni-CaO-La₂O₃ catalyst in the sorption enhanced steam reforming of bio-oil with acetic acid as the aqueous phase model compound. The objective of the work was to generate high purity hydrogen using catalysts with different Ni compositions (8, 16 and 20%). The materials were prepared via sol-gel methodology, and characterised by TGA, TPR, BET, SEM, XRD and XPS. In the catalytic tests, the catalyst with 20 wt.% Ni achieved 86.02% yield of hydrogen during the pre-breakthrough stage. The authors attributed this value to sufficient Ni active sites on the surface and good Ni dispersion. The catalyst remained stable during 9 cycles, however with a

reduction in capture capacity, due to CaO sintering. Gil et al. [120] also studied sorption enhanced steam reforming (SESR), considering acetic acid as the model bio-oil compound. The authors used a Pd/Ni-Co hydrotalcite (HT)-like material as a catalyst and a CaO-based material as a CO₂ sorbent. During the catalytic tests, in the pre-breakthrough stage, the authors obtained a high yield of H₂ (84.4%), with an H₂ purity of 99.8%. A zero concentration of CO was achieved, while that of CH₄ was 0.15% and that of CO₂ was 0.02%.

A thermodynamic assessment of the potential of conventional and advanced bio-oil steam reforming processes was studied by Singh et al. [121]. The researchers explored the thermodynamic potential of the process in four distinct scenarios: conventional steam reforming (CSR) and three advanced reforming approaches, namely sorption enhanced steam reforming (SESR), chemical loop steam reforming (CLSR), and steam reforming sorption enhanced chemical loop steam (SE-CLSR). The bio-oil was represented to include the following model compounds: acetic acid (22.53%), hydroxyacetone (18.30%), levoglucosan (4.22%), vanillin (7.04%), p- cresol (7.04%), furfural (14.08%), guaiacol (9.85%), phenol (14.08%) and toluene (2.86%). Several parameters were investigated in the process, such as the steam/carbon ratio, reforming temperature, among others. With regard to hydrogen yield, the SESR process presented higher values (0.216 kg H₂/kg of bio-oil), with a purity greater than 99%. CLSR, on the other hand, recorded the lowest yield and purity, with values of 0.178 kg H₂/kg bio-oil and 64.6%, respectively. Significant in situ heat generation was found in the reforming reactor for both SESR and SE-CLSR, suggesting a notable potential for autothermal operation. The researchers also found that the SE-CLSR process is highly intensified, featuring substantially lower energy requirements compared to all other processes. These results highlight the possibility of obtaining hydrogen with higher yields and purity, in addition to lower energy consumption, by combining CO₂ sorption and the chemical loop with traditional reforming.

Xie et al. [13] conducted a study on hydrogen production via SESR from corn cob bio-oil. Different adsorbent materials were prepared, but the one selected was CaO obtained by the calcination of Ca(CH₃COO)₂·H₂O, since it showed better capture capacity and better BET surface area. For both processes, the authors found that temperature and S/C effects were significant in the process. In the CSR process, the hydrogen concentration and yield increased with increasing temperature, stabilizing at 800 °C, reaching maximum values of 80 and 75%, respectively. In the process with CO₂

capture, these values increased to 85 and 90%, operating at the same temperature. The best operating conditions observed were S/C of 12 in the SESR process. Above this value, the yield and hydrogen concentration decreased, and the authors related this behaviour to a decrease in the partial pressure of CO₂. The carbon deposition on the catalyst was inhibited during the temperature range between 650 °C and 850 °C and the S/C range between 9 and 15.

2.4. Simulation process

The use of simulation has significant importance in the field of engineering and process industries for several reasons, as it allows the design and optimisation of processes, thermodynamic modelling, thermal and material balances, environmental impact assessment, solution process problems etc [40].

Kanatlı and Ayas [122] performed the simulation of the steam reforming of sunflower meal in Aspen Plus. In their studies, the authors included the reaction kinetics, and used several operational parameters and thermodynamic models in order to obtain data on the behaviour of the process. The composition of the sunflower and its characteristics were adopted to guarantee more realistic data on the process. Three models were simulated to obtain products in the steam catalytic reforming process. In these models, the difference is based on the products considered. The data obtained were compared with experimental data, where sunflower meal was used in the reforming process. Model II considers that all reactions occur simultaneously and that all species undergo combustion reactions (except biomass). The best results were obtained, with a similarity of 93% with experimental results. Using this model, an analysis of the effect of the water:biomass feed ratio on hydrogen yields was carried out, with the highest value obtained being 44.9 mol H₂/kg of sunflower flour, operating with a feed ratio of water:biomass ratio of 15:1 at a constant temperature of 800 °C and atmospheric pressure.

Hussain et al. [123] studied via Aspen Plus the effect of temperature and steam feed rate on steam reforming of drupe seed shells. The temperature range varied from 600 to 900 °C, and the steam flow range varied from 1 to 2 kg. The authors noted that the concentration and yield of hydrogen increased with increasing temperature (from 22.52 to 36.06 vol.%, with a steam flow rate of 1.56 kg/hr). In the simulation, formation reactions of H₂, CO, CO₂, CH₄ and H₂O were considered to occur quickly, with no loss of pressure in the system. In addition, the particles are uniform spheres of constant size, and the average diameter of the particles remains unchanged throughout the process.

Aiming to obtain the equilibrium composition and global heat of reaction of the bio-oil steam reforming process from thermodynamic data, Rodrigues et al. [124] carried out a study using Aspen plus software. The bio-oil model compound admitted was composed of acetic acid, phenol and acetone. The effects of process variables such as temperature and input S/C molar ratio were investigated over a wide range of conditions. Considering energy efficiency, the best operational conditions were identified in order to increase hydrogen production. With an S/C=10 and 577 °C, 2.28 mol H₂/mol C was obtained. The authors also highlighted that equilibrium calculations could be used to simulate these steam reforming reactions, given the behaviour of the catalyst.

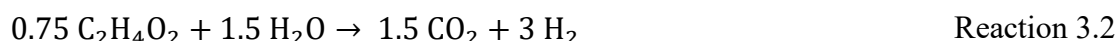
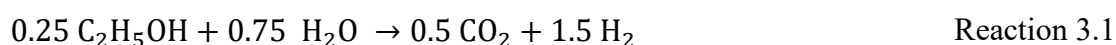
Taken together, the insights discussed contribute to a better understanding the potential in using bio-oil and its aqueous fraction in the steam reforming process with the aim of producing hydrogen. In terms of materials, some catalysts used in the process were seen, particularly the nickel-based. Regarding adsorbent materials, the use of calcium oxide was highlighted in processes where the aim is to capture the CO₂. The capture process proved to be more advantageous in energy and environmental terms, since carbon dioxide emissions are reduced with the use of these materials. The importance of simulation processes was also discussed, with works cited with the aim of showing the different approaches that can be carried out depending on the study interest. On the other hand, although there are many articles that deal with the reforming of pure components, such as ethanol or acetic acid, a gap in publications dealing with steam reforming with CO₂ capture of these mixed components was observed in the literature. This approach holds significance because conditions suitable for a pure compound might not yield the same results when the compound is part of a mixture.

Chapter 3 – SIMULATION AND EXPERIMENTAL METHODS

3.1. Thermodynamic analysis

NASA's Chemical Equilibrium with Applications (CEA) software was selected to perform the thermodynamic equilibrium calculations in order to compare them with experimental data obtained via catalytic tests. This model is based on the Gibbs free energy minimisation method (non-stoichiometric approaches) and it is used in situations where the reactions that occur in the system are unknown [125].

The operating parameters considered in this study are shown in Table 3.1. The possible products considered in the thermodynamic analysis were hydrogen (H_2), methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), unreacted water and carbon (C). For the SESR process, other solids were considered as calcium carbonate ($CaCO_3$), calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$). The effects of catalysts are not considered. Others products as methanal, methanol, ethylene, ethane, ethanal, ethanol, propane, propanal were also included, but calculations showed that their concentrations in equilibrium stream were negligible. The molar ratios used in the thermodynamic analysis are based on the Reaction 3.1 and Reaction 3.2: for a feed with 0.25 moles of C_2H_5OH and 0.75 moles of $C_2H_4O_2$, 2.25 moles of H_2O are stoichiometrically needed. Here, the stoichiometric steam/C is equal to 1.125. The amount of CaO required was calculated based on the number of moles of CO_2 stoichiometrically required, according to Reaction 3.3.



The overall reaction for the SESR of the blend is shown in Reaction 3.4.

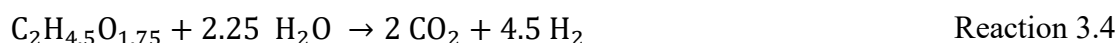


Table 3.1. Operating conditions in the equilibrium calculations for CSR and SESR.

Reformer Temperature ($^{\circ}C$)	500, 550, 600 and 650
Ethanol : Acetic acid : H_2O molar ratio	0.25: 0.75 : M, M=2.25, 4.5, 6.75 and 9
CaO/C molar ratio	0 (CSR) and 1 (SESR)

3.2.Plant simulation

Detailed in Chapter 8 (pg. 110).

3.3.Experimental

3.3.1. Materials

Bifunctional nickel and calcium oxide-based catalysts promoted with ZrO₂ and alkali metals

Nickel nitrate (II) hexahydrate (Ni(NO₃)₂·6H₂O, Vetec, 97%), calcium nitrate (Ca(NO₃)₂·4H₂O, Dinâmica, P.A), zirkon(IV)-oxidnitrat hydrat (ZrO(NO₃)₂·xH₂O, Aldrich, 99%), alkali metal precursors – Potassium carbonate (K₂CO₃, Vetec, P.A.) or Sodium carbonate (Na₂CO₃, Reagen, P.A.), anhydrous citric acid (C₆H₈O₇, 99.5%, Dinâmica), nitric acid (HNO₃, Ecibra, P.A.) and distilled water were used in the synthesis of bifunctional nickel and calcium oxide-based catalysts.

Bifunctional nickel and calcium oxide-based catalysts modified with aluminium and cerium

Anhydrous citric acid (C₆H₈O₇, 99.5%, Dinâmica), calcium carbonate (CaCO₃, 99%, Dinâmica), Aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, 98.0%, Nuclear), nickel nitrate (II) hexahydrate (Ni(NO₃)₂·6H₂O, 97.0%, Vetec), ammonium ceria(IV) nitrate (Ce(NH₄)₂(NO₃)₆, Sigma Aldrich, 98.5%) and distilled water were used in the synthesis of bifunctional nickel and calcium oxide-based catalysts.

Mineral waste used as CO₂ sorbent

High limestone content waste from Vale Fertilizante's apatite processing, composed of approximately of 82% calcium carbonate (CaCO₃), about 9.5% magnesium carbonate (MgCO₃), 6.5% Silicon dioxide (SiO₂) and 2.5% ferric oxide (Fe₂O₃).

Nickel supported on magnesium aluminate catalyst

Magnesium nitrate (Mg(NO₃)₂·6H₂O, 98%, Cinética), aluminium nitrate (Al(NO₃)₃·9H₂O, 98%, CAAL), ammonia solution (NH₄OH, 30%, Dinâmica), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 97%, Vetec) and distilled water.

Nickel supported on alumina catalyst

Boehmite ($\text{AlO}(\text{OH})$, Catapal A Sasol), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 97%, Vetec).

3.3.2. Catalyst preparation

Mineral waste used as CO_2 sorbent

The CO_2 sorbent used is a high limestone content waste from Vale Fertilizante's apatite processing from southeaster region of Brazil, which was previously homogenised using the quartering method. The material was dried overnight in an oven furnace at $100\text{ }^\circ\text{C}$, then calcined in a muffle furnace at $750\text{ }^\circ\text{C}$ for 4 hours in a flow of 50 mL/min of synthetic air with a heating rate of $10\text{ }^\circ\text{C/min}$. At the end of calcination, the material was crushed.

Nickel supported on magnesium aluminate catalyst

The material was prepared following methodology reported by Ferreira et al. [126] and Guo et al. [127]. To prepare 3 g of magnesium aluminate (MgAl_2O_4), 5.4069 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.021 mol) was mixture to 15.8211 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.042 mol), according to the MgAl_2O_4 molar stoichiometry ($\text{Al/Mg} = 2/1$). The nitrates were dissolved in 126 mL of distilled water in a 250 mL beaker, which was kept under magnetic stirring for 30 minutes at room temperature. An ammonium hydroxide solution 2 M was added slowly with constant stirring until pH attained the value of 9.7 and kept for 10 min. During the precipitation, temperature was maintained at $40\text{ }^\circ\text{C}$. The gel formed was filtered using a vacuum pump system (filter paper Qualy 80 g/m^2) and washed several times with distilled water. After, the material was dried at $100\text{ }^\circ\text{C}$ for 24 h in an over. The material obtained was macerated and calcined at $800\text{ }^\circ\text{C}$ for 4 h in a flow of 30 mL/min of synthetic air with a heating rate of $10\text{ }^\circ\text{C/min}$. Finally, the solid was ground to particle sized of 100 mesh. Supported nickel catalyst was prepared by wet impregnation method using an aqueous solution of nickel nitrate hexahydrate to obtain a 10% Ni loading. Briefly, nickel nitrate (0.8286 g) was dissolved in a small amount of distilled water in a beaker, which was kept under magnetic stirring for 20 minutes at room temperature. Then, 1.5 g of MgAl_2O_4 was added under continuous stirring. The sample was dried in an oven at $100\text{ }^\circ\text{C}$ for 12 h. The material obtained was macerated and calcined at $550\text{ }^\circ\text{C}$ for 5 h

in a flow of 80 mL/min of synthetic air with a heating rate of 10 °C/min. Finally, the solid was ground to particle sized of 100 mesh to obtain the catalyst used in this study.

Nickel supported on alumina catalyst

The preparation of the material adhered to the methodology outlined by Santos et al. [26]. Initially, boehmite underwent heating to 800 °C at a rate of 10 °C/min, maintaining this temperature for a duration of 6 hours. Subsequently, to attain a 10 wt.% Ni concentration, the support underwent impregnation with an aqueous solution of nickel hexahydrate via an incipient wet impregnation process. Following this, the sample underwent overnight drying at 100 °C, succeeded by calcination at 400 °C for a period of 3 hours, under an air atmosphere, at a heating rate of 10 °C/min.

Bifunctional nickel and calcium oxide-based catalysts promoted with ZrO₂ and alkali metals

Bifunctional materials were synthesized by the citrate sol-gel method according to the modified methodology of Wang et al. [128] maintaining the following mass ratios (Ni:CaO:MZrO₃ = 10:72:18), where M = Ca, K, and Na. To prepare 3 g of bifunctional material, appropriate amounts of Ni(NO₃)₂·6H₂O, Ca(NO₃)₂·4H₂O, ZrO(NO₃)₂ and alkali metal precursors (K₂CO₃ or Na₂CO₃) were solubilized in 150 mL of water at 40 °C under constant stirring (400 rpm) for 30 min. Then, C₆H₈O₇ and 10 drops nitric acid were added, and the solution was kept stirring for 10 minutes. Under stirring, the mixture was heated to 90 °C to evaporate the solvent until the formation of a gel. The gel was dried in an oven at 110 °C for 48 h and calcined in a muffle oven at 800 °C with a heating rate of 1 °C/min for 1 h under air atmosphere. Finally, the materials were titled as NiCaZr, NiCaKZr and NiCaNaZr.

Bifunctional nickel and calcium oxide-based catalysts modified with aluminium and cerium

Bifunctional nickel catalyst supported on CaO and alumina (NiCaAl), as well as nickel catalyst supported on CaO and alumina doped with ceria (NiCaAlCe) were prepared via citrate method [28]. Shortly, 0.0074 mols of C₆H₈O₇ and 0.0118 mols of CaCO₃ were dissolved into water, considering a molar ratio of C₆H₈O₇ to H₂O of 0.0033, to precipitate calcium citrate. The solution was kept under magnetic stirring at 75 °C for 15 minutes. Then, appropriate amounts of the precursor salts, Al(NO₃)₃·9H₂O,

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ were added into the mixture. The molar ratio of Al to Ca remained constant at 6:9 across all samples. For the NiCaAl catalyst, the molar ratio of Ni to Ca was 0.34, while for the NiCaAlCe catalyst, it was 0.23. Additionally, the molar ratio of Ce to Ca for the latter catalyst was 0.05. The solution was continuously stirred at 75 °C for approximately 4 hours and the materials were dried in an oven overnight at 100 °C. The material obtained was macerated and calcined under a synthetic air atmosphere (30 mL/min) using a two-step calcination method: the temperature was raised from 25 °C to 250 °C at a heating rate of 1 °C/min, and then increased to 900 °C at a rate of 10 °C/min, and held for 2 hours.

3.3.3. Characterisations

X-ray fluorescence (XRF) analysis was conducted using a Bruker spectrometer, model S8 Tiger, for semiquantitative composition determination of the samples. The material was mixed with a binder (Multimix, PXR-200) and formed into pellets using a hydraulic press, with varying masses according to the tablet preparation method. Data acquisition utilised the standardised QUANTEXPRESS analysis package.

A Shimadzu Lab X-XRD-6000 diffractometer was utilized for X-ray diffraction analysis, operating at 40 kV and 30 mA, with Cu K α radiation. Scanning covered a range from 10 to 80° (2 θ) with a step size of 0.01° and a rate of 0.6°/min at room temperature. The average crystallite size was determined using the Scherrer equation.

N₂ physisorption analysis was performed using a NOVAtouch Gas Sorption Analyzer LX1 to evaluate surface area of fresh and spent catalysts. Samples were heated overnight at 450 °C to remove impurities. Experiments were subsequently conducted at liquid nitrogen temperature (-196°C). The equipment's integrated software was then used to calculate the surface areas, applying the Brunauer, Emmett, and Teller (BET) method.

H₂-Temperature Programmed Reduction (TPR) was conducted using a gas chromatography method with a thermal conductivity detector (TCD). The experimental setup included a quartz reactor heated by a furnace controlled by a controller. Approximately 50 mg of sample was preheated under argon gas flow (30 mL/min) to 500 °C for 1 h and then cooled to room temperature. Catalyst reduction occurred with a continuous flow of 1.96% H₂ in Ar at 30 mL/min, increasing the temperature from room temperature to 1000 °C at a heating rate of 10 °C/min. Experimental H₂ consumption was determined by analysing peak areas during TPR, compared to a CuO calibration curve.

The reduction degree was calculated by comparing experimental and theoretical H₂ consumption ratios.

The stability and CO₂ sorption capacity of the samples were analysed using a Shimadzu TGA-50 Thermogravimetric Analyzer. Samples (8–10 mg) were heated to 800 °C under pure He for 10 minutes to remove impurities. Carbonation occurred at 600 °C for 30 minutes in a 15% CO₂/He stream, followed by calcination at 800 °C for 10 minutes under pure He. Each sample underwent 20 cycles, with CO₂ capture capacity calculated using Equation 3.1 and Equation 3.2.

$$\text{Capture capacity} \left(\frac{\text{g CO}_2}{\text{g cat}} \right) = \frac{m_t - m_0}{m_0} \quad \text{Equation 3.1}$$

$$\text{Capture capacity} \left(\frac{\text{g CO}_2}{\text{g CaO}} \right) = \frac{m_t - m_0}{m_0 * Y_{\text{CaO}}} \quad \text{Equation 3.2}$$

Where m_0 represents the initial sample weight at the start of each carbonation cycle, m_t represents the maximum sample weight at the end of each carbonation cycle, and Y_{CaO} represents the theoretical weight fraction of CaO in each sample.

3.3.4. Catalytic tests

Two reaction mixtures were tested for different materials. The first one was composed of a molar ratio of ethanol to water of 1:6. The second was a mixture of model molecules from the aqueous fraction of bio-oil, composed of a molar ratio of 0.25 ethanol to 0.75 acetic acid to 4.5 water. This ratio was selected within the experimental ranges already reported by Diebold [59]. Although there are different possible ranges, as the composition varies with numerous parameters related to the composition and processing of biomass, in this work, this value was chosen to represent a more stringent reforming condition, considering that acetic acid is a more complex molecule to reform. This choice is advantageous as it allows for the testing of catalysts under harsher conditions.

The SESR reaction was conducted in a fixed-bed quartz reactor filled with quartz wool, packed with catalyst. For mining waste mixed with Ni/Al₂O₃ or Ni/MgAl₂O₄, 2 g of physical sample mixture (50 wt.% catalyst: 50 wt.% sorbent) were used. For the bifunctional nickel and calcium oxide-based catalysts, 0.8 g of material was used.

During reduction, the material was heated to 800 °C (10 °C/min) under a mix of H₂ (30 mL/min) and Ar (100 mL/min) flows and held for 1 hour. Then, the reactor was cooled to 500 °C (reaction temperature) under Ar atmosphere. Liquid solution

(0.033 mL/min) was evaporated, generating a vapor phase flowing into the reactor with 100 mL/min of Ar. The vapor phase for the first reactional mixture consisted of 4.5 mL/min ethanol, 27 mL/min water vapor, while for the second reactional mixture consisted of 1.4 mL/min of ethanol, 4.4 mL/min of HAc, and 30.5 mL/min of water. Steam/C molar ratios were twice the stoichiometric ratio of each blend. Gas composition analysis used a gas chromatograph (Shimadzu GC-2014) equipped with a TCD detector and Carboxen-1010 plot column. The reactional products detected were H_2 , CO, CO_2 , and CH_4 . Reaction was conducted for 119 minutes at 1 atm. Regeneration involved heating the furnace to 800 °C at 10 °C/min and holding for approximately 60 minutes under Ar atmosphere to decompose $CaCO_3$.

Chapter 4 – THERMODYNAMIC ANALYSIS

4.1 Results and discussion

In this study, acetic acid and ethanol were chosen as representative molecules for the acids and alcohols present in the aqueous fraction of bio-oil. To have a greater understanding of the experimental conditions adopted in this work, analysis was conducted on the composition of the mixture with a molar ratio of 0.25 ethanol to 0.75 HAc. The production of hydrogen, as well CO₂, CO, and CH₄ was investigated at different temperatures, and steam/C molar ratios. All results are presented on a water and inert gas-free basis. Under all tested conditions, the conversion of the reaction mixtures was approximately 100%, indicating complete hydrocarbon conversion.

Figure 4.1 illustrates the equilibrium mole fractions of CSR products (dry basis) as a function of temperature, considering a steam/C ratio equal to 2.25.

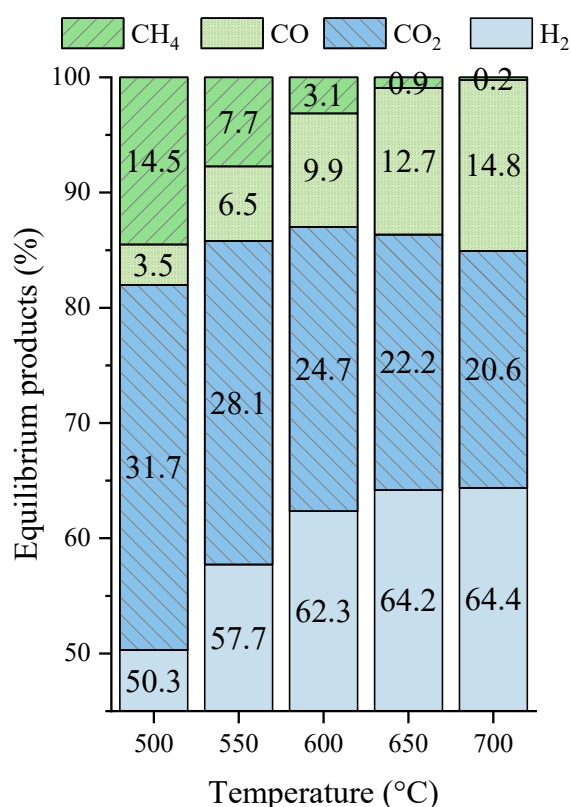


Figure 4.1. Equilibrium mole fractions of CSR products on a dry basis. Conditions:

Ethanol: Acetic acid: H₂O molar ratio = 0.25: 0.75: 4.5 (Steam/C=2.25); atmospheric pressure, Temperature range: 500 – 700 °C.

In general, the amount of hydrogen increases with increasing temperature, but stabilizes after 650 °C because of inhibition of the exothermic WGS reaction [129]. The

molar fraction of CH_4 decreases with increasing temperature across the entire range tested. On the other hand, the amount of CO_2 reached a maximum around $600\text{ }^\circ\text{C}$. As for CO , there is a significant increase with the rise in temperature, throughout the range tested. For a similar system investigated in this research, literature has reported an increase in CO with rising temperatures [15,130,131]. These studies, which analysed a wide temperature range, demonstrated that no CO is formed below $473\text{ }^\circ\text{C}$, attributing this to the exothermic nature of the WGS reaction, where higher temperatures negatively impact CO conversion. To minimize CO production, low temperatures combined with a high steam/fuel ratio are necessary. However, since higher temperatures are crucial for maximizing hydrogen production, this parameter condition is considered despite the increase in CO . Some studies, such as Wang et al. [132] the need for CO removal for applications in process like proton exchange membranes fuel cells (PEMFC).

The trends observed in the products with increasing temperature are in line with the thermodynamic analysis of ethanol steam reforming carried out by Lima da Silva, de Fraga Malfatti and Müller [131]. The authors performed a study using the Gibbs energy minimisation method. Different parameters, such as temperature ($127 - 927\text{ }^\circ\text{C}$) and water/ethanol ratio ($0 - 10$), were varied. The molar fractions of H_2 increased with temperature, while CH_4 showed the opposite behaviour. Regarding the formation of CO , it was not observed at low temperatures ($127 - 427\text{ }^\circ\text{C}$). However, at higher temperatures, its presence became significant, making it necessary to increase the $\text{H}_2\text{O}/\text{EtOH}$ ratio to minimize its production.

A second analysis was conducted to examine the products obtained in a SESR process, using CaO(s) as an adsorbent material. The advantage of using CaO in the steam reforming process lies in its ability to adsorb carbon dioxide formed during the reaction, through the carbonation reaction (Reaction 3.3). This allows the equilibrium of the SR reaction to be shifted, favouring the production of hydrogen and reducing the amount of CO_2 . Furthermore, the regenerated CaO can be recycled, thus extending the catalyst life and reducing operating costs [133]. Results for solids CaO , Ca(OH)_2 and CaCO_3 were not presented because excess CaO becomes a by-product. This occurs because, according to Reaction 3.3, a stoichiometric amount of CaO will convert all CO_2 to CaCO_3 . Consequently, any excess CaO remains unreacted and does not influence the equilibrium composition.

The results shown in Figure 4.2 highlight the significant effect of temperature on the SESR process. At the lowest temperature tested ($500\text{ }^\circ\text{C}$), higher amounts of hydrogen

and CH₄ were produced, with only trace amounts of CO₂ and CO detected. As the temperature increased, the quantities of hydrogen and CH₄ decreased, while CO and CO₂ levels rose. This shift occurred because the methanation reaction becomes thermodynamically less favourable at higher temperatures, whereas the steam reforming of methane is kinetically enhanced, resulting in lower CH₄ concentrations [32,134].

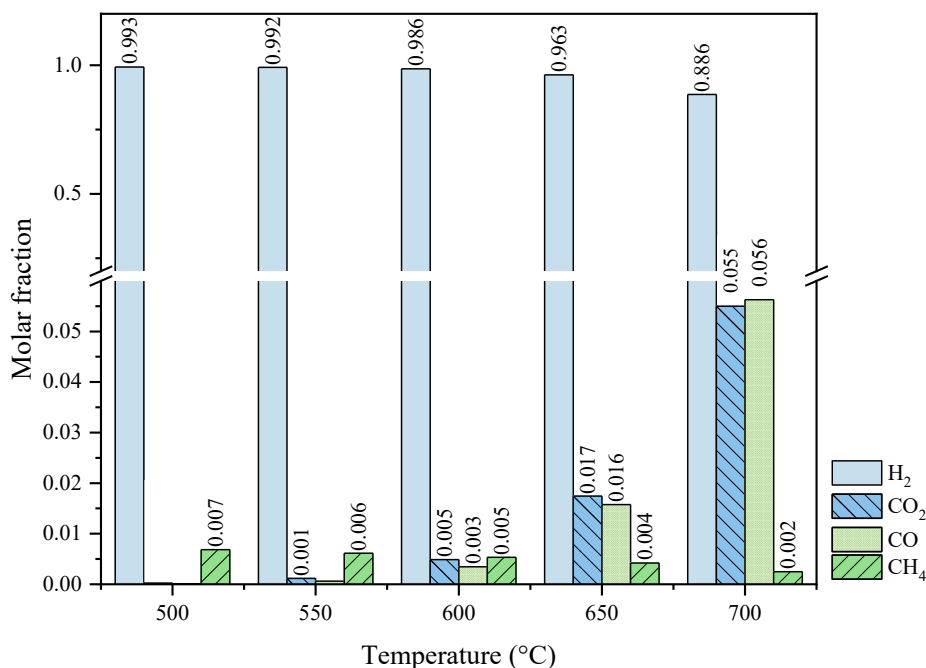


Figure 4.2. Equilibrium mole fraction of SESR products on a dry basis. Conditions: Ethanol: Acetic acid: H₂O molar ratio equals to 0.25: 0.75: 4.5 (Steam/C=2.25); atmospheric pressure, Temperature range: 500 – 700 °C, mols of CaO = 2.

The low concentration of CO at lower temperatures is related to the WGS reaction being favoured under these conditions. The carbonation reaction is also promoted at low temperatures, which explains the low concentration of CO₂. As the temperature increases, the concentration of this product rises, as these reactions are not favoured. Furthermore, the process of decarbonation of calcium carbonate begins to occur at approximately 600 °C, which may contribute to the changes in CO₂ concentration as the temperature increases. The results obtained for all reaction products are in agreement with those reported in the literature [32,134,135].

Figure 4.3 displays hydrogen mole fraction results for various temperatures and steam to carbon (S/C) ratios. The S/C ratio is vital for optimising both the steam reforming process and the WGS reaction. In steam reforming, it directly affects hydrogen production efficiency by influencing raw material conversion and reducing unwanted by-products like methane and coke. Properly adjusting the S/C ratio maximises hydrogen yield while

minimising energy consumption. In the WGS reaction, the S/C ratio is crucial for converting carbon monoxide (CO) to carbon dioxide (CO₂) and hydrogen (H₂). An optimal ratio ensures complete conversion of reactants, enhancing hydrogen production and the purity of the final product [83].

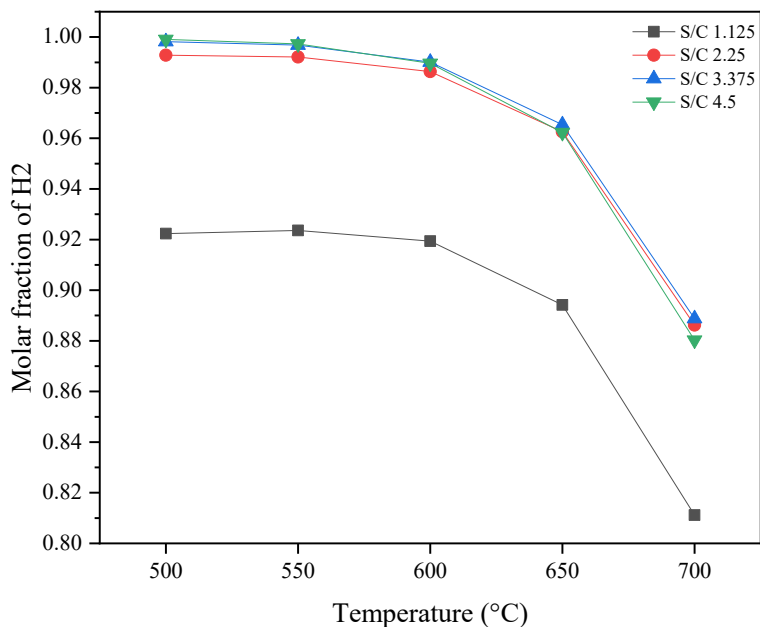


Figure 4.3. Molar fraction of hydrogen obtained with different S/C ratios, varying the temperature. Conditions: Steam to carbon (S/C) range: 1.125 – 4.5; stoichiometric quantity = 1.125; atmospheric pressure, Temperature range: 500 – 700 °C, mols of CaO = 2.

Results show that hydrogen molar fractions peaked at temperatures around 550 °C, decreasing with increasing temperature. As for the S/C ratio, the stoichiometric amount of 1.125 resulted in a lower hydrogen yield of 0.922. In contrast, higher S/C ratios of 2.25, 3.375, and 4.5 yielded similar and higher hydrogen values of 0.993, 0.998, and 0.999, respectively. This is because this amount of water is insufficient to meet the demand of the reforming process and the WGS reaction. With an S/C ratio ≥ 2.25 , the H₂ mole fraction values were greater than 0.99 and very similar to each other. Therefore, in experimental approaches, using twice the stoichiometric amount of water is generally a good option, as a higher excess of water can lead to problems such as dilution of the carbon feed, reducing its concentration and thus decreasing the efficiency of the process. It also increases energy consumption for heating and vaporising the water, leading to higher operating costs. Additionally, surplus water can complicate the separation and purification of final products, increasing processing costs [40,42].

4.2 Conclusion

This chapter evaluated the sorption enhanced steam reforming (SESR) of a mixture of acetic acid and ethanol as model compounds of the aqueous fraction of bio-oil (AFB). Thermodynamic analysis was carried out for the conventional steam reforming (CSR) and SESR, considering different operational parameters, such as temperature, adsorbent addition, and steam/carbon ratio effects. At varying temperatures, the hydrogen yields for CSR were 50.3% at 500°C, 57.7% at 550°C, 62.3% at 600°C, 64.2% at 650°C, and 64.4% at 700°C. These values are lower than those for SESR, which were 99.3%, 99.2%, 98.6%, 96.3%, and 88.6%, respectively. This difference is directly related to the absence of the CO₂ capture process in the conventional system. In the SESR process at 500 °C, the stoichiometric steam-to-carbon (S/C) ratio of 1.125 resulted in a hydrogen yield of 92.2%. However, doubling the stoichiometric ratio to 2.25 produced a significantly improved hydrogen yield of 99.3%, which is comparable to the higher S/C ratios of 3.375 (99.8%) and 4.5 (99.9%). Additionally, operating at 500 °C also yielded a higher molar fraction of hydrogen. This indicates that a S/C ratio of 2.25 at 500°C is advantageous, achieving yields similar to those obtained with even higher ratios.

Chapter 5 – SORPTION ENHANCED STEAM REFORMING OF ETHANOL USING A MINING WASTE RICH IN CALCIUM AND MAGNESIUM OXIDE AS ADSORBENT MATERIAL FOR CARBON DIOXIDE CAPTURE

5.1. Results and discussion

5.1.1. Characterisation of fresh samples

Table 5.1 shows the composition of the mining waste, determined via X-Ray Fluorescence.

Table 5.1. Chemical composition (wt.%) of mining waste.

Molecular formula	CaO	MgO	Fe ₂ O ₃	SiO ₂	P ₂ O ₅	Al ₂ O ₃	Others
Content (wt.%)	73.18	14.02	3.08	2.55	1.43	1.28	3.75

Table 5.2 presents the semi-quantitative results from X-ray fluorescence (XRF) of the synthesized catalysts. While discrepancies exist between theoretical values and experimental results, the deviations are less than 10%. These variations may arise from impurities, hydration of reagents, and losses during the experimental procedures.

Table 5.2. Chemical composition (wt.%) of Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts via XRF (wt.%).

Catalyst	NiO	Al ₂ O ₃	MgO	Others
Ni-Al ₂ O ₃	12.54	86.95	-	0.51
Ni-MgAl ₂ O ₄	13.62	65.49	20.49	0.40

Figure 5.1 shows the X-ray patterns of mining waste and reduced and passivated Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts. The main phases identified in the MW diffractogram consist of calcium compounds, including Ca(OH)₂ (PDF 84-1265) at 2θ values of 17.98, 28.96, 34.07, 46.68, 50.80, and 54.53°, as well as CaCO₃ (PDF 85-1108) and CaMgCO₃ (PDF 89-1304) at 23.03, 29.45, 39.48, 47.64, 48.61, and 48.73°. Additionally, the presence of hematite phase Fe₂O₃ (PDF 79-7) in the X-ray patterns correlates with the iron content identified by XRF results. Both material showed peaks at 2θ angles of 44.5, 51.81, and 76.45°, indicating the presence of metallic nickel (PDF 4-850), which suggests the reduction of NiO to Ni [126]. Ni-Al₂O₃ catalyst exhibits peaks associated with δ-Al₂O₃ (PDF 46-1131) and γ-Al₂O₃ (PDF 47-1308). This finding aligns with the research of Cho et al. [137], where commercial γ-Al₂O₃ was utilised, and δ-Al₂O₃ was obtained

through the thermal decomposition of boehmite at 950 °C. The Ni-MgAl₂O₄ catalyst also exhibited characteristic peaks of the spinel phase (PDF 75-1797), consistent with findings by Ferreira et al. [126]. Peaks corresponding to Ca(OH)₂ and CaCO₃ were identified, and Ca(OH)₂ arises from the hydration of calcium oxide, occurring as CaO reacts with atmospheric water. The presence of calcium carbonate is attributed to the carbonation of CaO, where atmospheric carbon dioxide reacts with CaO to form CaCO₃ [128].

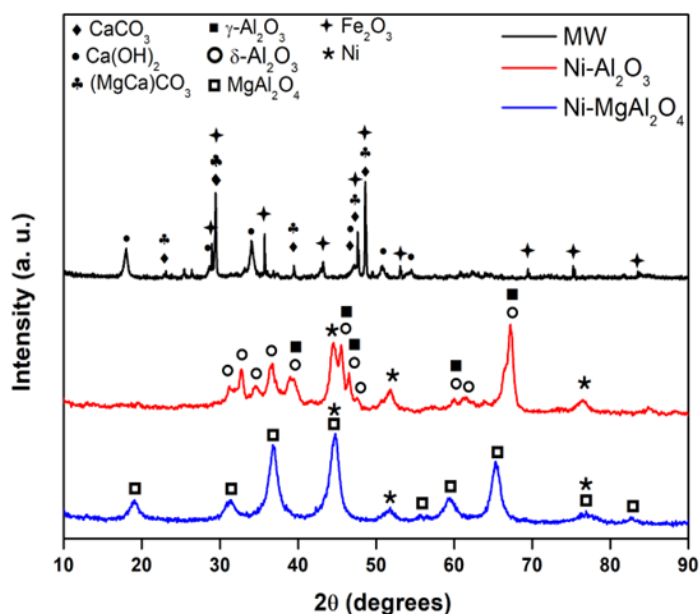


Figure 5.1. XRD results of MW and Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts.

The reducibility of the synthesized Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts was analysed by TPR, as illustrated in Figure 5.2. The peak profiles showed typical behaviour of NiO reduction in the range of 400 to 800 °C with varying interaction strengths with the support [138]. Three distinct reduction peaks were observed for the Ni-Al₂O₃ catalyst: the peak at approximately 500 °C corresponds to the reduction of larger NiO particles with minimal support interaction, the peak around 650 °C suggests a medium interaction with the support, and the small peak near 750 °C is related to a strong interaction between NiO and alumina [139].

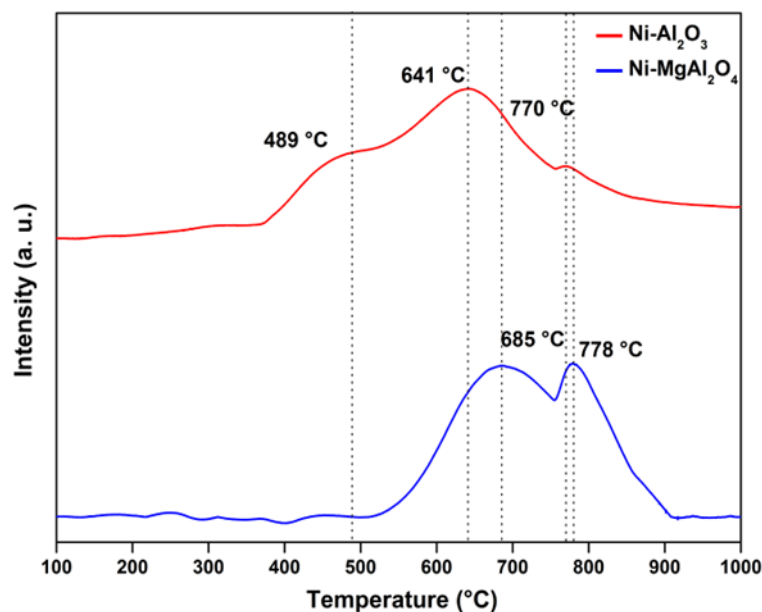


Figure 5.2. TPR profile for fresh Ni-Al₂O₃ and Ni-MgAl₂O₄ catalysts.

For the Ni-MgAl₂O₄ catalyst, no reduction peak of NiO species with weak interaction with the catalyst support was observed at low temperatures. Instead, two peaks were noted above 650 °C, indicating significant interaction between nickel oxide particles and magnesium aluminate. Furthermore, the greater interaction of NiO-Ni-MgAl₂O₄ reflects the lower reducibility of the catalyst, as shown in Table 5.3. Akiki et al. [140] also reported a low reducibility for Ni/MgAl₂O₄ catalysts, attributing it to the greater interaction between the reducible phase and the support, which was promoted by the diffusion of Ni²⁺ cations within the support at temperatures above 550 °C.

Both catalysts exhibited peaks around 750 °C, with the Ni-MgAl₂O₄ catalyst showing a significantly larger peak compared to Ni-Al₂O₃. This peak could be attributed to the reduction of the highly dispersed NiAl₂O₄ spinel phase, despite its absence from identification by X-ray diffraction in either material. This transformation may also explain the lower degree of reduction observed in the Ni-MgAl₂O₄ catalyst, as some Ni may not be fully reduced to metallic nickel likely due to the interaction with the spinel phase [141–143].

Table 5.3. H₂ consumption and reducibility data obtained by TPR.

Catalyst	H ₂ consumption (μmol.g ⁻¹ cat) ^(a)	Reducibility (%)
Ni-Al ₂ O ₃	1540	90
Ni-MgAl ₂ O ₄	1145	67

^(a)It was calculated from TPR peaks and H₂ pulses.

The mining waste underwent 20 carbonation and decarbonation cycles using thermogravimetric analysis, as shown in Figure 5.3. The material exhibited a weight increase of 28.6% in the 1st cycle and 13.6% in the 20th cycle. These weight increases are related to the ability of CaO (44 g/mol) to carbonate under a dilute CO₂ atmosphere, converting into CaCO₃ (100 g/mol). The decrease in carbon dioxide absorption capacity can be attributed to the sintering process of calcium oxide particles [27]. During sintering, CaO particles agglomerate and compact when exposed to high temperatures, resulting in a decrease in specific surface area and changes to the material's physical structure. This loss of porosity reduces the reactivity and ability of CaO to absorb gases such as CO₂. Consequently, the reactive surfaces become less accessible, compromising the material's efficiency in CO₂ capture and release during carbonation and decarbonation cycles [144].

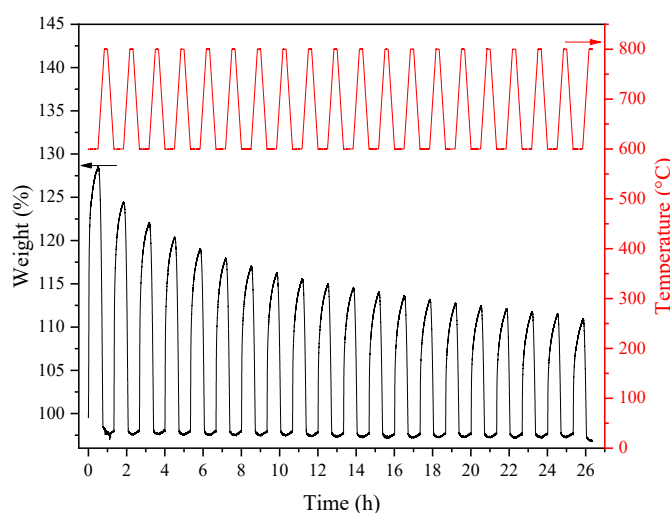


Figure 5.3. 20 carbonation and decarbonation cycles from mining waste used as adsorbent material. Conditions: Temperature of carbonation of 600 °C, under 15% CO₂/He atmosphere, and temperature of decarbonation of 800 °C, under pure He atmosphere.

Following the analysis, the amount CO₂ adsorbed per gram of CaO was calculated, considering the CaO content in the mining waste as 44.12% (XRF). Figure 5.4a illustrates that as the number of cycles increases, the sorbent's CO₂ capture capacity decreases. Initially, the adsorbent had a capture capacity of 0.65 gCO₂/gCaO in the 1st cycle and dropped to 0.31 gCO₂/gCaO, showing a loss of capture capacity of 52.5%. The decrease in performance is mainly attributed to the sintering process of CaO, a well-documented phenomenon in the literature owing to the low thermal stability of this material [145,146]. Various approaches have been explored to mitigate this phenomenon, including the

incorporation of inert materials into the structure. These materials act as physical barriers, preventing direct contact between the active particles of the catalyst. This helps maintain the dispersion of active particles and preserves their surface area, ensuring more stable and prolonged catalytic efficiency [147]. In this sense, Hu et al. [148] conducted a study emphasising the importance of gaining a better understanding of the influence of inert materials integrated into CaO-based sorbents designed for CO₂ capture at high temperature. They evaluated several inert stabilisers to enhance the cyclic performance of CaO/CaCO₃ particles. The study highlighted Y- and Al-based supports for their superior cyclic performance, with Mn, Mg, La, Yb, and Nd-based supports also showing promising results. The authors emphasised that factors such as melting point and surface area significantly influence the effectiveness of each support, crucial for optimising the functionality of the sorbent.

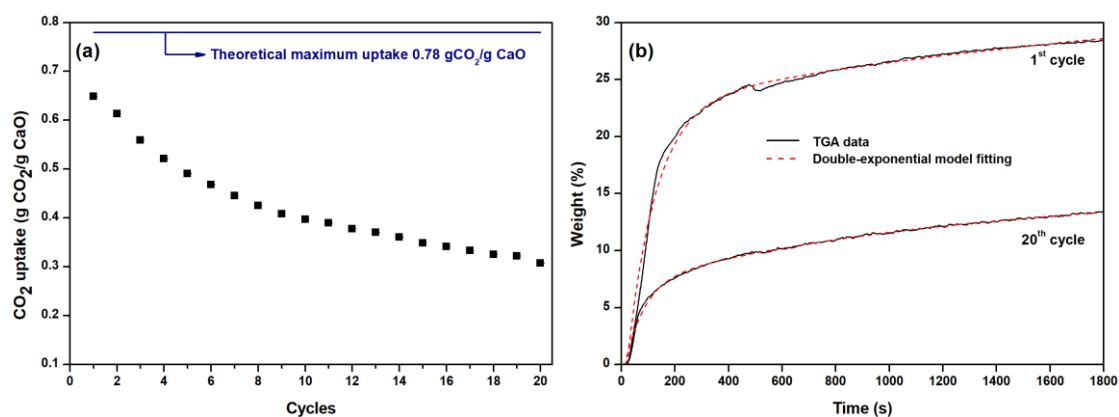


Figure 5.4. Results of (a) CO₂ capture capacity (MW); (b) Double exponential fitting.

Conditions: capture 600°C (15% CO₂/He) and regeneration 800°C (He).

Although the MW capture capacity has fallen by more than 50%, capture capacity is still in line to those reported in the literature. Vieira, Santos and Hori [30] prepared a bifunctional Ni and Ca catalysts by the sol-gel citrate method using P.A. reagents and obtained results of capture capacity of 0.4 gCO₂/g CaO in the 1st cycle and 0.15 gCO₂/gCaO in the 18th, with a loss of capture capacity of 62.5%. Krödel et al. [149] studied the use of CaO-based sorbents for CO₂ capture. A reference material, CaCO₃ nanoparticles (Ca-NP) without Zr, was prepared. Two core-shell materials with different ZrO₂ contents (wt.%) were also prepared: Ca-15Zr and Ca-26Zr. Additionally, three different yolk-shell materials were developed: Ca@12Zr, Ca@16Zr, and Ca@55Zr. The cyclic CO₂ uptake of the zirconia-stabilized yolk-shell sorbents, the reference Ca-NP, and the core-shell particles were assessed over 20 carbonation-calcination cycles. The

reference material, Ca-NP (without Zr), showed a high capture capacity in the first cycle of 0.63 gCO₂/gSorb, decreasing to 0.21 gCO₂/gSorb (loss of capacity of 73%). The yolk-shell materials yielded significantly better-performing sorbents compared to the core-shell architecture (and the Ca-NP reference). The Ca@12Zr, Ca@16Zr, and Ca@55Zr materials presented initial capture capacities of 0.69, 0.65, and 0.17 gCO₂/gSorb, decreasing to 0.61, 0.38, and 0.04 gCO₂/gSorb, respectively. This means the materials presented a loss of capture capacity of 12%, 42%, and 76%, respectively. The lowest verified capture value (Ca@55Zr) was attributed to the large fraction of CO₂ capture inactive tetragonal zirconia and CaZrO₃ in this material.

To understand the kinetics of CO₂ capture, mathematical models can be applied. In this case, the use of a model such as the double-exponential can describe the kinetic and diffusional regimes in adsorption. In the first case, considered a rapid stage of the process, the regime is dominated by surface interactions and fast initial adsorption kinetics. Generally observed in the early stages of adsorption, the speed is governed by the rate of collision of CO₂ molecules with the adsorbent surface. In the diffusional period (slow phase), the process is controlled by the diffusion of CO₂ molecules within the pores of the material. This regime is dominant in later stages of adsorption, where CO₂ molecules need to move through pores to reach internal adsorption sites [150].

The obtained TGA data was adjusted to a double exponential model (Equation 5.1) to analyse the influence of the kinetic and diffusion regimes of CO₂ adsorption and the results are shown in

Table 5.4 and Figure 5.4b. The double exponential model is used to help describe the CO₂ capture process through kinetic k_1 and diffusion k_2 parameters. The pre-exponential factors A and B corresponds to the capture capacity in the kinetic and diffusion periods, respectively. The C factor corresponds to the maximum capture capacity is the percentage of CO₂ adsorbed at the equilibrium [151,152]. When the constant k_1 is greater than k_2 , it's an indication that the diffusion of CO₂ into the CaCO₃ layer is the slowest step in the reaction, which is the case of the present work. In the opposite scenario, the surface reaction is the rate-determining step [153].

$$wt\% = -Ae^{-k_1t} - Be^{-k_2t} + C \quad \text{Equation 5.1}$$

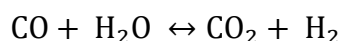
Table 5.4. Fitting parameters to the double-exponential model.

Cycle	A	B	C	k ₁ (s ⁻¹)	k ₂ (s ⁻¹)	k ₁ /k ₂	R ²
1 st	27.843	11.856	34.534	0.569	0.023	24.509	0.990
20 th	8.673	8.251	15.343	0.824	0.047	17.431	0.996

5.1.2. Catalytic tests

In the catalytic tests, 10 reaction and regeneration cycles were carried out, using Ni-Al₂O₃/MW and Ni-MgAl₂O₄/MW catalysts. Figure 5.5 displays the molar fractions on a dry basis of reaction products (H₂, CO₂, CO and CH₄) obtained from sorption enhanced steam reforming of ethanol, alongside equilibrium results for H₂ derived from thermodynamic analysis (depicted in orange). Three different stages can be delineated in the product distribution profiles obtained: The first corresponds to the pre-breakthrough stage. At this initial stage, the system exhibits the highest molar fraction of H₂ and optimal adsorbent capacity. This phase emphasises maximum CO₂ capture efficiency, where the adsorbent effectively captures CO₂ produced during the reaction. In stage II (breakthrough), the adsorption capacity gradually decreases as the adsorbent becomes saturated. Consequently, the CO₂ capture efficiency diminishes, marking the onset of the breakthrough period. In stage III (post-breakthrough), the system transitions to behaving like conventional steam reforming without CO₂ capture. Here, the entire adsorbent is saturated, and CO₂ is no longer effectively captured, resembling typical steam reforming reactions. This characterisation illustrates the dynamic behaviour of the SESR process over successive stages, impacting both hydrogen production and CO₂ capture efficiency [154].

One primary motivation for employing SESR is to achieve high-purity and high-yield hydrogen production. This is facilitated by leveraging Le Chatelier's Principle in the water-gas shift reaction, represented by Equation 5.2 [145]. By capturing CO₂ with the adsorbent, the reaction equilibrium is driven forward to counteract the CO₂ removal effects, thereby increasing hydrogen formation.



Equation 5.2

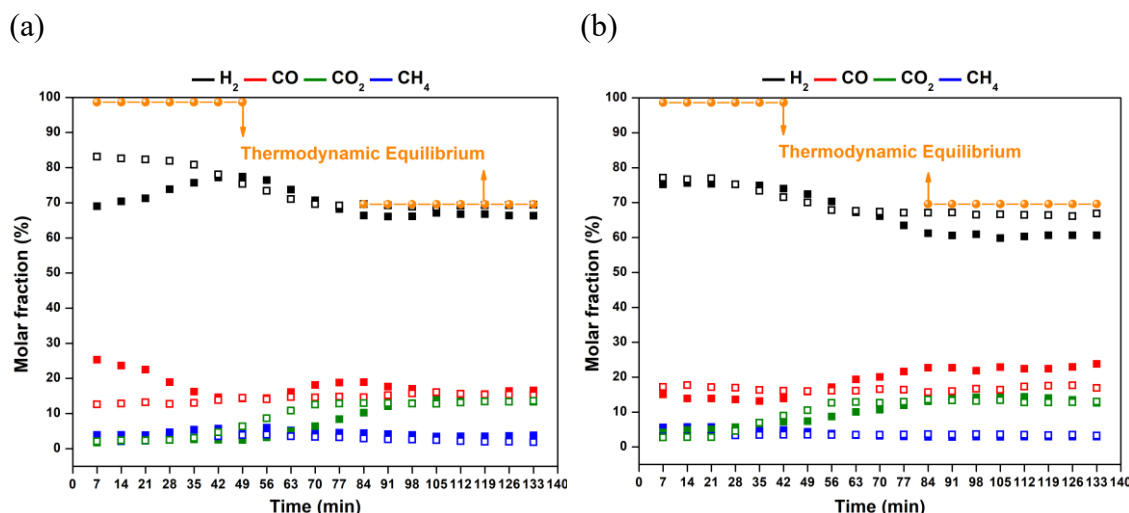


Figure 5.5. Molar fraction on a dry basis of the products of the sorption enhanced steam reforming reaction with the catalysts (a) Ni-Al₂O₃/MW and (b) Ni-MgAl₂O₄/MW. Conditions: Temperature 600 °C, steam/ethanol=6 and liquid flow of 0.033 mL/min. Filled symbol (■) represents the 1st reaction cycle, and unfilled symbol (□) represents the 10th cycle.

During the pre-breakthrough period, the molar fraction of H₂ remained close to 80% for both catalysts studied. Substantial levels of CO were detected with the Ni-Al₂O₃/MW and Ni-MgAl₂O₄/MW catalysts, comprising 20% and 15% of molar fractions, respectively. For CO₂, molar fractions of 2% and 5% were observed with the Ni-Al₂O₃/MW and Ni-MgAl₂O₄/MW catalysts, respectively. The high concentration of CO observed in the catalytic tests can be explained by the limitations of the WGS reaction. In this scenario, although water vapour is beneficial in the CO₂ adsorption process, the sorbent-water interaction can reduce the availability of free water and hinder the reaction [155]. The low fraction of CO₂ observed, along with the prolonged duration of the pre-breakthrough period (~42 min) for the Ni-Al₂O₃/MW catalyst, indicates the good capture capacity and stability of the material. For the Ni-MgAl₂O₄/MW catalysts, the pre-breakthrough period decreases to around 28 min, remaining during all 10 cycles. However, the high concentration of CO observed throughout the catalytic test contributed to reduce the molar fraction of hydrogen obtained in both cases. The difference in pre-breakthrough periods can be attributed to different interactions between the catalyst and the adsorbent, even though the adsorbent is the same in both cases. In the nickel alumina system, the distribution and accessibility of the adsorbent may be more efficient, prolonging the CO₂ capture, while magnesium nickel aluminate may not offer the same

efficiency, possibly due to a smaller active area or blocking of adsorption sites. In addition, magnesium aluminate may promote secondary reactions that interfere with capture, reducing the pre-breakthrough period.

During the 1st reaction cycle with Ni-Al₂O₃ catalyst (Figure 5.5a), a decrease in the hydrogen fraction was observed in the initial moments of the catalytic test, which can be explained by the possible oxidation of the active site due to the initial contact of the reaction mixture, rich in water [121,156]. In this way, the produced H₂ was consumed in order to regenerate the catalyst and, after about 30 minutes, it began to reach its maximum amount, followed by the beginning of the breakthrough period. Oliveira and Hori [27] achieved comparable outcomes by employing bifunctional Ni/CaO and Ni/CaAlMg catalysts in sorption enhanced steam reforming of ethanol. Additionally, the presence of Ni may be facilitating a certain level of reduction of Mg, leading to increased interaction with H₂O and preventing the reoxidation of Ni. This could explain the behaviour of the hydrogen profile observed in Figure 5.5. Furthermore, when considering the pre-breakthrough time, since all the Ni is reduced, it is likely that more CO₂ is being produced in the second sample, which would account for the shorter breakthrough time.

Studies by Aissaoui et al. [157] and Zhang et al. [158] have highlighted the improvement in the thermal stability of catalysts due to the presence of compounds such as MgO and Fe₂O₃. In the present study, the presence of these materials was confirmed via XRF analysis, and the stability of the catalysts during the catalytic tests was verified. During both cycles 1 and 10, the materials maintained the same pre-breakthrough period duration of approximately 40 minutes.

In both profiles, a difference can be observed between the thermodynamic data and the experimental data. One factor that may explain this behaviour is the low availability of active sites to promote the complete reforming. Quan et al. [159] prepared Ni/Ce catalysts with different Ni contents for steam reforming of ethanol and found that with Ni contents lower than 10%, the catalysts were not stable due to the lack of active sites. For the Ni-MgAl₂O₄ catalyst, (Figure 5.5b), this discrepancy is more pronounced and could be related to the lower content of Ni⁰ active sites, which is in agreement with TPR results.

5.1.3. Characterisation of spent catalysts

After the 10th cycle, the catalysts underwent regeneration, passivation, and subsequent XRD analysis, as depicted in Figure 5.6. Both catalysts presented peaks in 2θ

equal to 32.24, 37.40, 53.92, 64.20, 79.85 and 88.55° referring to CaO (PDF 77-2376) and 2θ equal to 42.95 and 62.41° referring to MgO (PDF 78-430). As the presence of the MgO phase was not identified in the fresh catalyst, it is suggested that this phase was formed after decomposition of (CaMg)CO₃ present in the MW. Furthermore, the diffractogram revealed the presence of the metallic Ni⁰ phase, indicating that the catalysts retained active sites even after exposure to air.

The Ni⁰ average crystallite sizes were calculated for both fresh and spent catalysts. Specifically, the Ni-MgAl₂O₄ catalyst exhibited an increase in average crystallite size from 7 nm (fresh) to 13 nm (spent). Similarly, the Ni-Al₂O₃ catalyst showed an increase in average crystallite size from 6 nm (fresh) to 15 nm (spent). The increase in this parameter for both catalysts can be related to the sintering process. Elevated temperatures during synthesis or operation can enhance the mobility of Ni atoms, facilitating their aggregation and coalescence into larger crystallites. Prolonged exposure to high temperatures or aggressive reaction environments accelerates these growth mechanisms, reducing the available surface area for catalytic reactions and consequently diminishing catalytic activity [160,161].

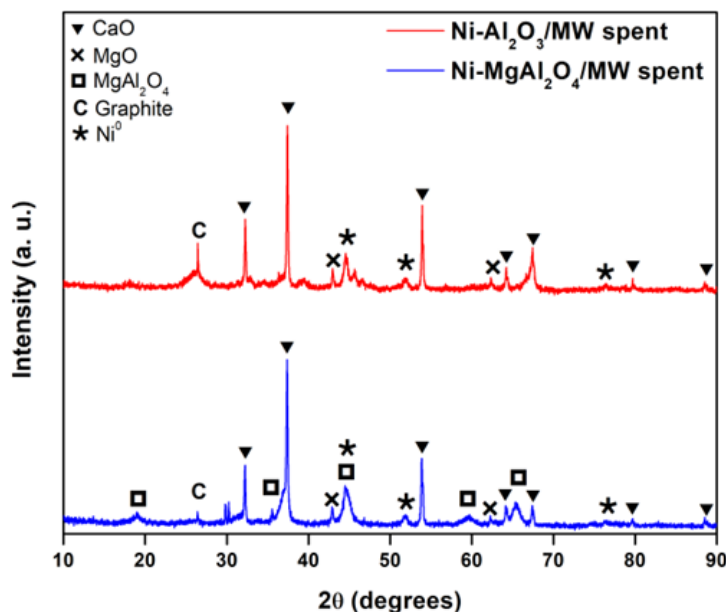


Figure 5.6. XRD analysis of the spent and regenerated catalysts at 800 °C under a flow of Ar 100 mL/min and H₂ 30 mL/min for 1 h.

A peak related to the graphitic carbon (PDF 8-415) phase was observed in both catalysts at 2θ equal to 26.5°. However, the peak's intensity in the Ni-MgAl₂O₄/MW catalyst was significantly lower compared to that in the Ni-Al₂O₃/MW catalyst. This is also another indication of higher CO₂ production when this catalyst is used. Similar

results were reported by Kim et al. [162] who investigated the addition of MgO to Ni and Al₂O₃ catalysts for steam reforming of methane. The authors found less carbon deposition in catalysts promoted by MgO, attributing this effect to greater basicity and greater interaction between supporting metal.

TGA analysis examined the average carbon deposition rates of two spent catalysts over a total of 22.6 hours (133 minutes per cycle across 10 cycles). Ni-Al₂O₃/MW catalyst showed the highest carbon deposition rate at 25.91 mgC g⁻¹cat h⁻¹, followed by the Ni-MgAl₂O₄/MW catalyst at 17.09 mgC g⁻¹cat h⁻¹. Previous discussions suggest that MgO may mitigate carbon deposition on catalyst surfaces. Oliveira and Hori [27] and Chen et al. [163] studied carbon deposition in various Mg-Al modified Ni catalysts, finding a lower deposition rate associated with the presence of MgO. The latter author further reported deposition rates ranging from 32.2 to 12.7, correlating with different Mg contents.

5.2.Conclusion

The development of bifunctional materials, Ni-Al₂O₃/MW and Ni-MgAl₂O₄/MW, for hydrogen production through SESR of ethanol utilising mining waste as a source of CaO was investigated. Both catalysts demonstrated high bioethanol conversion rates (>99%) and excellent stability during the hydrogen production process. Specifically, during the pre-breakthrough period, the Ni-Al₂O₃ catalyst achieved a H₂ molar fraction of 82.2%, while the Ni-MgAl₂O₄ catalyst achieved 75.8%. The duration of the pre-breakthrough period for the Ni-Al₂O₃/MW catalyst was ~ 42 min, which indicated the good capture capacity and stability of the material. For the Ni-MgAl₂O₄/MW catalysts, the pre-breakthrough period decreased to around 28 min, remaining during all cycles. The use of MW as an adsorbent not only provided an increase in the H₂ fraction due to the capture of CO₂ and displacement of the WGS reaction equilibrium, but was also responsible for the thermal stability of the material as it contained other oxides, such as MgO and Fe₂O₃, helping to reduce sintering of the adsorbent. Although capture using synthetic sorbents may be superior, the application of MW in the process is promising, being able to minimize environmental impacts in the industrial sector with lower costs.

**Chapter 6 – USE OF BIFUNCTIONAL NICKEL AND CALCIUM
OXIDE-BASED CATALYSTS PROMOTED WITH ZIRCONIUM
OXIDE AND ALKALI METALS IN THE SORPTION ENHANCED
STEAM REFORMING OF MODEL COMPOUNDS OF AQUEOUS
FRACTION OF BIO-OIL**

6.1. Results and discussion

6.1.1. Characterisation of fresh samples

All catalysts were prepared with 10 wt.% Ni. The NiCaZr catalyst contained 77.63 wt.% CaO, while both the NiCaKZr and NiCaNaZr catalysts contained 72 wt.% CaO. In addition to these components, the NiCaKZr catalyst included 10.20 wt.% ZrO₂ and 7.80 wt.% K₂O, whereas the NiCaNaZr catalyst contained 11.98 wt.% ZrO₂ and 6.02 wt.% Na₂O. Table 6.1 shows the results obtained via X-ray fluorescence (XRF). Therefore, given that the results obtained via this type of analysis are semi-quantitative, there is an agreement between what was obtained and what was theoretically expected. These differences noted in values can also be justified by experimental errors, losses throughout the material synthesis process and the purity of the reagents.

Table 6.1. Chemical composition (wt.%) of catalysts (NiCaZr, NiCaKZr, NiCaNaZr) obtained by X-ray fluorescence.

	Ni	CaO	ZrO ₂	Na ₂ O	K ₂ O	Others
NiCaZr	11.07	77.01	11.29	0	0.07	0.56
NiCaKZr	10.83	70.94	7.7	0.58	9.14	0.81
NiCaNaZr	11.5	70.69	9.53	6.5	0.13	1.65

The materials were prepared in order to obtain a bifunctional nickel supported on calcium oxide and ZrO₂ promoted with alkali metals. Figure 6.1 shows the diffractograms obtained for the fresh (reduced and passivated) materials. Ni phase (PDF 4-850) was identified at 2θ equals to 44.5 and 51.8°, indicating total reduction of NiO to Ni⁰. Ca(OH)₂ phase (PDF 84-1266) was also identified in all catalysts at 2θ equals to 17.9, 28.6, 33.9, 50.7°. Its occurrence could be linked to the catalyst reduction process, typically involving the removal of oxygen or other oxidizing elements from the catalyst surface, often conducted in a controlled atmosphere like hydrogen (H₂). As explained in the work of Jacob [164], if H₂ reacts with oxygen present on the surface of the catalyst, water is

formed. As the material is rich in CaO, which is highly hygroscopic, this phase may hydrates and forms $\text{Ca}(\text{OH})_2$. Another possibility that justifies the presence of $\text{Ca}(\text{OH})_2$ is the hydration of calcium oxide with the water present in the atmosphere [128]. M-ZrO₃ phases, where M represents Ca, Na, or K, was expected to be detected. However, only the CaZrO₃ phase (PDF 35-790) was identified (in all catalysts) at various angles: 22.1°, 31.1°, 31.4°, 45.2°, 50.4°, 50.9°, 55.8°, 56.7°, and 65.9°. The synthesis of calcium zirconate species involves a direct solid-solid reaction between CaO and ZrO₂. Throughout the synthesis steps, Ca^{2+} ions diffuse into the interface and lattice of ZrO₂ [165]. Its presence offers benefits to the catalyst, given its high Tammann Temperature (1218°C), which can significantly enhance the material's stability [128].

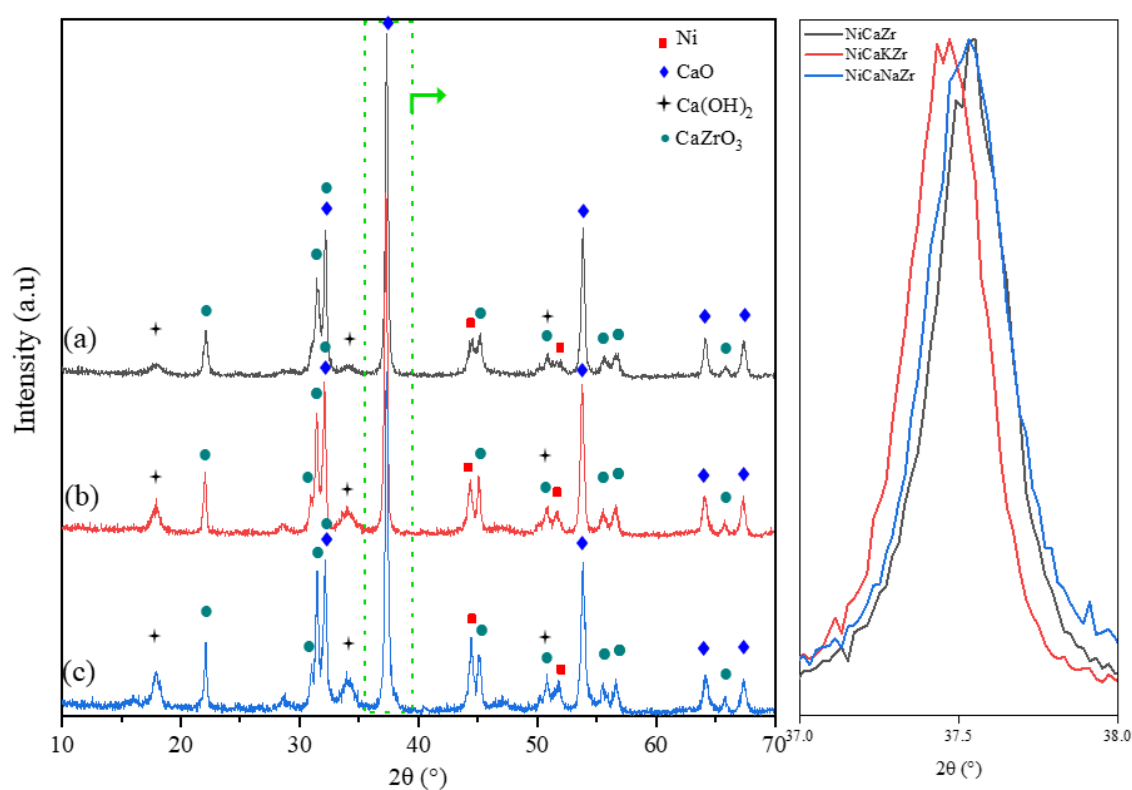


Figure 6.1. X-ray diffraction patterns of reduced and passivated catalysts at room temperature. Legend: (a) NiCaZr, (b) NiCaKZr and NiCaNaZr.

Although XRF analysis detected the presence of Na and K species, their addition did not induce the formation of additional crystalline phases. Several studies [92,166–168] have reported that the incorporation of alkali metals did not result in changes in the crystal structure detectable by X-ray diffraction (XRD). Osaki and Mori [168] found that the XRD patterns of K-modified Ni/Al₂O₃ catalysts lacked peaks for K species, even at a high K loading of 10 wt.%. Bacariza et al. [166] incorporated 15 wt.% of alkali metals (Li, K, and Cs) into Ni/USY catalysts and did not observe clear diffraction peaks

attributed to K or Cs. Additionally, Hu et al. [29] prepared a bifunctional Ni/CaO catalyst doped with 5 wt.% of alkali metals (Li, Na, and K) and were also unable to identify new crystalline phases associated with these components. In general, despite the incorporation of metals such as sodium, potassium and caesium into various matrices, the primary crystalline structure has remained unchanged. The aforementioned studies attribute this result to the likelihood of alkali metals being integrated into the existing crystal lattice in an amorphous and/or highly dispersed state across the catalyst surface.

The average crystallite size of the metallic nickel and calcium oxide for fresh catalysts were estimated using the Scherrer Equation, at diffraction angles of 44.5° and 37.1° . NiCaZr catalyst presented the lowest Ni average crystallite size (14 nm). In catalysts with the addition of alkali metals, the Ni average crystallite sizes were larger than in the first case, and similar to each other (~ 23 nm). The CaO average crystallite sizes of the fresh catalysts were quite similar, with a maximum variation of only 10%. Among the catalysts, the NiCaKZr exhibited the largest average crystallite size (33 nm), followed closely by NiCaKZr and NiCaNaZr (31 nm).

The peak corresponding to pure calcium oxide (CaO) in the NiCaZr catalyst appears at the expected 2θ position. After doping the material with alkali metals, a shift of this peak to smaller angles was observed. A possible reason for this shift is the incorporation of these alkali metals into the CaO crystal structure, which results in an expansion of the lattice, since Na and K atoms could occupy the Ca sites in the crystal structure. This is related to the different atomic radii of materials: 186 pm for sodium, 220 pm for potassium and 180 pm for calcium. According to Bragg's law (Equation 6.1), the position of the diffraction peaks (2θ) is inversely proportional to the interplanar spacing (d). Therefore, doping with alkali metals such as Na and K, which have larger atomic radii than Ca, results in an increase in the interplanar spacing of the CaO crystal lattice. This increase causes the diffraction peaks to shift to smaller 2θ angles, as observed experimentally and being more pronounced for NiCaKZr.

$$n\lambda = 2d\sin\theta \quad \text{Equation 6.1}$$

Where n is an integer (order of diffraction), λ is the wavelength of X-radiation, and θ is the angle of diffraction. When dopant atoms (Na and K) replace Ca atoms, the increase in interplanar spacing d due to the larger atomic radius of the dopants causes the angle θ to decrease, shifting the diffraction peaks to smaller 2θ positions.

Literature studies demonstrate the feasibility of doping the CaO crystal structure with alkali metals, as elucidated by Wang et al. [169]. Effects of Li, Na, K, Rb, and Cs doping in metal oxides (MgO, CaO, SrO, BaO) using DFT-D simulations were investigated. Their findings indicate that alkali metal doping can create basic sites, where the electron donated by the alkali metal resides within defects such as oxygen vacancies (F^+ centres). These vacancies represent sites within the crystal lattice where an oxygen atom is absent, facilitating the localisation of additional electrons. Consequently, these sites form F^+ centres, characterised by an additional positive charge attributable to the presence of the extra electron. Additionally, Marí et al. [170] conducted a study characterising CaO, SrO, and CaSrO_2 phosphors co-doped with Eu^{3+} and alkali metal ions. The authors presented diffractograms of CaO co-doped with Eu^{3+} and M^+ ($M = \text{Na}$ and K). Similar profiles were obtained, suggesting that the co-doping of alkali metal ions with Eu^{3+} did not induce significant structural changes in CaO. This phenomenon was attributed to the comparable ionic radii of Eu^{3+} (94.7 pm, coordination number = 6) and Na^+ (102 pm, coordination number = 6), which closely resemble those of Ca^{2+} (100 pm, coordination number = 6), facilitating their efficient substitution. Despite the notably larger ionic radius of K^+ (138 pm), its successful incorporation into the CaO lattice was observed, causing minor structural distortions that affected the diffraction peak intensities. Furthermore, a shift to smaller angles 2θ was observed for the $\text{CaO}:\text{Eu}^{3+}$, $\text{Na}^+/\text{CaO}:\text{Eu}^{3+}$ and $\text{K}^+/\text{CaO}:\text{Eu}^{3+}$ materials, presenting values at 37.342° , 37.276° and 37.258° , respectively. This behaviour was explained by the variation in the atomic radii of the alkali metals inserted in the CaO crystal lattice.

The reducibility of the catalysts was inspected by TPR experiments and results are shown in Figure 6.2. All samples exhibited reduction peaks within the temperature range of 300 to 650 °C. The addition of alkali metals resulted in a shift of the peaks from approximately 500 °C to about 450 °C. Usually, the reduction peaks at lower temperatures are associated with the reduction of free NiO species, while the ones that appear at higher temperatures correspond to the reduction of complex NiO species with significant interaction with the support [171,172]. Additionally, in catalysts incorporating alkali metals, an additional peak was detected around 810 °C. Fu et al. [173] prepared a CaO-based bifunctional catalysts with Ni, Co, Mn and Fe to be used in the calcium-looping and reverse-water-gas-shift reaction. For the Ni-CaO catalyst, a reduction peak around 650 and 900 °C was observed, and this profile was assigned to the reduction of NiO incorporated into the CaO adsorbent and interacting strongly with CaO. All catalysts

showed the formation of CaZrO_3 , suggesting that NiO might be supported also on CaZrO_3 . Therefore, peaks related to weak and strong NiO- CaZrO_3 interactions are expected between 400 and 630 °C [174].

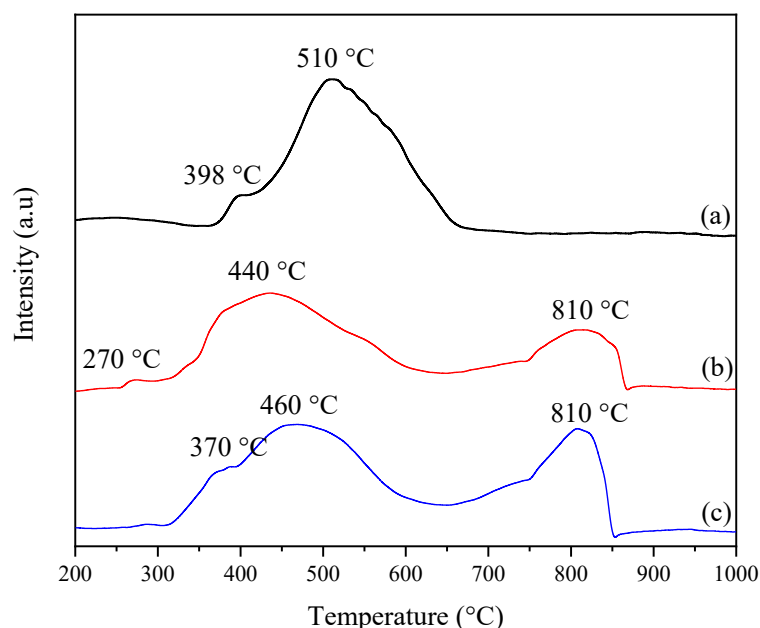


Figure 6.2. H_2 -TPR profiles for the bifunctional catalysts: (a) NiCaZr, (b) NiCaKZr, (c) NiCaNaZr.

Jang et al. [172] carried out a study of metal oxide (MgO , CaO , and La_2O_3) promoted Ni- $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalysts for H_2 and CO production from two major greenhouse gases. In their work, the authors reported TPR results and verified peaks around 813 °C for the catalyst with alkali metal Mg. The presence of this peak was related to the reduction of complex NiO species, which could be located in the subsurface layers of the MgO , showing interaction between NiO and MgO species. Similarly, in our study, the presence of the peak at 810 °C could also be ascribed to the interaction between NiO and alkali metal oxides species.

Hu and Lu [175] reported on the utilisation of $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts modified with a series of promoters (Li, Na, K, Mg, Fe, Co, Zn, Zr, La, Ce) in the acetic acid reforming reaction. The reduction profile of different catalysts was assessed via TPR, with temperatures ranging from 100 to 800 °C. In the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, the reduction profile exhibited a main peak around 610 °C. With the addition of K and Na, the authors observed the presence of two peaks, the first at around 400 °C and the second at around 800 °C. By shifting the first reduction peak to lower temperatures, the authors concluded that the inclusion of alkali metals promoted the reduction of NiO species. Similar behaviour was reported by Yang, Feng, and Chu [171]. They found that for the K-Ni/ Al_2O_3 catalyst, the

NiO reduction peaks shifted to a lower temperature, and that the H₂-uptake for the K-modified Ni/Al₂O₃ catalyst was significantly higher than that of the bare catalyst, a result akin to that reported in Table 6.2. Furthermore, the authors correlated XRD data with TPR, emphasizing that the reduced Ni metal exists in the form of aggregates with large crystallite size. This same behaviour was observed in the present work (Table 6.5).

Table 6.2 presents the experimental H₂ consumption and reduction degree for all catalysts. The incorporation of alkali metals enhanced the reduction of NiO species, increasing the reduction degree from 72% to 80% and 83%, with the Na-containing catalyst showing the highest value. This outcome aligns with expectations and previous discussions based on literature reports.

Table 6.2. H₂ experimental consumption ($\mu\text{mol/g}_{\text{cat}}$) and degree of reduction (%) for the NiCaZr, NiCaKZr and NiCaNaZr catalysts.

Catalyst	H ₂ _{experimental} consumed ($\mu\text{mol/g}_{\text{cat}}$)	Degree of reduction (%)
NiCaZr	1231	72
NiCaKZr	1363	80
NiCaNaZr	1422	83

A thermal pre-treatment was carried out on the materials to remove impurities, moisture, and carbonates. After this step, the materials underwent 20 cycles of carbonation and calcination, lasting approximately 26 hours (Figure 6.3). In the first cycle, weight increases of 52%, 45%, and 47% were observed for the NiCaZr, NiCaKZr, and NiCaNaZr catalysts, respectively. By the end of the 20th cycle, these values had decreased to 33%, 32%, and 30%, respectively. Consequently, the loss of CO₂ capture capacity for these materials was 37%, 29%, and 38%, respectively. Thus, under the operating conditions of the TGA technique, the NiCaKZr catalyst exhibited the best results over the cycles. Regarding the influence of alkali metal addition on the thermal stability test, the NiCaKZr, and NiCaNaZr catalysts exhibited a lower capture capacity in the first cycle compared to NiCaZr. However, they also maintained good thermal stability throughout the process.

In general, the loss of CO₂ capture capacity observed for all catalysts can be linked to the sintering process. This process is related to the high temperatures at which CaCO₃ calcination occurs, which can affect the CaO product layer. This phenomenon involves structural changes in the particle, potentially affecting pore size, distribution, and overall

porosity. Consequently, the effective diffusivity of CO_2 passing through the CaO layers is impacted [176].

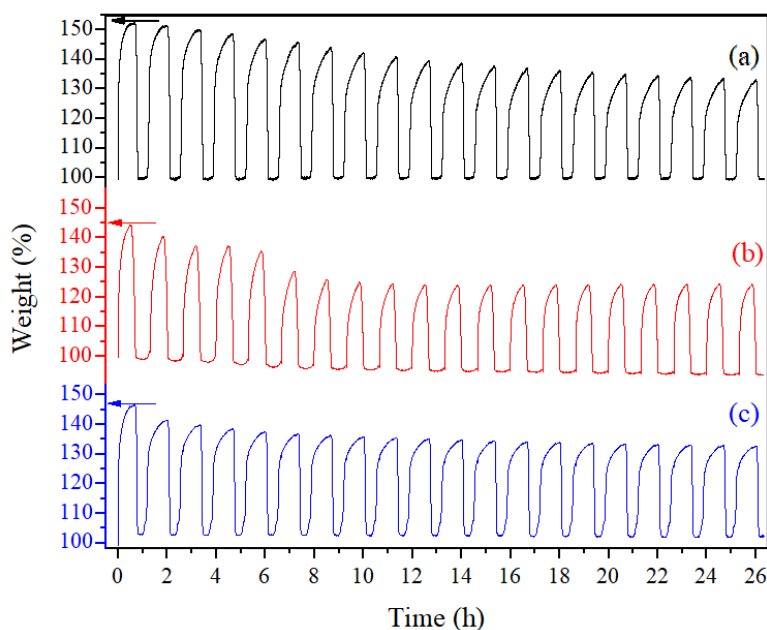


Figure 6.3. Carbonation and regeneration cycles obtained via thermogravimetric analysis (TGA). Conditions: carbonation at 600 °C under 15% CO_2/He , Regeneration at 800 °C under pure He atmosphere. (a) NiCaZr, (b) NiCaKZr, (c) NiCaNaZr.

In the study conducted by Oliveira et al. [145], propane SESR was investigated using three different bifunctional catalysts, one of which had a theoretical composition of 10% Ni supported on 72% CaO and 18% CaZrO_3 . 20 carbonation and calcination cycles were conducted via TGA under operational conditions similar to those in this work. The authors observed that the Ni-CaO- CaZrO_3 catalyst exhibited a weight gain of approximately 50% in the first cycle, decreasing to around 33% in the 20th cycle. In comparison to the catalyst containing only CaO, this material demonstrated greater thermal stability during the carbonation test. This increased stability was attributed to the minimisation of CaO sintering due presence of CaZrO_3 . In the present study, a catalyst with a similar composition was tested (NiCaZr), and the initial and final weight gain for the material were very similar with the findings reported by Oliveira and collaborators.

Figure 6.4 presents the CO_2 capture capacity results per mass of the catalyst. The initial capture capacities of the NiCaZr, NiCaKZr, and NiCaNaZr catalysts were 0.60, 0.40, and 0.28 g CO_2/g catalyst, respectively. By the end of the 20th cycle, these capacities had decreased to 0.22, 0.31, and 0.22 g CO_2/g catalyst. Throughout the entire process, the catalyst doped with K demonstrated a higher capture capacity than the catalyst doped with

Na. Despite having a higher initial capacity, the NiCaZr catalyst showed a significant reduction in capture capacity. Quantitatively, the loss was greater for the NiCaZr catalyst (63%). In contrast, the NiCaNaZr and NiCaKZr catalysts exhibited similar reductions, with losses of 21% and 23%, respectively.

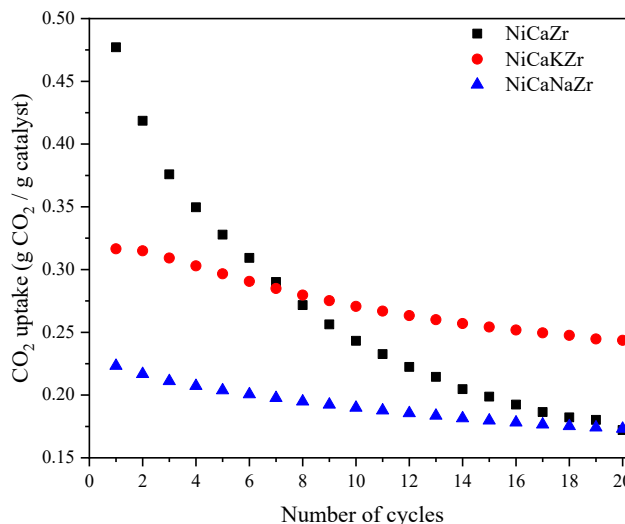


Figure 6.4. CO₂ capture capacity of catalysts (NiCaZr, NiCaKZr, NiCaNaZr).

Conditions: carbonation at 600 °C under 15%CO₂/He, Regeneration at 800 °C under pure He atmosphere.

Luisetto et al. [177] investigated the impact of CaO content on cyclic stability during the CO₂ capture process. The authors synthesized CaO-CaZrO₃ catalysts with theoretical CaO concentrations of 40, 60, and 80 wt.% using the auto-thermal combustion method. Quantitative phase analysis was conducted using the reference intensity ratio (RIR) method, determining the phase amounts of CaZrO₃, CaO, Ca(OH)₂, and CaCO₃ in each catalyst. For the 40 wt.% CaO catalyst, the phase amounts were 52.8% CaZrO₃, 20.4% CaO, 25.5% Ca(OH)₂, and 0.3% CaCO₃. In the 60 wt.% CaO catalyst, the phase amounts were 35.8% CaZrO₃, 44.8% CaO, 18.9% Ca(OH)₂, and 0.5% CaCO₃. For the 80 wt.% CaO catalyst, the phase amounts were 14% CaZrO₃, 3% CaO, 73.5% Ca(OH)₂, and 9.5% CaCO₃. The inclusion of CaZrO₃ was justified by its role as a spacer, which prevents the sintering of CaO grains at high temperatures, and by its ability to reduce the diffusional resistance of CO₂ migrating towards the internal grains of the synthetic sorbent. 13 carbonation and calcination cycles were conducted. Regarding the CO₂ capture capacity per gram of sorbent, initial values of 0.31, 0.47 and 0.57 were obtained, with final values of 0.30, 0.34 and 0.42 for the 40%-CaO, 60%-CaO and the 80%-CaO catalysts, respectively. Comparatively, in the present work the NiCaZr catalyst presented

a composition similar to the 80 wt.% CaO catalyst reported by the authors. Regarding the capture capacity, the materials presented comparable results, with final values of 0.42 gCO₂/gsorb.

Different models can describe CO₂ capture kinetics, including the double-exponential model (Equation 6.2). This model involves two distinct phases: a rapid phase and a slow phase. Initially, CO₂ rapidly sorbs onto the surface of unreacted CaO particles, forming a core-shell structure where unreacted CaO is enveloped by a layer of CaCO₃. Subsequently, CO₂ begins to diffuse towards the unreacted nucleus, initiating an additional sorption step. However, this diffusion process is slow and challenging, thus limiting the overall mechanism. In the case of smaller CaO particles, the distance for CO₂ diffusion is shorter, resulting in a faster and easier sorption process compared to larger particles [150]. CO₂ uptake capacity data obtained from TGA analysis were fitted to Equation 6.2, where y represents the weight percentage of sorbed CO₂, A and B are the pre-exponential factors related to the amount of CO₂ capture, and C is the pre-exponential factor that indicates the maximum CO₂ captured. Exponential constants are represented by k_1 and k_2 . Specifically, k_1 represents the CO₂ chemisorption step, and k_2 represents the CO₂ diffusion step.

$$y = A e^{-k_1 x} + B e^{-k_2 x} + C \quad \text{Equation 6.2}$$

Table 6.3 presents the kinetic parameters for all catalysts, along with the coefficient of determination (R^2) values and the k_1/k_2 ratio. Analysing this ratio helps determine the controlling step of the process. According to Oliveira et al. [27], k_1/k_2 ratios greater than 1 indicate that CO₂ diffusion through the external CaCO₃ layer is the controlling step. This was the case in this study, as all k_1/k_2 values exceeded 1.

Table 6.3. Kinetic parameters of carbonation process for the bifunctional catalysts estimated by fitting the CO₂ uptake data to a double exponential model.

Catalyst	Cycle	A	B	C	$k_1(\text{s}^{-1})$	$k_2(\text{s}^{-1})$	k_1/k_2	R^2
NiCaZr	1 st	-51.400	-15.860	57.131	0.484	0.038	12.603	0.984
	20 th	-1.900	-48.090	50.088	0.168	0.005	37.178	0.999
NiCaKZr	1 st	-33.310	-21.210	47.708	0.453	0.060	7.547	0.992
	20 th	-17.940	-17.200	32.205	1.410	0.095	14.811	0.996

NiCaNaZr	1 st	29.520	-22.140	46.947	1.140	0.096	11.910	0.998
	20 th	-0.420	-6.740	7.070	0.685	0.032	21.186	0.998

Yoon and Lee [150] calculated the kinetic parameters for the different catalysts studied: unmodified CaO (CaO) and CaO modified with Zr (CaZr) (ZrO₂ was added in a minor proportion, maintaining a Ca/Zr molar ratio of 30). In all analyses, the authors obtained k_1 higher than k_2 , concluding that the limiting stage of the process corresponded to the diffusion of CO₂ through the carbonate layer. In addition to this analysis, the authors adjusted the experimental data from the capture tests to a deactivation model to verify the cyclic CO₂ sorption performance of the sorbents. This type of data processing has been reported in the literature for different materials [27,30,178]. A lower deactivation coefficient value indicates better cyclic stability of the material, once this coefficient reflects the expected reduction in CO₂ sorption performance per cycle. For the CaO and CaZr sorbents prepared via the solid-state method, values of 0.1096 and 0.0675 were obtained, respectively. Similarly, the deactivation coefficient for the catalysts used in this work was calculated using Equation 6.3, and the results are presented in Table 6.4.

$$a = K x e^{-k_d N} \quad \text{Equation 6.3}$$

In this equation, N stands for the number of carbonation/decarbonation cycles, k_d represents the deactivation coefficient, K is a pre-exponential constant in the model. The sorbent activity a is defined as the amount of CO₂ sorption uptake during the Nth cycle, divided by the maximum CO₂ sorption capacity of CaO.

Table 6.4. Parameters estimated through the deactivation model utilising TGA data.

	K	- k_d	R ²
NiCaZr	0.5777	0.0563	0.9566
NiCaKZr	0.4065	0.0149	0.9794
NiCaNaZr	0.2791	0.0130	0.9680

According to the Table 6.4, the highest k_d value was observed for the NiCaZr catalyst. In contrast, the alkali metal-doped catalysts showed quite similar k_d values. This indicates that the doped catalysts experienced less deactivation over the operating time compared to the NiCaZr catalyst, thereby retaining their catalytic activity and effectiveness during use.

6.1.2. Catalytic tests

Catalytic tests were conducted using a reaction mixture representing the aqueous fraction of the bio-oil, composed by water, acetic acid and ethanol. Ten reaction cycles were performed, each lasting 96 minutes. The identified products were H_2 , CO_2 , CH_4 , and CO , with only the fractions of the first two being shown in the Figure 6.5. In all cases, ethanol and acetic acid exceeded 99% and 95%, respectively. The dashed lines represent the thermodynamic equilibrium data for each reaction product, calculated using the CEA software. It is important to note that, in the graphs, the values obtained by the thermodynamic analysis are presented only to illustrate the maximum values that can be achieved at equilibrium, for comparison purposes with the catalytic results obtained. For this, in the pre-breakthrough period, the equilibrium molar fractions (with the effect of the adsorbent) were considered. In the post-breakthrough period, the equilibrium molar fractions without adsorbent effect were considered.

Figure 6.5 shows the SESR product distribution using three different catalysts: NiCaZr (a), NiCaKZr (b), and NiCaNaZr (c). In all cases, during the 1st reaction cycle at pre-breakthrough stage (labelled as "I" in the graph), the molar fractions of hydrogen obtained are above 90%. At this point, the adsorbent material presents its maximum CO_2 adsorption capacity, increasing the purity of the H_2 produced. The duration of this stage in the 1st cycle varied, with NiCaNaZr showing the highest value (48 min), followed by NiCaKZr (30 min), and NiCaZr (18 min). In absolute terms, the NiCaKZr catalyst retained its capture capacity more effectively throughout the 10 cycles, exhibiting a pre-breakthrough time variation of 18 minutes, compared to 36 minutes for the NiCaNaZr catalyst. This performance aligns with the TGA results, which also indicated superior stability for the NiCaKZr catalyst. This shows that the alkali metal-doped catalysts were able to maintain the CO_2 capture process for longer.

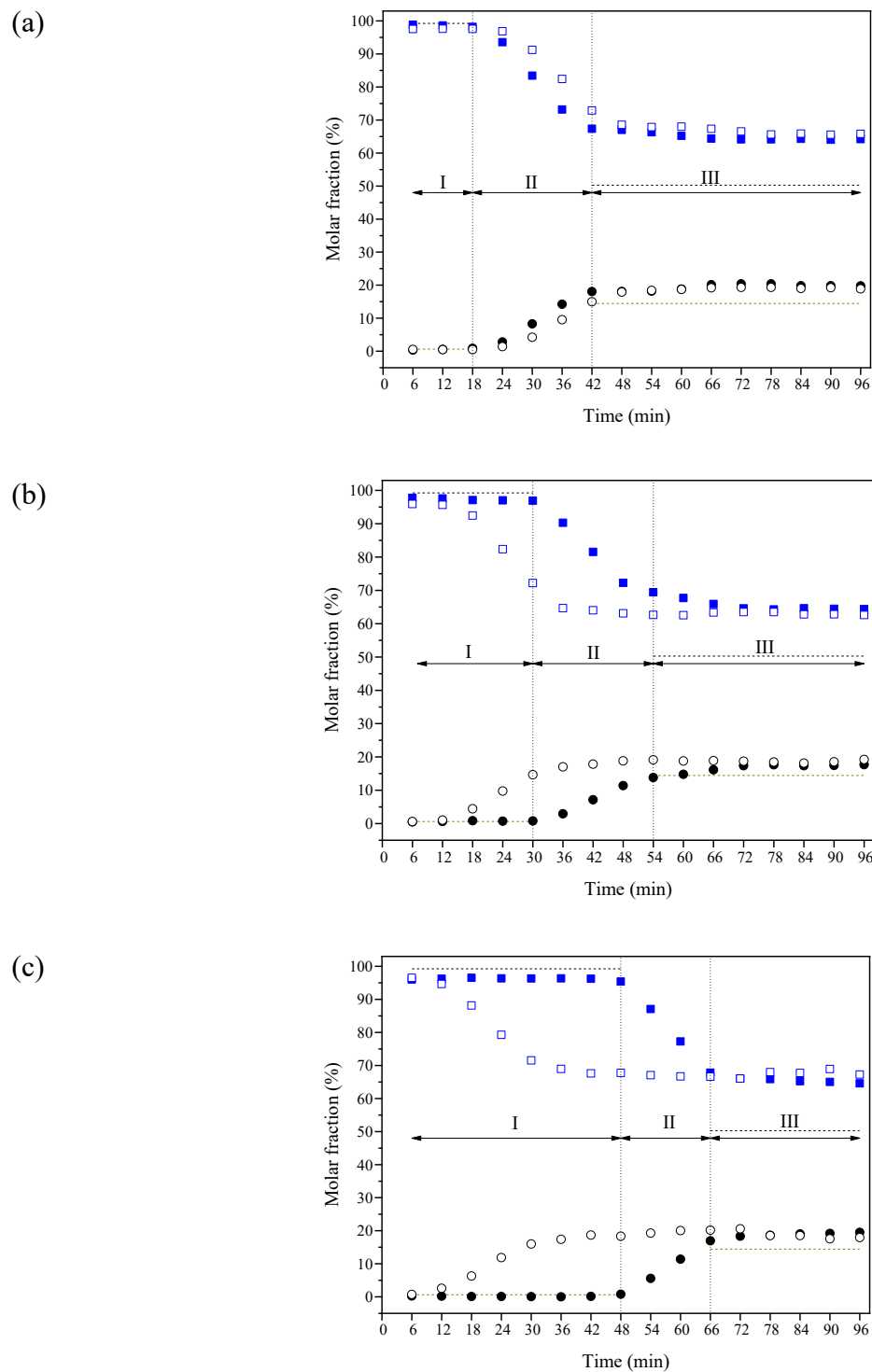


Figure 6.5. Profiles of H_2 (■) and CO_2 (●) molar fraction on dry basis as a function of time during the SESR for 1st (filled symbol) and 10th (empty symbol) cycles for (a) NiCaZr, (b) NiCaKZr, and (c) NiCaNaZr. Conditions: $T = 500\text{ }^\circ\text{C}$, $S/C = 2.25$, $m_{\text{cat}} = 0.80\text{ g}$, Ar flow = 100 mL/min. Dashed line: thermodynamic equilibrium.

Once the post-breakthrough stage began, indicated as "III" in the graph, the adsorbent material ceased to capture CO₂, leading to the conventional steam reforming. NiCaNaZr lasted the longest during stages I and II (66 min in the 1st cycle, decaying to 30 min in the 10th cycle), followed by NiCaKZr and NiCaZr catalysts (54 and 42 min in the 1st cycle, decaying to 30 and 18 min in the 10th cycles, respectively).

During the 10 cycles of steam reforming with CO₂ capture, the NiCaZr catalyst maintained a constant pre-breakthrough time of 18 minutes, demonstrating good stability. Although this consistent performance is commendable, the initial pre-breakthrough time was relatively modest. In contrast, the NiCaKZr and NiCaNaZr catalysts started with significantly longer pre-breakthrough times (54 and 48 minutes, respectively), indicating their efficiency at capturing CO₂. Despite experiencing a reduction in pre-breakthrough time, decreasing to approximately 12 minutes, these catalysts still ended up with times comparable to the NiCaZr catalyst. This suggests that, although they underwent degradation, the doped catalysts exhibited superior initial CO₂ capture capacity.

As for the thermodynamic equilibrium data, the values for the experimental mole fractions of H₂ are smaller, but similar during stage I, especially in the 1st cycle. As the process progresses, these values become more distant, which can be attributed to the increase in the mole fraction of other hydrogenated products, as CH₄. Additionally, as mentioned earlier, divergences may occur due to the operating conditions of the system, since equilibrium calculations assume an isobaric and isothermal system without the input of external matter [30].

Since this study uses a novel reaction mixture, directly comparing catalyst performance in SESR processes with the same raw materials is unfeasible. However, it is possible to draw comparisons with studies that have explored the use of catalysts doped with alkali metals in the steam reforming of different reaction mixtures. Frusteri et al. [179] investigated the effects of alkali metals (Li, Na, K) on Ni/MgO catalysts in bio-ethanol steam reforming. Experiments were conducted in a fixed-bed quartz microreactor at atmospheric pressure, using 0.010–0.060 g of catalyst diluted with 150–300 mg of carborundum (SiC). Each catalyst (bare, Na-doped, K-doped, Li-doped) was tested for 20 hours at 550–650 °C and a steam/carbon ratio of 4.2. They found that doping Ni/MgO catalysts with alkali metals was highly effective in enhancing catalysts performance. The dopants promoted NiO reduction and improved catalyst stability by reducing metal sintering, achieving H₂ selectivity above 95%. Evin et al. [180] studied alkali doping (Li and Na) of Pt/ceria catalysts for low-temperature water–gas shift and methanol steam

reforming. Catalysts with alkali metals showed greater activity than undoped ones, as these additives improved methoxy decomposition at 160 °C by weakening C–H bonds, thus enhancing methanol conversion. Additionally, the Na-doped catalyst exhibited greater CO₂ selectivity than the undoped Pt/ceria catalyst across all tested temperatures. Yu et al. [181] investigated the steam reforming of acetic acid with nickel catalysts, assessing the impact of alkali metals (Na and K) and a range of other additives, including alkali earth, transition, and rare earth metals (Mg, Ca, Sc, Cr, Mn, Fe, Co, Cu, Zn, Zr, La, Ce). The catalysts were tested in a fixed-bed quartz reactor at temperatures between 300 and 600 °C using 0.5 g of material. Nitrogen flowed at 60 mL/min, and reactions were conducted for 30 minutes at each temperature. Acetic acid was introduced at a flow rate of 0.12 mL/min, with a steam/C of 5:1. The authors observed that alkali metals (K and Na), transition metals (Co), and rare earth metals (La and Ce) significantly improved catalyst activity by facilitating the reduction of nickel oxides.

6.1.3. Characterisation of spent samples

After the end of the reaction cycles, the catalysts were subjected to different characterisation techniques to verify possible changes in their structures. XRD of the spent catalysts (reduced and passivated) are shown in Figure 6.6. The results obtained were quite similar to those of fresh catalysts. Ni, CaO, Ca(OH)₂, and CaZrO₃ phases were identified in all cases. The presence of the Ni⁰ phase indicates that the metallic phase of the catalyst was preserved, suggesting that the catalyst maintained its ability to catalyse the reaction after the regeneration process. The average crystallite sizes for the Ni⁰ and CaO phases were calculated for the fresh and spent catalysts, and the result is shown in Table 6.5.

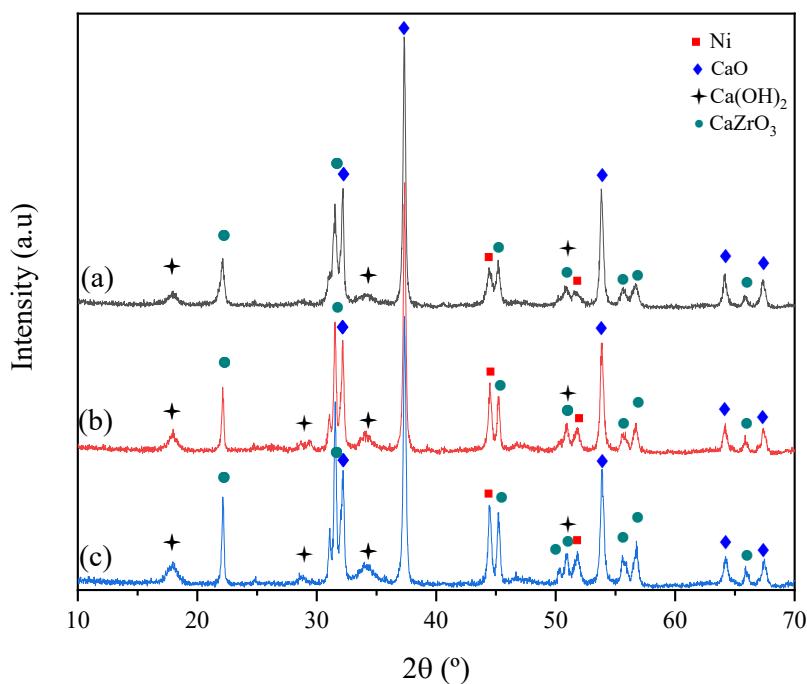


Figure 6.6. X-ray diffraction patterns of spent catalysts at room temperature: (a) NiCaZr, (b) NiCaKZr and (c) NiCaNaZr.

Table 6.5. Properties of fresh and spent catalysts.

	Catalyst	Average Crystallite size (nm)		Surface area (m ² /g)
		Ni	CaO	
Fresh	NiCaZr	14	33	39.1
	NiCaKZr	23	32	44.4
	NiCaNaZr	24	30	53.3
Spent	NiCaZr	20	37	37.8
	NiCaKZr	27	36	77.2
	NiCaNaZr	27	34	60.7

In the spent catalysts without the addition of alkali metals, the Ni average crystallite size increased considerably, by 42%. However, when K and Na were added, this increase was smaller (17 and 12%, respectively), indicating a less pronounced sintering process. Among fresh catalysts, an increase in Ni average crystallite size was observed with addition of alkali metals.

In this study, alkali metals were incorporated into the NiCaZr catalyst to act as spacers aimed at preventing the agglomeration of active nickel (Ni) particles and enhancing their dispersion. However, the calculated average crystallite size for the fresh catalysts did not reflect this intended outcome. This finding is not uncommon in the

literature, having already been reported in the work of Chen and Chen [167] and Yu et al. [181]. For instance, Yu et al. observed larger metallic nickel particle sizes when alkali metals were introduced in the nickel catalysts (e.g., from 14 nm for Ni/Al₂O₃ to 19.8 nm and 17 nm for Na-Ni/Al₂O₃ and K-Ni/Al₂O₃, respectively).

The explanation for the effect of doping alkali metals in different fresh catalysts remains relatively unexplored. Chen and Chen [167] studied strategies to mitigate coke formation and sintering in Ni-alumina catalysts using alkali and alkaline earth metals (1 wt.%) as promoters. The fresh-unpromoted catalyst had an average crystallite size of 16.1 nm. When adding potassium to the material, a significant increase in average crystallite size was observed (20.6 nm), while adding sodium had no notable effect (15.8 nm). However, the authors did not provide an explanation for these changes. After 5 hours of catalytic cracking of n-hexane, particle sizes increased: unpromoted Ni (25.9 nm), Ni-K (21.4 nm), and Ni-Na (23.1 nm). The increase was attributed to nickel sintering or site blocking by carbon deposits.

In the present work, the rationale for the increase in the nickel average crystallite size in the fresh catalysts is grounded in the alkali metal precursors utilised. For synthesising the NiCaZr catalyst, nickel and calcium nitrates were employed through the citrate sol-gel method, without precipitation of precursors. Conversely, in NiCaKZr and NiCaNaZr catalysts, sodium and potassium carbonates were added alongside nitrates as precursors, leading to visible precipitation during preparation. Wu et al. [182] explored the preparation of the bifunctional Ni-CaO-CeO₂ catalyst using various techniques including wet mixing, coprecipitation, and sol-gel. They found that the physicochemical properties of the materials were influenced by the choice of precursors and preparation methods, impacting the nickel grain size in the catalysts. Specifically, the sol-gel method yielded a smaller Ni grain size (19.66 nm) compared to coprecipitation (25.56 nm). In summary, the selection of precursors and synthesis method played a pivotal role in shaping the structure of the catalysts under investigation. In this present work, the use of carbonates in the alkali metal catalysts introduced a precipitation step during preparation, and as discussed by Wu et al., this variation may have affected the average crystallite size of these materials.

Regarding the CaO average crystallite size, a slightly increase for the spent catalysts was observed in all cases. And this result is in line with the results observed via TGA and catalytic test. This can occur due to several factors, such as the sintering of CaO particles, which can affect material properties such as specific surface area and catalytic

activity [108]. It should be noted, however, that the increase was not substantial ($\sim 10\%$), which is attributed to the presence of spacers in the material. In a study by Yoon and Lee [150], the role of zirconium oxide in CaO-based sorbents was examined. It was discussed that homogeneously distributed and chemically bonded CaZrO_3 on the CaO surface effectively creates spacing between CaO molecules, thereby protecting the material from sintering. Following this insight, the amount of inert material (CaZrO_3 , K_2O , and Na_2O) present in each catalyst in this study was quantified using theoretical values. Despite a consistent weight content across all materials (18 wt.%), the mole quantities differed, being 3.01×10^{-3} , 7.45×10^{-3} and 8.75×10^{-3} for the NiCaZr, NiCaKZr, and NiCaNaZr catalysts, respectively. These variations suggest that the reduced sintering observed in catalysts doped with alkali metals can be attributed to the higher number of spacer atoms in the material.

The surface area results are shown in Table 6.5. For fresh catalysts, the addition of alkali metals led to an increase in surface area. Compared to the NiCaZr catalyst, the NiCaNaZr and NiCaKZr catalysts showed increases of 36% and 13%, respectively. This outcome underscores the benefits derived from the inclusion of these metals in order to enhanced the physical characteristics of the catalysts. A similar effect was obtained by Santos, Oliveira and Hori [92] when doping the catalyst with Na. The authors investigated the performance of Na_2CO_3 -CaO sorbent in SESR of methane. Two catalysts based on nickel and calcium oxide were prepared, one doped with Na. In fresh materials, an increase in surface area was observed in the case where Na was added (from 94 to 98 m^2g^{-1}). Regarding the spent catalysts, Na-catalyst showed a much less pronounced surface area reduction than the unpromoted catalyst (83 m^2g^{-1} and 94 m^2g^{-1} for NiCa and NiCaNa catalysts, respectively).

Additionally, a comparison of the surface areas of fresh and used catalysts was conducted. For the spent NiCaKZr and NiCaNaZr catalyst, a significant increase in surface area was noted. In contrast, for NiCaZr catalyst, a slight decrease in surface area was observed upon use, but remaining quite similar (from 39.1 to 37.8 m^2g^{-1}). With a similar catalyst to the one in the present work, Wang et al. [183] also observed a decrease in the surface area of the material after 10 reactional cycles of ethanol SESR. The authors employed a bi-functional Ni-CaO- CaZrO_3 catalyst with theoretical compositions of 10% CaZrO_3 and 90% CaO, and varied the Ni content from 5% to 25%. The authors observed a decrease in surface area for all tested materials upon characterisation of the spent

material. Notably, the surface area of the Ni₁₀-Ca₉₀Zr₁₀ material slightly decreased from 18.7 m²g⁻¹ to 10.5 m²g⁻¹.

The variation in surface area in fresh and spent materials can be linked to several factors. A decrease in BET surface area can result from sintering or particle aggregation during heat treatments, which reduces the available adsorption surface due to particle fusion. Aggregation during preparation or handling can also reduce the exposed area [68]. Another common cause is contamination or blocked pores. Adsorbed substances such as gases, vapours or contaminants during material preparation or storage can block the pores, preventing the measuring gas from reaching the entire internal surface during BET analysis. Additionally, structural changes such as recrystallisation, phase transitions, or surface reactions can alter morphology and reduce surface area [184,185]. In contrast, an increase in BET surface area may indicate material hydration. When CaO is exposed to water, it reacts to form Ca(OH)₂, which has a more porous structure and greater surface area compared to CaO. This reaction creates new calcium hydroxide crystals with fine particles and plates, enhancing the specific surface area. Additionally, the volumetric expansion of Ca(OH)₂ compared to CaO leads to additional microcracks and pores, further increasing the total area available for adsorption [186,187].

To verify the rate of carbon deposition in the three spent catalysts and the effect of the addition of alkali metals on this parameter, the materials were subjected to TGA analysis. In the reforming process, the challenge lies in having a catalyst capable of breaking the bonds in the structure of what is being fed and, at the same time, effectively eliminating the carbon formed [188]. The objective is to have a regenerated catalyst at the beginning of each cycle. The carbon deposition rates obtained were 18.5, 9 and 18 mgC g⁻¹cat h⁻¹ for the NiCaZr, NiCaKZr and NiCaNaZr catalysts, respectively. The results suggest that the addition of alkali metals, particularly potassium (K), contributed to decreasing the rate of carbon deposition on the catalyst surface. Findings from Bennett and Price [189] demonstrated that alkali metals and other inorganic components can increase coke gasification due to the oxygen transfer mechanisms that are responsible for carbon oxidation. This is intensified when there are carbonates or oxides of Na, K, Li, Rb, Cs, Ba and Mr on the coked surface. The experimental results indicated that potassium (K) was the most effective in inhibiting carbon deposition, followed by sodium (Na), rubidium (Rb), caesium (Cs) and lithium (Li). An additional explanation for the improved performance of materials with the addition of alkali metals can be attributed to the fact that alkali metals increase the basicity of the catalyst, promoting dehydrogenation

and reforming of intermediate carbonaceous species, reducing the formation of coke [190].

Literature reports various approaches aimed at mitigating coke deposition on catalysts. These include optimizing reaction conditions, selecting different catalysts and preparation methods, adding additives or promoters to the catalyst, and employing catalyst regeneration processes to burn off coke deposits, thus restoring the activity of these materials [68,175,191]. For instance, Hu and Lu [175] studied modifications in Ni/Al₂O₃ catalysts with a series of promoters (M = Li, Na, K, Mg, Fe, Co, Zn, Zr, La, Ce) to be subjected to the steam reforming of acetic acid. The catalyst was loaded with 30 wt.% nickel and promoters were added to achieve a M/Al atomic ratio of 0.1. Based on experiments performed at 600 °C with an S/C ratio of 1.5, coke deposition analysis revealed that the Ni-K/Al₂O₃ catalyst exhibited a coke formation rate (14.7 mgC g⁻¹cat h⁻¹) significantly lower compared to the Ni/Al₂O₃ catalyst (24.6 mgC g⁻¹cat h⁻¹), due to the promotion of K in the gasification of the coke deposit. Kumar, Singh and Sinha [68] surveyed materials used for acetic acid steam reforming, highlighting transition metals like Ni, Co, and Cu, often paired with supports such as Al₂O₃, ZrO₂, and CeO₂. However, among these possibilities, the issue of sintering and coke deposition on the materials was emphasised as a significant challenge. During the reforming of oxygenated components, CO bonds contribute to side reactions. This effect is pronounced when using acetic acid as a fuel due to its thermal instability, which results in carbonaceous deposits. The formation of secondary products such as ethylene, CO, and acetone further accelerates carbon formation. To address this issue, the authors suggested that catalyst stability could be enhanced by incorporating ZrO₂, an amphoteric oxide with both acidic and basic sites. This structure facilitates the adsorption of steam and carbon oxides on the catalyst surface.

Carbon deposition rates in ethanol reforming processes are commonly lower than those in the acetic acid reforming process. This behaviour is a result of the combination of ethanol's simpler molecular structure, its more direct decomposition reactions and the lower propensity to form solid intermediates [188]. In order to compare carbon deposition rates during the steam reforming of ethanol, some works from the literature can be cited. Wurzler et al. [192] applied Ni/MgO catalysts in the steam reforming of ethanol. Reactions was carried out at atmospheric pressure, at a temperature of 500 °C, with S/C = 3. The catalyst prepared via precipitation and aging presented a carbon deposition rate of 6.2 mgC g⁻¹cat h⁻¹. Oliveira and Hori [27] used bifunctional nickel and calcium-based catalysts doped with Mg and Al in the ethanol SESR process. Ni/Ca, Ni/CaMgAl-

68, and Ni/CaMgAl-79 catalysts were submitted to catalytic tests at 600 °C, S/C=3, and the average carbon deposit rates obtained were 11.5, 6.2, and 7.4 mgC g⁻¹cat h⁻¹, respectively.

The aforementioned studies offer a comparative analysis of carbon deposition rates in the reforming of different fuels, providing a insight into how operational conditions and feedstock affect carbon deposition.

6.2. Conclusion

This study focused on investigating the sorption enhanced steam reforming of blend comprising acetic acid and ethanol, serving as model compounds to represent the aqueous fraction of bio-oil. Employing bifunctional catalysts comprising nickel, calcium oxide, and alkali metals dopants, the research achieved promising outcomes. Ni⁰, CaO, Ca(OH)₂, and CaZrO₃ were the predominant phases identified in the fresh and reduced catalysts. For the spent catalysts, the phases initially identified remained. The catalysts demonstrated proficiency in producing high-purity hydrogen, with compositions aligning with theoretical expectations. Catalytic tests revealed high conversions of ethanol (99%) and acetic acid (95%), alongside consistent hydrogen molar fractions exceeding 90%. Specifically, during the pre-breakthrough period of 18, 30, and 48 min, the NiCaZr, NiCaKZr, and NiCaNaZr catalysts exhibited H₂ molar fractions of 98.6%, 97.3%, and 96.2%, respectively. Doping the catalysts with alkali metals proved to be satisfactory, resulting in longer pre-breakthrough times (30 and 48 min for NiCaKZr, and NiCaNaZr catalysts) compared to the non-doped catalyst (18 min).

Chapter 7 – USE OF BIFUNCTIONAL NICKEL AND CALCIUM OXIDE-BASED CATALYSTS PROMOTED WITH ALUMINIUM AND CERIUM IN THE SORPTION ENHANCED STEAM REFORMING OF MODEL COMPOUNDS OF AQUEOUS FRACTION OF BIO-OIL

7.1. Results and discussion

7.1.1 Characterisation of fresh samples

Both catalysts were formulated to contain 20 wt.% of NiO. The NiCaAl catalyst comprised 75.5 wt.% CaO and 4.5 wt.% Al₂O₃. On the other hand, the NiCaAlCe catalyst consisted of 66 wt.% CaO, 4 wt.% Al₂O₃, and 10 wt.% CeO₂. To evaluate the oxides incorporated into catalysts, XRF analyses were carried out. The results obtained are shown in Table 7.1. Discrepancies with the calculated theoretical values can be related to experimental errors, impurities in the precursors, losses throughout the preparation process etc. However, the results obtained are in line with the expected range.

Table 7.1. Semi-quantitative analysis for chemical composition by XRF for NiCaAl and NiCaAlCe catalysts.

%	NiO	CaO	Al ₂ O ₃	CeO ₂	Others
NiCaAl	21.07	73.77	4.13	-	1.03
NiCaAlCe	20.21	62.80	2.98	13.17	0.84

Figure 7.1 shows the diffractograms obtained for the reduced and passivated materials. Figure 7.1a presents the CaO phase with the highest intensity peak at 37.4°, and this phase is also identified at diffraction angles of 32.2°, 53.9°, 64.2°, and 67.4°. Figure 7.1b, however, does not exhibit the CaO phase. Instead, the most intense phase present corresponds to Ca(OH)₂ (PDF 84-1266), which is identified at diffraction angles of 17.9°, 28.6°, 33.9°, 46.8°, 50.7°, 54.2°, 62.7°, and 64.3°. The predominance of the Ca(OH)₂ phase in profile (b) can be attributed to the high hygroscopic capacity of CaO, which tends to absorb moisture from the atmosphere and convert to Ca(OH)₂. Furthermore, the presence of ceria in the catalyst, indicated by CeO₂ peaks at 28.5°, 33.1°, 47.5°, and 56.3°, may have facilitated the adsorption of atmospheric water onto the material, as suggested by Fronzi et al. [193]. Al₂O₃ peaks were not detected, being a strong indication of its complete conversion into other amorphous phases, such as highly dispersed calcium aluminates. [194,195].

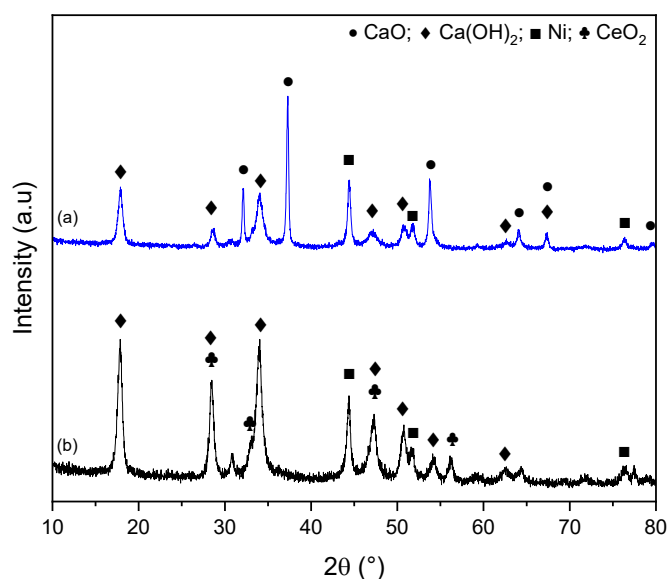
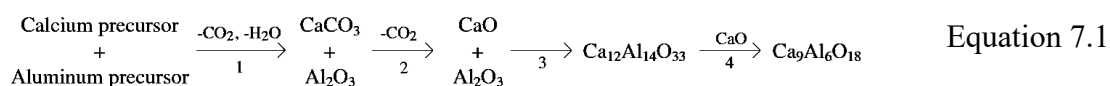


Figure 7.1. XRD patterns for the NiCaAl (a) and NiCaAlCe (b) reduced and passivated catalysts.

Diffraction peaks assigning to NiAl_2O_4 were not identified. Peaks corresponding to reduced nickel (PDF 4-850) were detected at 44.5° , 51.8° , 76.4° , indicating the transformation from NiO to Ni^0 after reduction. Despite the preparation process, the catalysts did not exhibit peaks corresponding to $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (18.1° , 33.4°) and/or $\text{Ca}_9\text{Al}_6\text{O}_{18}$ (33.2°). It is possible that during the reaction pathways, some of the aluminium in the structure (confirmed via XRF) did not react with the available calcium, resulting in the formation of CaO . Additionally, the low concentration of Al_2O_3 may explain why it is not detected in the XRD analysis.

The catalysts used in this work were prepared using a synthesis method similar to that of Zhou et al. [196]. In their study, the authors prepared a CaO -based CO_2 sorbents derived from various calcium and aluminium precursors. They identified different phases among the prepared materials, including CaO and $\text{Ca}_9\text{Al}_6\text{O}_{18}$, CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (mayenite), and only CaO . The study enabled the authors to propose a mechanism for forming the inert support (Equation 7.1).



In Equation 7.1, a correlation is established between the formation of Al_2O_3 and the calcination of aluminium precursors (step 1). Likewise, the authors proposed the formation of CaO from the calcination of calcium precursors (step 2). The formation of

calcium aluminates was associated with solid-solid reactions between CaO and Al₂O₃. However, as these reactions are under the control of Ca²⁺ diffusion across the surface of the reactants, some factors as particle size of the precursors, composition, and the interparticle contact of the reactants, are decisive in the process. This highlights the importance of precursors in determining the final product. The authors suggested that the non-formation of calcium aluminates may be attributed to the difficulty in diffusing Ca²⁺ across the Al₂O₃ interface, where high resistance may prevent alumina conversion. As for the formation of Ca₁₂Al₁₄O₃₃ or Ca₉Al₆O₁₈, previous studies conducted by Mohamed and Sharp [197] and Ghoroi and Suresh [198], demonstrated that the mayenite structure is initially formed, and if Ca²⁺ continues to diffuse into this structure, then Ca₉Al₆O₁₈ can be produced. In this context, the characteristics of the mayenite layers play a crucial role in determining whether or not the Ca₉Al₆O₁₈ structure is formed: if too tight layers are formed, the diffusion of Ca²⁺ can be significantly diffculted, resulting in the absence of the Ca₉Al₆O₁₈ structure.

The carbonation and decarbonation cycles were conducted using thermogravimetric analysis, with each sample undergoing 20 cycles over approximately 26 hours. Prior to the start of the cycles, each sample underwent thermal pre-treatment to eliminate impurities, moisture, calcium hydroxide, and calcium carbonate. The weight increase for the NiCaAl catalyst was 48.10% and 33.17% in the 1st and 20th cycles, respectively, as shown in Figure 7.2. The NiCaAlCe catalyst showed an increase of 47.92% in the 1st cycle and 36.37% in the 20th cycle. During the carbonation process occurring under a CO₂ atmosphere, the conversion of CaO to CaCO₃ takes place. This chemical reaction explains the observed weight increase. Following this step, the CaO must be regenerated at a higher temperature. In this process some pores are produced in the CaO particles and sintering may occur, resulting in incomplete conversion of CaCO₃ into CaO. The decline in CO₂ uptake capacity and cyclic stability observed in Figure 7.2a and Figure 7.2b can be attributed to the changes in the particle structure during the calcination-regeneration cycles [199].

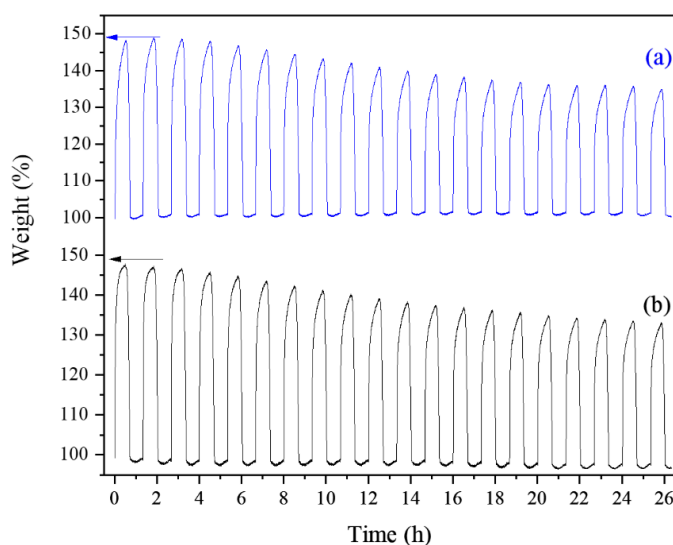


Figure 7.2. Cyclic CO₂ sorption and desorption behaviour of (a) NiCaAl and (b) NiCaAlCe catalyst. Conditions: $T_{\text{carbonation}} = 600\text{ }^{\circ}\text{C}$ (15% of CO₂ in He atmosphere); $T_{\text{descarbonation}} = 800\text{ }^{\circ}\text{C}$ (pure He atmosphere, 50 mL/min).

In Figure 7.3 is shown the CO₂ uptake performance of NiCaAl and NiCaAlCe catalysts. Between the 1st and 10th cycles, both catalysts showed similar capture capacity values (gCO₂/gcatalyst). However, throughout all 20 cycles, the NiCaAlCe catalyst showed better performance, so it can be stated that under those operating conditions, the addition of ceria to the structure contributed to improving the performance of the catalyst, working as a stabiliser. Yancheshmeh, Radfarnia and Iliuta [28] reported similar results in their work. They studied the use of $x\text{NiO}/\text{Ca}_9\text{Al}_6\text{O}_{18}\text{--CaO}$ ($x = 15, 20$, and $25\text{ wt. \%}$) and $20\text{NiO--}y\text{CeO}_2/\text{Ca}_9\text{Al}_6\text{O}_{18}\text{--CaO}$ ($y = 5, 10$, and $15\text{ wt. \%}$) catalysts in the steam reforming of glycerol. During cyclic carbonation-calcination tests, the materials enhanced with CeO₂ demonstrated excellent CaO conversion and maintained good cyclic stability. This improved performance was attributed to the formation of a thin shell-connected structure resulting from the addition of CeO₂ and the oxygen mobility characteristic of CeO₂. 5 cycles of catalytic tests were carried out, and it was observed that the material promoted with 10 wt.% of CeO₂ presented a better performance. This was related to the CeO₂ content in the material, which can influence the number of adjacent nickel active sites, the degree of CaO sintering and the extent of coke deposition.

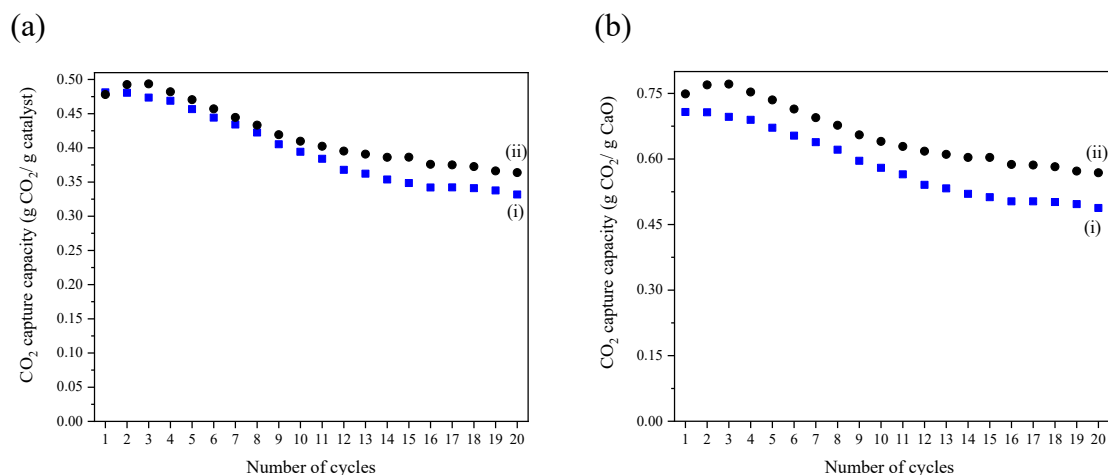


Figure 7.3. Comparison between cyclic CO₂ uptake capacity of (i) NiCaAl and (ii) NiCaAlCe catalysts: (a) $g_{CO_2}/g_{catalyst}$ and (b) g_{CO_2}/g_{CaO} . Conditions: Adsorption under 15 vol.% CO₂ at 600 °C and regeneration under Ar at 800 °C.

The amount CO₂ adsorbed per gram of CaO was calculated, considering the CaO content identified by XRF in order to have a normalised comparison between the catalysts, and the results are displayed in Table 7.2. The initial capture capacity values (g_{CO_2}/g_{CaO}) for the NiCaAlCe catalyst are similar to the theoretical value of pure CaO ($0.785 \text{ g}_{CO_2}/g_{CaO} = 44 \text{ g mol}^{-1} \text{ CO}_2/56 \text{ g mol}^{-1} \text{ CaO}$). There is no consensus in the literature regarding the specific role of CeO₂ in enhancing the cycle stability of CaO-based sorbents, but as mentioned before, the enhanced stability of NiCaAlCe compared to NiCaAl could be attributed to the oxygen mobility characteristics of CeO₂ [28,200]. Some research findings have suggested that under specific conditions, the presence of oxygen vacancy sites within the structure of CaO-based sorbents can enhance their cyclic stability. The presence of ceria could facilitate the diffusion of CO₂ through the CaCO₃ product layer, as well as through agglomerated or even sintered CaO particles [200,201].

Table 7.2. Loss of CO₂ uptake capacity (g_{CO_2}/g_{CaO}) from NiCaAl and NiCaAlCe catalysts, comparing 1st and 20th cycles.

Catalyst	1 st cycle	20 th cycle	Loss of CO ₂ sorption capacity (%)
NiCaAl	0.71	0.49	31.04
NiCaAlCe	0.75	0.57	23.88

The stability and good capture capacity observed in both catalysts may be related to the good dispersion of the calcium aluminate formed. Calcium aluminate can act as a

stabilising agent, helping to maintain the dispersion of active components within the catalyst matrix. When the catalyst undergoes sintering, which involves the particles coalescing and growing together, the presence of calcium aluminate can hinder excessive particle growth. This is because calcium aluminate promotes the formation of smaller crystallite sizes, which limits the extent of sintering. As a result, the particle size of the catalyst remains relatively small even during sintering, which is beneficial for maintaining the catalytic activity and surface area [202].

Fitting the experimental data of the carbonation process to a double exponential model allows us to explain the occurrence of two distinct stages in the process. This model provides a more comprehensive understanding of the carbonation kinetics by accounting for two separate rate constants, reflecting the complex nature of the carbonation reaction [178,203]. The initial stage involves chemisorption, which is the reaction between CO₂ and CaO, occurring on the surface of CaO particles. The subsequent phase of the carbonation process entails the diffusion of CO₂ through the CaCO₃ layer formed, allowing for further interaction with CaO. However, as the process progresses, CaO gradually becomes scarce and challenging to access due to the sorbent's gradual saturation. Moreover, this model enables a quantitative comparison of the kinetics of CO₂ capture by CaO-based sorbents [30]. To comprehend the dynamic carbonation process, the double exponential model (Equation 7.2) was applied. The parameters resulting from the adjustment of experimental data with the double exponential model for the catalysts are shown in Table 7.3, calculated for cycles 1 and 20. In addition to these parameters, the values of the k_1/k_2 ratio and the coefficient of determination (R^2) were also calculated.

$$y = A e^{-k_1 x} + B e^{-k_2 x} + C \quad \text{Equation 7.2}$$

In the provided equation, y represents the weight percentage of CO₂ captured, while A , B , and C denote the pre-exponential factors. k_1 and k_2 represents the exponential constants, and x stands for the reaction time. The chemisorption step is represented by k_1 , while the CO₂ diffusion step is denoted by k_2 . Additionally, the term C corresponds to the maximum CO₂ capture capacity.

Table 7.3. Parameters obtained for the double exponential model, using ATG data from NiCaAl and NiCaAlCe catalyst.

Catalyst	Cycle	A	B	C	$k_1(\text{s}^{-1})$	$k_2(\text{s}^{-1})$	k_1/k_2	R^2
NiCaAl	1 st	-36.148	-31.580	60.527	0.356	0.031	11.383	0.991
	20 th	-25.240	-16.674	37.074	0.895	0.047	19.103	0.994
NiCaAlCe	1 st	-43.781	-12.503	48.350	0.599	0.097	6.207	0.993
	20 th	-30.251	-14.491	38.516	0.944	0.056	16.902	0.990

As reported by Guo et al. [204], k_1 denotes the chemisorption, and k_2 represents the slow stage – diffusion. When $k_1/k_2 > 1$, the CO_2 capture mechanism is controlled by diffusion through the CaCO_3 . On the other hand, for values of $k_1/k_2 < 1$, the CO_2 capture mechanism is controlled by the chemical reaction. In this case, it indicates the predominance of surface reactions in the total adsorption process. This phenomenon occurs due to the sintering of CaO particles, leading to a decrease in active calcium sites on the surface [26]. Vieira, Santos and Hori [30] reported in their studies k_1/k_2 ratios greater than 1 for the 1st and 20th cycles, similar results obtained in this study, indicating that the CO_2 diffusion is the rate-limiting process. The NiCaAlCe catalyst exhibits the highest values for both k_1 and k_2 , which can be explained by its lower loss of capture capacity. Furthermore, for both catalysts, the values of k_1 and k_2 tend to be lower in the 20th cycle, which may be related to the growth of the CaO crystallite diameter and lower reaction and diffusion rates, due to the sintering process [27]. The lower loss of capture capacity in this catalyst could be related to the presence of cerium (Ce), which acts as a dopant, enhancing the thermal stability of calcium oxide (CaO) and retarding sintering at high temperatures. This stabilization helps maintain the structural integrity and active sites of the catalyst during operation. The formation of intermediate phases induced by Ce can also improve microstructural properties, minimising sintering and preserving a high surface area, essential for effective capture performance [205]. The correlation coefficients (R^2) exceeded 0.99, indicating a good correlation in the regression analysis, as shown in Table 7.3.

Investigating the addition of Zr to CaO-based sorbents, Yoon and Lee [178] utilized a deactivation model to characterise the decrease in CO_2 capture capacity during each carbonation-regeneration cycle. This model, built on the assumption of first-order decay, allows for the calculation of deactivation coefficients, k_d , for the materials according to Equation 7.3, where N is the number of carbonation/decarbonation cycles,

k_d is the deactivation coefficient, K is a model pre-exponential constant and a represents the sorbent activity at the N^{th} cycle. The latter refers to the amount of CO_2 sorption uptake at the N^{th} cycle divided by the maximum CO_2 sorption capacity of CaO , 78.5%. Sorbents with lower deactivation coefficient values tend to present a good cyclic stability.

$$a = K \times e^{-k_d N} \quad \text{Equation 7.3}$$

Table 7.4 provides detailed information on the calculated values from the deactivation model. By the analysis of k_d values, the NiCaAlCe catalyst presented a value around 78% lower than the NiCaAl catalyst. This observation aligns with previous stability analyses, confirming the superior stability of the ceria-doped catalyst. Oliveira and Hori [27] applied the deactivation model to Ni/CaMgAl catalysts and found $-k_d$ values of 0.0563, 0.0149 and 0.0130. Vieira, Santos and Hori [30] performed the same analysis for bifunctional Ni/CaO catalysts modified with CeO_2 and inert $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and obtained similar values of $-k_d$ parameter (0.048, 0.016 and 0.022).

Table 7.4. Parameters estimated by the deactivation model using TGA data for the NiCaAl and NiCaAlCe catalysts.

	K	$-k_d$	R^2
NiCaAl	0.7391	0.0229	0.97
NiCaAlCe	0.7875	0.0179	0.95

In Figure 7.4 is shown the H_2 -TPR profiles for the (a) NiCaAlCe and (b) NiCaAl catalysts. NiCaAlCe catalyst presented three peaks at 450, 620 and 770 °C. For NiCaAl catalyst, four peaks were detected at 480, 610, 685 and 775 °C.

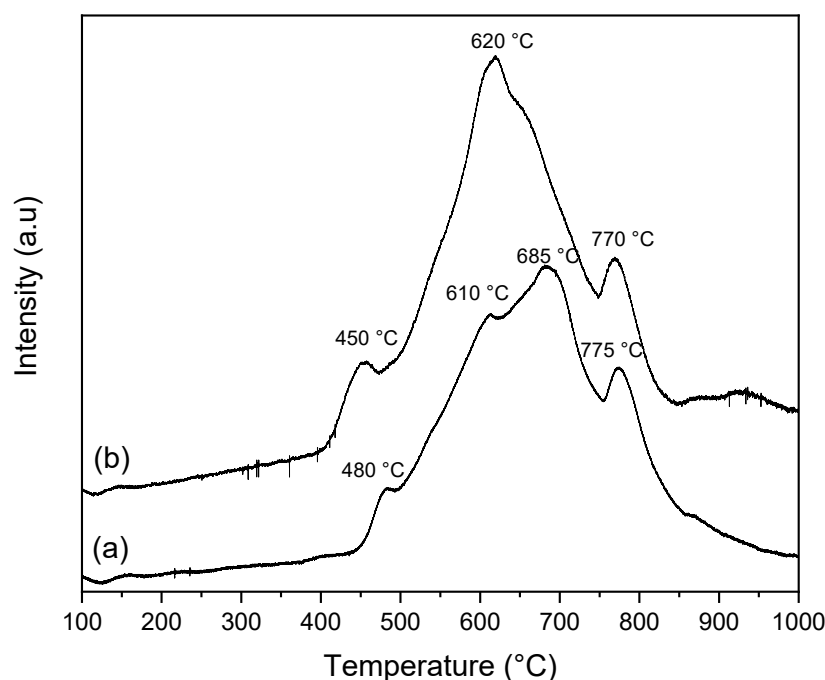


Figure 7.4. TPR of calcined (a) NiCaAl and (b) NiCaAlCe catalysts.

As expected for Ni catalysts, it is observed that the reduction for both catalysts begins around 450 °C [174,195,206]. Due to the high nickel content in the material (20% NiO), hydrogen consumption is high, as confirmed by the large reduction profile observed for both catalysts, which extends over a wide temperature range. At lower temperatures, there is a reduction of free NiO species, in which larger Ni particles interact less with the support. Around 600 °C, peaks are observed indicating that Ni interacts slightly more with the support, resulting in slightly smaller particles. For temperatures above 700 °C, the peaks are generally more pronounced for Ni with greater interaction with the support, mainly Al. This may suggest the formation of NiAl_2O_4 , even if it has not been identified via XRD [88], and is consistent with the CaCO_3 calcination temperature used in this work, 800 °C. In this case, even if NiAl_2O_4 did not form in the fresh catalyst, it would eventually occur in the regeneration cycle. Therefore, part of the Ni is in the aluminate phase, and its presence in steam reforming is beneficial primarily due to its structural and indirect catalytic effects. While Ni in the spinel structure is not active for reforming, under reducing conditions, it can release Ni^0 gradually, replenishing active sites and prolonging catalyst life. NiAl_2O_4 also prevents sintering by acting as a spacer and improves Ni-support interaction, reducing the risk of particle migration and coke formation. Additionally, it stabilises the support and can influence reaction mechanisms indirectly, such as through hydrogen spill over or modifying support properties to enhance water

activation [207]. In the profile of the catalyst with Ce (b), a greater area of hydrogen consumption and a peak of greater intensity at intermediate temperatures (620 °C) are observed, which may be related to the reduction of ceria in the structure ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$). Research conducted by Abou Rached et al. [205] revealed that the reduction of CeO_2 typically occurs between 400–600 °C. However, was emphasized that in situations with a high nickel content, these peaks could be masked by the nickel reduction, which occurs in the same temperature range.

The addition of Ce reasonably decreased the reduction temperature of the catalyst, as showed in profile (b). When comparing the results with data obtained by Aziznia et al. [208], there is an agreement between them, especially for high temperatures. The authors studied a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, with Ni contents of 5, 10 and 20%. A single peak with a maximum at around 390 °C was found for a pure NiO sample, while a NiAl_2O_4 sample showed a single peak with a maximum at around 820 °C. Dantas [209] reported the temperature-programmed reduction profile of nickel catalysts with CeO_2 and CeZrO_2 -based supports. Hydrogen consumption in the temperature range between 377 and 927 °C was identified, and this profile was related to the reduction of NiO species with different interactions with the support, as well as the reduction of CeO_2 promoted by the metal. Furthermore, the addition of CeO_2 to $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts increased hydrogen consumption, providing more intense reduction peaks.

The measured H_2 consumption for total NiO reduction in NiCaAl catalyst was 2198 $\mu\text{mol/gcat}$ and 2472 $\mu\text{mol/gcat}$ for the NiCaAlCe catalyst. This increase in the H_2 consumed is related to the fact that in the catalyst containing ceria, both NiO and CeO_2 are reducible phases, causing greater hydrogen consumption. The degree of reduction achieved during the H_2 -TPR procedure for the NiCaAl catalyst was around 87%, and this lower reduction value can be justified by the presence of nickel aluminate, as it is not possible to reduce all the Ni. For NiCaAlCe catalyst, the degree of reduction was not calculated since the reduction process is not restricted to nickel, but also occurs with ceria present in the structure.

7.1.2. Catalytic tests

Experiments were carried out to investigate sorption enhanced steam reforming of mixtures of acetic acid and ethanol. For this purpose, 10 reaction and decarbonisation cycles were conducted in all cases and the identified products were H_2 , CO_2 and CO^* and CH_4^* (not showed due low concentration*). Figure 7.5 shows the molar fraction of H_2

and CO₂ (1st and 10th cycle) resulting from the reaction using the (a) NiCaAl and (b) NiCaAlCe catalysts. The experimental curves demonstrate three typical stages: pre-breakthrough (I), breakthrough (II), and post-breakthrough (III). The dotted lines indicate the distribution of predicted products at thermodynamic equilibrium, calculated by CEA software. The mole fractions presented were calculated on Ar and H₂O free basis. For all analyses, the ethanol conversion was higher than 99%, and for HAc the average conversion through the cycles was higher than 92%.

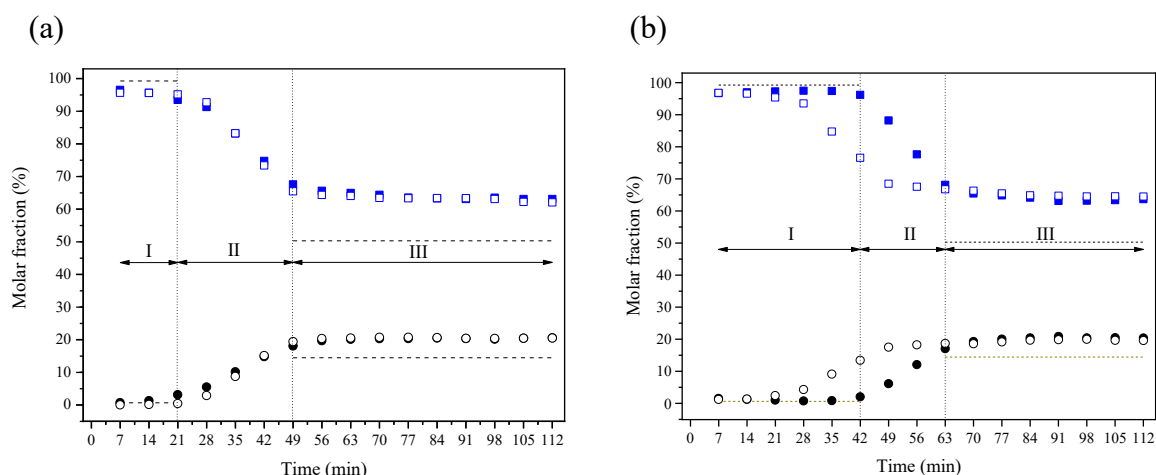


Figure 7.5. Product distribution (dry basis) from the SESR using (a) NiCaAl and (b) NiCaAlCe catalysts. Reactional conditions: $T = 500\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 0.8\text{ g}$. Legend: ■ H₂, 1st cycle; □ H₂, 10th cycle; ● CO₂, 1st cycle; ○ CO₂, 10th cycle. Dashed line: thermodynamic equilibrium.

For both cases, low concentrations of CO₂ are observed in stage I, as the bifunctional catalyst captured part of this by-product generated by the reforming and WGS reactions. As a result, the molar fraction of H₂ reached high values (96.6% - a and 97.0% - b), remaining so throughout stage I. The concentrations of CO and CH₄ (not shown) were maintained at relatively low levels. In stage II, the capture capacity of the adsorbent material began to drop, and the CO₂ concentration gradually increased. In the third region, the adsorbent became saturated, meaning that CO₂ adsorption was no longer effective, with average molar fractions of 20% being obtained for both cases. The difference in H₂ concentration in the I (~ 95%) and III (~ 65%) stages provided direct evidence of the effect of CO₂ adsorption on the process. The duration of stage I in the 1st and 10th cycles remained around 21 min in profile a, and decrease from 42 to 21 min in profile b. This suggests that in the first case, the catalyst was stable throughout the reaction cycles, but with a short capture period. This behaviour could be related to the lower CO₂ capture capacity observed in the TGA tests, compared to the NiCaAlCe

catalyst. For the second case, the duration was higher, but with a pronounced decrease, which could be attributed to catalyst aging and the diminishing capacity for CO₂ capture. The catalyst's extended pre-breakthrough duration in the first cycle suggests that CeO₂ might have played a role in reducing sintering, and this could explain the prolonged effectiveness of the catalyst during CO₂ capture. However, the catalyst still showed signs of sintering over time. After multiple reaction/decarbonation cycles, the sorbent reduced its CO₂ capture capacity and, consequently, the capture time [210]. The initial effect of increased pre-breakthrough may be related to the fact that the NiCaAlCe catalyst does not desorb CO₂ as efficiently as the non-promoted catalyst. Another hypothesis is that, initially, the Ce was fully reduced, but in subsequent cycles, this condition was not achieved due to the reduction time and the hydrogen flow available. To assess this possibility, the amount of each phase present in the catalyst was calculated and converted to moles. Based on the reduction reactions of NiO and CeO₂, the required amount of hydrogen was estimated considering the stoichiometry. Subsequently, the hydrogen supplied by the flow during the reduction time was compared to the required amount, concluding that the hydrogen was sufficient for both reductions. Furthermore, the deposition of coke on the catalyst could also contribute to this decline in capture capacity. Coke acts by restricting the access of CO₂ to the active CaO sites, obstructing pores, and adhering to the sorbent's surface at elevated temperatures [28]. Yancheshmeh, Radfarnia and Iliuta [28] conducted five reaction cycles of steam reforming of glycerol using CeO₂-promoted NiO/Ca₉Al₆O₁₈-CaO bifunctional material. They observed a hydrogen concentration of 98.3% in the initial cycle during stage I, which gradually decreased to 65.5% in stage III. Additionally, the authors noted a reduction in pre-breakthrough time from 57 to 30 minutes, attributing this change to coke deposition and CaO sintering.

Based on TGA analyses and literature reports [200,201,204], the presence of ceria was expected to enhance catalytic activity. However, this anticipated behaviour was not observed under the reaction conditions used in this study. Regarding the hydrogen molar fraction obtained, both catalysts presented similar maximum values (~97%). Regarding the duration of the pre-breakthrough period, the NiCaAlCe catalyst even presented a longer duration in the first cycle, but in the second cycle (not shown) it decreased to 21 min and remained so until the 10th cycle. Similar result was obtained by Vieira and Hori [30] in the study of ethanol SESR. A maximum hydrogen molar fraction of 85% was obtained in stage I, in the first cycle, accompanied by a significant formation of CO (10.3%). Regarding the pre-breakthrough stages, a duration of 55 minutes was maintained

throughout the cycles, indicating that the presence of inert mayenite and CeO_2 enhanced the cyclic stability of CaO in the catalyst. Upon comparing the results with those obtained using a catalyst lacking Ce (NiCaAl), the author concluded that the addition of CeO_2 did not yield significant benefits to the properties of NiCaAl , and no superior catalytic performance was observed for the ceria-containing catalyst compared to NiCaAl .

Regarding the thermodynamic limit delineated in the product distribution profiles, it's noted that during stage I, the experimental molar fractions of H_2 tend to be lower, while those of CO_2 remain similar. Moving to stage III, across all cases, the experimental molar fractions exceed those predicted in equilibrium calculations. This difference can be justified by the operating system used. Essentially, equilibrium composition calculations assume an isothermal and isobaric system without external matter input. However, continuous reactions were carried out, which implies that the equilibrium composition could not be reached, as the contact time between reactants was not sufficient. Therefore, it is expected that experimental results will be different from those predicted via software [64,211]. Another justification is that for stage I, as there is a CO_2 capture process, it is expected that hydrogen production will be maximized, with by-products being formed in low concentration. Therefore, similar values of equilibrium data can be seen with experimental data for the two products identified. In stage III, when the capture process ceases, there is an increase in by-products, so the thermodynamic limit data are more distant from the experimental data obtained.

7.1.3. Characterisation of spent samples

X-ray Diffraction (XRD) analysis of the reduced and passivate catalysts after 10 reaction cycles revealed that the phases present were similar to those in the fresh catalysts. In both catalysts, Ca(OH)_2 , CeO_2 and Ni^0 phases remained. In the latter, its presence suggests that the material retained active metallic sites, even after passivation. The average crystallite sizes were calculated for Ni^0 , Ca(OH)_2 and CeO_2 using the Scherrer Equation and the results are displayed in Table 7.5. Due to the hydration of the CaO peaks, calculate these parameters for this phase was not possible.

Table 7.5. Textural properties of fresh and spent NiCaAl and NiCaAlCe catalysts

		Average crystallite size (nm)		Superficial area (m ² /g)
	Catalyst	Ni ⁰	Ca(OH) ₂	
Fresh	NiCaAl	23	9	62
	NiCaAlCe	17	10	112
Spent	NiCaAl	25	15	116
	NiCaAlCe	26	14	110

The average crystallite size of Ca(OH)₂ remained consistent across both fresh samples, while the average crystallite size of Ni decreased with ceria incorporation. Smaller nickel average crystallite size in catalysts can have advantages such as increasing active surface area (as confirmed by the superficial area results), improving particle distribution, reducing sintering, and minimising coke deposition. In spent materials, the observed increase in the average crystallite size of both Ni and Ca(OH)₂ suggests the effect of sintering, a behaviour previously reported in the literature. Li et al.[212] observed that increasing Ni loading in a Ni/ZrO₂ catalyst enhanced activity but led to aggregation, particularly when loadings exceeded 20%, resulting in larger crystallites and accelerated sintering and coke deposition. Similarly, Artetxe et al. [213] noted that higher Ni content boosted active sites and H₂ yields but also increased coke formation, leading to faster deactivation. In this sense, the average rate of coke deposition on the catalysts was analysed.

At the end of the 10th cycle, the spent catalysts were subjected to thermogravimetric analysis in order to gasify the carbon accumulated on the material during the reaction. For the NiCaAl and NiCaAlCe catalysts, a slightly decrease was observed from 9.95 to 9.59 mgCgcat⁻¹h⁻¹, respectively. Given the similar carbon deposition values for both materials, a correlation with their catalytic activity can be inferred. Since the amounts of H₂, CH₄ and CO were similar in both cases, it is likely that the Boudouard reaction (Equation 7.4) and the decomposition of CH₄ (Equation 7.5) occurred in a similar manner, resulting in equivalent amounts of carbon. In this context, seems like the influence of ceria did not have a significant impact on the reduction of carbon deposition or on the increase in the catalytic activity of the material [214].



The catalysts, fresh (calcined) and spent (reduced), were subjected to textural characterisation using the N_2 physisorption technique. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) model applied to N_2 adsorption data, and the results obtained are shown in Table 7.5. The surface area of the catalysts was higher than that of similar structures reported in the literature [28,195,196]. For the NiCaAl catalyst, there was an increase in surface area after 10 cycles of reaction in all compositions tested. Similar results have already been reported in the literature [27,215,216]. Since there is an excess of water in the steam reforming process, it is possible that the bifunctional catalyst underwent a hydration process. In this scenario, water molecules react with fresh CaO to form $Ca(OH)_2$. The increase in the molar volume of $Ca(OH)_2$, compared to the original CaO, is the main factor that triggers the expansion and cracking of particles on the CaO surface. The resulting fracture expands the surface area and porosity of the CaO, making it more available for further reactions [186,187,217].

The addition of ceria contributed to improved structural properties, as evidenced by the decrease in the average crystallite size of Ni in the fresh material and the nearly doubled surface area compared to the NiCaAl catalyst. Furthermore, the material showed superior retention of its structural characteristics after use, with the surface area remaining nearly unchanged, with a slightly decrease. About this decrease, similar results were obtained by Vieira, Santos and Hori [30] and Micheli et al. [218], and this behaviour can be related to the sintering or particle aggregation during heat treatments, where particle fusion reduces the available adsorption surface. Additionally, aggregation during preparation or handling can also limit the exposed surface area [68].

7.2. Conclusion

This study evaluates the efficacy of bifunctional catalysts in steam reforming bio-oil components. Two catalyst types, including one doped with ceria oxide, were tested. Results showed high conversion rates of ethanol and HAc. XRD analysis revealed crystalline phases of Ni^0 , CaO, $Ca(OH)_2$ and CeO_2 , for the case where Ce was added to the material. BET analysis showed structural differences between catalysts, with ceria addition improving properties. In the catalytic tests, similar molar fractions of hydrogen were observed during the pre-breakthrough period for both catalysts, with values of 96.7% for NiCaAl and 97% for NiCaAlCe. Regarding the duration of this stage, the NiCaAl catalyst consistently maintained a duration of 21 minutes between the 1st and 10th

cycles. In contrast, the NiCaAlCe catalyst had a duration of 42 minutes in the 1st cycle, which decreased to 21 minutes by the 4th cycle and remained at this level through the 10th cycle. In this sense, although the addition of ceria improved the textural properties of the catalyst, its addition did not bring significant benefits in terms of hydrogen production and extension/stability of the pre-breakthrough time.

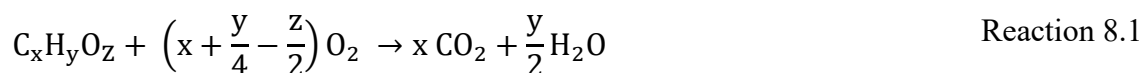
Chapter 8 – PROCESS SIMULATION AS A TOOL FOR TECHNICAL PERFORMANCE EVALUATION

8.1. Methodology

In Aspen Plus software, modelling a system is carried out in two distinct phases. The first phase involves the specification of the properties, where the chemical components present in the system are identified and the thermodynamic model to be used in calculating the properties is selected. In the second phase, which comprises the simulation specification, the system flow diagram is developed, covering all equipment and currents involved. Furthermore, the supply currents and operating conditions of all equipment are determined.

Model description

The simulation of conventional and sorption enhanced steam reforming of bio-oil model compounds (ethanol and acetic acid blend) was carried out using Aspen Plus software (v.10). The thermodynamic model chosen was the NRTL for the liquid phase, modified with the Peng Robinson equation of state for the vapor phase. The reformer and a combustor are both represented by RGibbs units, i.e. equilibrium reactors solved by minimisation of Gibbs energy. The bagasse was defined as a non-conventional solid stream. To determine the properties of this material, such as density and enthalpy, DCOALIGT and HCOALGEN models were adopted, which make use of ultimate, proximate and sulphur analyses. The Aspen model analysis tool determined the required biomass to feed the plant. Based on this mass, 20% excess air was employed to ensure efficient combustion, as per literature for industrial processes [219]. This approach ensured safe and optimized system operation. To determine the stoichiometric air for burning biomass, the air needed for a unit mass was first calculated. Biomass, composed of carbon, hydrogen, and oxygen, required specific oxygen amounts for complete combustion (generic equation given in Reaction 8.1). Assuming atmospheric air contains about 21% oxygen, the required air was calculated and then scaled to the total biomass. For sugarcane bagasse, this equated to 5.26 kg of air per 1 kg of biomass. Amount of biomass was determined from a sensitivity analysis of the parameters, using the Model Analysis Tool, included in the program.



The use of biomass from agricultural waste is of great interest to Brazil, since the country has great potential for producing this material. Bagasse from sugarcane is categorized as a non-inert solid, class IIA (ABNT, 2004), indicating the feasibility of reusing this material without generating toxic waste or the need for controlled disposal. Although only a third of the energy contained in sugar cane is used to convert it to ethanol, the remainder is intrinsically linked to the processing of waste generated, such as bagasse and straw. As for the use of bagasse, around 93% is used in burning boilers to generate steam. In this sense, sugarcane bagasse was used as biomass to be burned in the process, in order to produce energy [220]. Some studies have analysed the feasibility of using this material in a thermo-chemical conversion process, aiming to generate energy from direct combustion, gasification, liquefaction and pyrolysis with or without physical conversion [221–223]. The ultimate and proximate analyses data of sugar cane bagasse used in the simulation are summarized in Table 8.1.

Table 8.1. Ultimate Analysis and Proximate analysis of sugar cane bagasse [220].

Ultimate Analysis (wt.%)		Proximate analysis (wt.%)	
Carbon	45.15	Volatile matter	78.6
Hydrogen	5.40	Moisture content	5.9
Oxygen	41.80	Ash content	7.4
Nitrogen	0.20	Fixed carbon	14.0
Sulphur	0.02		
Chlorine	0.03		
Ash	7.40		

The components used for the simulation included acetic acid, ethanol, water, hydrogen, methane, carbon monoxide, carbon dioxide, and air. The solids included calcium oxide, calcium carbonate, coke, and ash (the latter two as non-conventional). The main assumptions in the simulation were that the system was in steady state, no catalytic effect was considered, and the reactors operated adiabatically. The separation efficiency of the separators was fixed at 1. The reference environment was taken as 25 °C and 1 atm. The fuel submitted to the reforming process was pressurised to 5 atm using a pump (with an efficiency of 0.85). The air composition was admitted as 21% O₂ and 79% N₂. The

sorbent CaO was fully regenerated, and deactivation caused by multiple utilisations was not considered (with a molar ratio of CaO/C = 1).

The plant was simulated to process a capacity of 100 kmol/h (745 kg/h) of the aqueous phase of bio-oil, consisting of a mixture of acetic acid and ethanol in a molar ratio of 0.75:0.25, respectively. This processing capacity was selected as it represents a typical range for pilot-scale or small-scale industrial applications [224,225]. In this proportion the feed molar steam/carbon ratio is 2.25 compared to the stoichiometric requirement of 1.125 for CO₂ and H₂ products. In the plant, the CaO and CaOH streams are the same, but not indicated as recycle since this type of approach makes it difficult to converge simulated data. Depending on the raw material, bio-oils have low levels of sulphur (around 0.05 wt.%) [226]. Thus, published works assumed that the desulfurization step was not necessary [226–229], and the same is assumed in this present work.

Thermal efficiency

Based on work of Lind, Heyne and Johnsson [230], the thermal efficiency of the process was calculated using Equation 8.1 and Equation 8.2.

$$\eta_{th, process} = \frac{\sum_i \dot{Q}_{prod, i} + (P_{el}^- - P_{el}^+) + (Q_{th}^- - Q_{th}^+)}{\sum_i \dot{Q}_{fuel, j} + (P_{el}^+ - P_{el}^-) + (Q_{th}^+ - Q_{th}^-)} \quad \text{Equation 8.1}$$

$$\dot{Q} = n * LHV = \left(\frac{\text{kmol}}{\text{h}} \right) * \left(\frac{\text{kJ}}{\text{kmol}} \right) \quad \text{Equation 8.2}$$

Where $\dot{Q}_{prod, i}$ and $\dot{Q}_{fuel, j}$ are the energy values of products and inputs, calculated on a lower heating value (LHV). For the aqueous fraction of bio-oil and model compounds, the LHV, in J/mol, were obtained from Aspen Plus (1.33×10^6 – ethanol, 7.88×10^5 – HAc, 4.73×10^5 – biomass, 2.44×10^5 – hydrogen and 8.00×10^5 – methane). P_{el} stands for the electricity, n refers to molar flow (kmol/h) and $\dot{Q}_{th}$ represents the heat imported (+) or exported (–). For Q and P , only the net flows are included, so that the terms appear either in the numerator (net exports) or denominator (net imports).

CO₂ emissions

$$\text{CO}_{2, \text{steam reform}} = \text{CO}_{2, \text{REACPROD stream}} + \text{CO}_{2, \text{CO}_2 \text{ stream}}^* \quad \text{Equation 8.3}$$

* Only in the SESR process

$$\text{CO}_{2\text{whole process}} = \text{CO}_{2\text{steam reform}} + \text{CO}_{2\text{FLUEGOUT stream}}^* \quad \text{Equation 8.4}$$

CO₂ emissions were calculated under two scenarios: firstly, by considering only the stream from reaction products (CO₂) of the reforming process (Equation 8.3) and secondly, by incorporating the total CO₂ emissions from both the reforming process and biomass burning (Equation 8.4).

8.2. Results and discussion

The Aspen Plus® simulation software was utilised for simulating the processes and acquiring stream data to assess the impact of operating conditions in the system. Table 8.2 and Table 8.3 displays the material balances for both processes, while Table 8.4 and Table 8.5.

Simplified schemes of conventional steam reforming (CSR) and SESR are shown in Figure 8.1 and Figure 8.2, respectively. The flowsheet of the whole system modelled by Aspen Plus is shown in Figure A.1 and Figure A.2, and the conversion of simulated aqueous phase of bio-oil was 100% for both process. In both processes, biomass (sugarcane bagasse) is burned to provide energy for the plant. The biomass (BM stream) is fed into a dryer (DRYER), which operates at 100 °C. Subsequently, the water is removed in a separator (WATER stream) to obtain dry biomass (stream 4). Further treatment involves directing the dry biomass to the first ‘Ryield’ reactor (DECOMP). This first reactor (DECOMP), played the role of decomposing the biomass structure, preparing it to be directed to the combustion reactor (COMBUST). In Aspen Plus, the simulation of equilibrium units with nonconventional solid feed, such as the combustion of solid biomass streams, requires this type of combination. The Ryield reactor (DECOMP) converts the non-conventional solid stream of chemically bound CHNSO elements of the biomass into a stream of conventional compounds, typically C, H₂, N₂, O₂ and S. This is followed by an RGibbs combustor (COMBUST). This allows the computation of the minimisation of Gibbs energy solution with input streams of conventional compounds, as it cannot provide an equilibrium solution directly from non-conventional solid input. However, the decomposition is endothermic, and therefore, in order to simulate an overall adiabatic combustor (e.g. a well-insulated furnace), the RGibbs unit of the combustor needs to provide the heat duty for the RYield unit of the combustor. The RGibbs is therefore simulated with a negative heat duty, where the negative heat duty is matched by the RYields’ heat duty. Enthalpy from the flue gases of the RGibbs COMBUST unit can

then be used to provide heat to different parts of the plant via heat exchangers. The residual heat in cooler3 unit could potentially be repurposed to supply energy to the dryer, reformer (CSR), or regenerator (SESR), as the outlet temperature in the cooler was carefully maintained higher than that of these units to comply with the second law of thermodynamics. However, to facilitate this reuse, a secondary processing of flue gases after the cooler would be necessary. This study only highlights the potential for such reuse. In the COMBUST unit, biomass combustion occurs (stream 5), with a concomitant supply of air (AIR stream). The air is heated to a temperature slightly lower than the auto-ignition temperature of sugarcane bagasse (between 250 and 263 °C [231]). Preheating of the air is a crucial aspect in the plant, since this stream represents the largest material flow during combustion and contains a significant amount of nitrogen that does not actively participate in the process, and is thus a heat sink. The combustion reactor provides energy to the plant in the form of heat and generating the hot current to be used in the heat exchangers. Amounts of biomass and air were determined from a sensitivity analysis of the parameters, using the Model Analysis Tool, included in the program. After the combustor's module (DECOMP-COMBUST), a separation unit is used to obtain two streams, a flue gas stream and the ash stream. The bio-oil aqueous phase model mixture molecule, in liquid phase, is fed into the plant (AFB stream), being pumped to a heat exchanger (HE1). In this first exchanger, the temperature is raised to the vaporisation temperature at the given pressure, and in the second heat exchanger (HE2), the temperature is raised to the temperature of superheated steam. Subsequently, the mixture is directed to the RGibbs reformer unit (REFORMER). In the CSR process, the reaction products (stream 13) are then directed to a heat exchanger (HE3). In this exchanger, the reaction products are cooled, while the air is heated to be fed into the combustor chamber. Stream 15 is directed to a WGS reactor (RGIBBS), in order to obtain more hydrogen from these generated products. Subsequently, the products are cooled and separated (REACPROD stream), and the excess water from reforming is removed from the process (WATER1 stream). In the SESR process, the reaction products (stream 13) are directed to a separator (CYC1), so that the adsorbent material (saturated CaO, in the form of CaCO₃) is regenerated (stream 14) in the REGENER unit. This configuration is commonly used in the simulation of this type of process, being reported in previously published works [232–234]. The gaseous products (stream 18) are directed to a heat exchanger (HE3), preheating the air, with the reaction products subsequently cooled (stream 19), and the water separately (stream 21). The REGENER unit supplies a stream of CO₂ and CaO

(stream 15), which is then directed to a second separator (CYC2), with the CO₂ being separated into stream 16 and the CaO separated, which is recycled in the reformer (CaO1), not shown as a connected stream, since the calculations were done separately to avoid problems with the convergence of values.

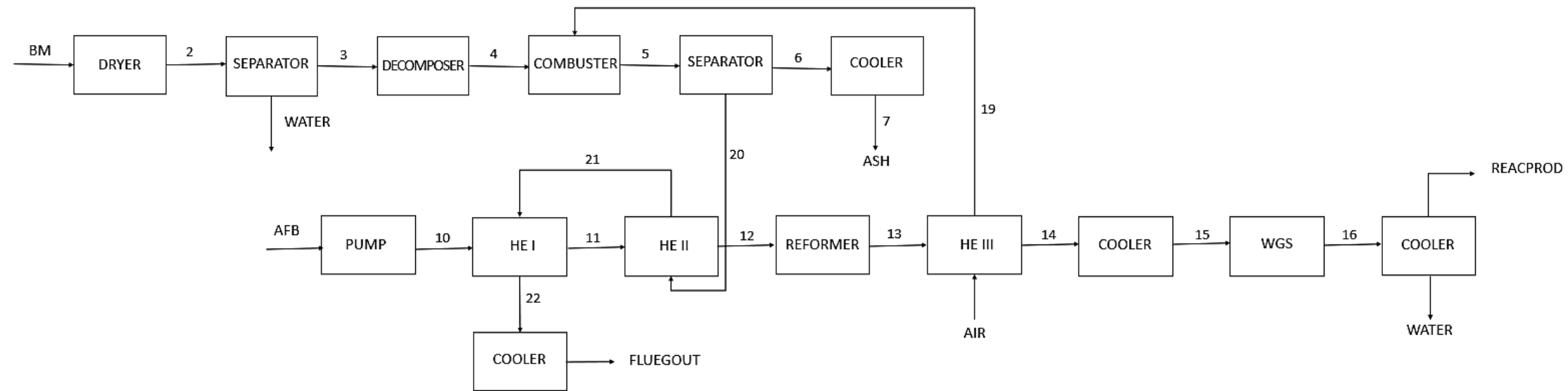


Figure 8.1. Layouts of conventional steam reforming (CSR).

Table 8.2. Stream summary for CSR process.

Streams	BM	2	Water	3	4	5	6	7	Air	19	20	21	22	FLUEOUT
T (°C)	25	100	100	100	700	1798	1798	110	30	230	1798	1530	892	615
P (bar)	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mass fraction														
Vapor		0.06	1		0.47	0.99			1	1	1	1	1	1
Liquid														
Solid	1	0.94		1	0.53	0.01	1	1						
F (kg/h)														
H_2O		43.96	43.96			337.13					337.13	337.13	337.13	337.13
H_2					37.86	0.12					0.12	0.12	0.12	0.12
CO						10.75					10.75	10.75	10.75	10.75
CO_2						1142.88					1142.88	1142.88	1142.88	1142.88
CH_4						0.00								
N_2					1.40	3716.33			3714.93	3714.93	3716.33	3716.33	3716.33	3716.33
O_2					293.04	144.03			987.51	987.51	144.03	144.03	144.03	144.03
Biomass	745.00	701.05		701.05										
Ash					51.88	51.88	51.88	51.88						
C					316.52									
S					0.14									
HCl						0.22					0.22	0.22	0.22	0.22
H_2S						0.15					0.15	0.15	0.15	0.15
Cl_2					0.21									
Total	745.00	745.00	43.96	701.05	701.05	5403.48	51.88	51.88	4702.44	4702.44	5351.61	5351.61	5351.61	5351.61

Table 8.2. (Continued)

Streams	AFB	10	11	12	13	14	15	16	REACPRO	WATER1
T (°C)	30	30	153	550	600	375	360	360	85	85
P (bar)	1	5	5	5	5	5	5	5	5	5
Mass fraction										
Vapor			1	1	1	1	1	1	1	
Liquid	1	1								1
Solid										
F (kg/h)										
H_2O	1473.97	1473.97	1473.97	1473.97	1173.75	1173.75	1173.75	1088.32	41.77	1046.55
H_2					76.75	76.75	76.75	86.31	86.31	
CO					132.82	132.82	132.82			
CO_2					962.50	962.50	962.50	1171.19	1171.19	
CH_4					156.42	156.42	156.42	156.42	156.42	
N_2										
O_2										
C_2H_6O	209.38	209.38	209.38	209.38						
C_2H_4O	818.88	818.88	818.88	818.88						
Total	1473.97	1473.97	1473.97	1473.97	2502.23	2502.23	2502.23	2502.23	1455.68	1046.55

Table 8.3. Stream summary for SESR process.

Streams	BM	2	WATER	3	4	5	6	7	AIR	23	24	25	26	FLUEGOUT
<i>T</i> (°C)	25	100	100	100	700	1804	1804	30	30	230	1804	1659	1320	815
<i>P</i> (bar)	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Mass fraction														
Vapor		0.06	1		0.47	0.99			1	1	1	1	1	1
Liquid														
Solid	1	0.94		1	0.53	0.01	1	1						
<i>F</i> (kg/h)														
<i>H</i> ₂ <i>O</i>		80.89	80.89			621.05					621.05	621.05	621.05	621.05
<i>H</i> ₂					69.67	0.17					0.17	0.17	0.17	0.17
<i>CO</i>						15.80					15.80	15.80	15.80	15.80
<i>CO</i> ₂						2109.47					2109.47	2109.47	2109.47	2109.47
<i>CH</i> ₄														
<i>N</i> ₂					2.58	6635.88			6633.30	6633.30	6635.88	6635.88	6635.88	6635.88
<i>O</i> ₂					539.27	459.05			2014.14	2014.14	459.05	459.05	459.05	459.05
<i>Biomass</i>	1371.00	1290.11		1290.11										
<i>Ash</i>					95.47	95.47	95.47	95.47						
<i>C</i>					582.49									
<i>S</i>					0.26	0.26					0.26	0.26	0.26	0.26
<i>Cl</i> ₂					0.39	0.39					0.39	0.39	0.39	0.39
Total	1371.00	1371.00	80.89	1290.11	1290.11	9937.55	95.47	95.47	8647.44	8647.44	9842.08	9842.08	9842.08	9842.08

Table 8.3. (Continued)

Streams	AFB	10	11	12	CAO1	13	14	15	16	CO2	CAO	18	19	REACPROD	WATER1
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T (°C)	30	30	153	550	800	600	600	800	800	120	800	600	153	85	85
P (bar)	1	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Mass fraction															
Vapor			1	1		0.24		0.44	1	1		1	1	1	
Liquid	1	1													1
Solid					1	0.76	1	0.56			1				
F (kg/h)															
H_2O	1474.01	1474.01	1474.01	1474.01		837.39						837.39	837.39	38.53	798.86
H_2						142.70						142.70	142.70	142.70	
CO						3.08						3.08	3.08	3.08	
CO_2						8.58		1467.02	1467.02	1467.02		8.58	8.58	8.58	
CH_4						43.97						43.97	43.97	43.97	
N_2															
O_2															
CaO					1869.28			1869.28			1869.28				
$CaCO_3$						3336.31	3336.31								
C_2H_6O	209.61	209.61	209.61	209.61											
C_2H_4O	819.12	819.12	819.12	819.12											
Total	2502.74	2502.74	2502.74	2502.74	1869.28	4372.03	3336.31	3336.31	1467.02	1467.02	1869.28	1035.72	1035.72	236.86	798.86

Utilising the information provided in Table 8.2 and Table 8.3, the CO₂ emissions for both processes were calculated under two scenarios: firstly, by considering only the stream from reaction products of the reforming process (Equation 8.3) and secondly, by incorporating the total CO₂ emissions from both the reforming process and biomass burning (Equation 8.4). In the case of the process considering only the CO₂ emitted in the steam reforming process, the emissions were 13.57 kg_{CO₂}/kg_{H₂} produced for CSR and 10.34 kg_{CO₂}/kg_{H₂} produced for SESR (CO₂ from REACPROD and CO₂ streams). Considering the CO₂ emission of the entire plant, accounting for that generated when burning biomass, the emissions for CSR and SESR were 27.14 kg_{CO₂}/kg_{H₂} produced and 25.12 kg_{CO₂}/kg_{H₂} produced, respectively.

When comparing the CO₂ emissions from the reforming process with those from reforming combined with biomass combustion, the value is approximately double. In the context of the SESR process, this higher CO₂ production is compounded by the fact that the regenerator in the process requires approximately four times more energy than the reformer in the CSR process. This results in a significantly higher energy demand to keep the unit operational, requiring 1.84 times more biomass mass to be burned. From an environmental standpoint, it is crucial to examine the impact of these gas emissions into the atmosphere, with a focus on exploring pre-treatment options to minimise potential negative effects on the environment.

Regarding the calculation of hydrogen yield, values of 0.43 mol_{H₂}/mol_{aqueous phase of bio-oil} and 0.71 mol_{H₂}/mol_{aqueous phase of bio-oil} were obtained for the CSR and SESR processes, respectively. Vagia and Lemonidou [9] studied the thermodynamic analysis of hydrogen production via steam reforming of selected components of the aqueous fraction of bio-oil. The model molecules of the aqueous fraction of bio-oil were acetic acid, ethylene glycol and acetone at 4/1/1 molar ratio. The authors carried out tests varying temperature, pressure and steam/fuel ratio. As for the hydrogen yield, the authors obtained 0.64 mol_{H₂}/mol_{aqueous phase of bio-oil}. The authors also performed a total net energy analysis for the CSR plant, operating without a sufficient secondary energy source. For a plant composed of preheater, reforming reactor, cooler and shift reactor equipment were considered. The total net energy found was 4.9E+04 kW.

In Table 8.4, for the SESR, the negative energy demand in the reformer block (- 9.55E+02) shows that CO₂ sorption in the reactor released much more energy than was needed for the steam reforming reaction. As a result, the reactor could run without any external heat, and the extra heat could be used elsewhere in the plant for other utilities. Similar behaviour was reported in the work of Singh et al. [82]. The authors performed a

comparative analysis between 4 hydrogen production routes from bio-oil reforming: CSR, SESR, chemical looping steam reforming (CLSR) and sorption enhanced chemical looping steam reforming (SE-CLSR). In their study, they accounted for heaters and coolers but did not consider heat exchangers or a secondary energy supply. Another observation similar to the cited work refers to the SESR process. In this case, a higher H_2 yield ($0.216 \text{ kgH}_2/\text{kg}_{\text{bio-oil}}$) was obtained, but with an increase in energy demand. The SE-CLSR process was the one that presented substantially lower energy requirements than all the other processes.

Table 8.4. Energy balance for each block in the CSR and SESR flowsheets.

Block	Model pallet	Parameters inserted in the program	<i>Energy balance (kW)</i>	
			CSR	SESR
HE1	HeatX	Vapor fraction = 1	1.27E+03	1.27E+03
HE2	HeatX	T cold stream = 550 °C	5.54E+02	5.54E+02
HE3	HeatX	T cold stream = 263 °C	2.86E+02	4.94E+02
Reformer	RGibbs	P, Heat duty = $Q = \Delta H_{(\text{stream13-stream12})}$	4.45E+02	- 9.55E+02
WGS	RStoic	Reaction, P = 5 bar, $T_{\text{in}} = 360 \text{ °C}$	5.04E+01	-
Regenerator	RGibbs	P, Heat duty = $Q = \Delta H_{(\text{stream15-stream14})}$	-	1.82E+03
Dryer	RStoic	Reaction, P = 5 bar, $T_{\text{in}} = 360 \text{ °C}$	5.38E+01	1.06E+02
Decomp	RYield	P = 1 bar	1.20E+03	2.35E+03
Combuster	RGibbs	$Q_{\text{Decomp} \mp \text{Combuster}} = 0$, Reaction, P = 5 bar	- 4.45E+02	- 8.46E+06
Cooler (sum)	Heater	T_{out}	- 1.66E+03	- 2.71E+03
Pump	Pump	Pressure increase, Efficiency = 0.85		
CYC1, CYC2	Ssplit	Split ratio, solid = 1	-	-

Faheem et al. [233] conducted a comparative study of steam methane reforming (SMR), sorption enhanced steam methane reforming (SE-SMR), autothermal reforming (ATR), and sorption enhanced autothermal reforming (SE-ATR). Using Aspen Plus, they simulated the process flowsheets and compared the processes based on energy consumption and production. In their calculations, methane energy was defined as the energy that could be supplied if the methane were burned directly in a burner. The energy

content of the consumed methane and the produced hydrogen was also determined. The study found that the SESR process had the highest methane demand ($4.6\text{E}+3$ MJ), followed by SE-ATR, ATR, and SMR ($2.2\text{E}+3$ MJ). In terms of hydrogen production, SE-SMR performed the best ($3.2\text{E}+3$ MJ), followed by SMR ($2.5\text{E}+3$ MJ), SE-ATR, and ATR. These findings are consistent with the results of the present work, where SESR consumed more energy but yielded higher hydrogen production.

Table 8.5. Net energy analysis of CSR and SESR processes.

	Variable	CSR ¹	SESR ²
		kW	kW
Primary fuel supply (reformer)	$Q_{\text{Et}} + Q_{\text{HAc}}$	4.66E+03	4.67E+03
Secondary fuel supply (combuster)	Q_{Biomass}	8.20E+03	1.52E+04
	Σ_{fuel}	1.29E+04	1.98E+04
Process electricity demand	P_{pump}	3.30E-01	3.30E-01
Process electricity co-generation		0	0
	$\Delta P = P_{\text{gen}} - P_{\text{dem}}$	-3.30E-01	-3.30E-01
Process heat demand	$Q_{\text{ref}}^1 / \text{reg}^2 + Q_{\text{dryer}}$	5.04E+02	1.93E+03
Useful process excess heat	$Q_{\text{WGS}} + Q_{\text{coolers}}$	-	2.86E+03
	$Q_{\text{ref}}^2 + Q_{\text{coolers}}$	1.71E+03	-
	$\Delta Q = Q_{\text{exc}} - Q_{\text{dem}}$	6.89E+01	1.05E+03
Energy value main product	Q_{H_2}	2.90E+03	4.80E+03
Energy value by-product 1	Q_{CH_4}	2.17E+03	6.09E+02
	Σ_{prod}	5.07E+03	5.41E+03
Sum of energy getting back from the plant (a)	$\Sigma_{\text{prod}} + \Delta Q (>0)$	6.28E+03	6.34E+03
Sum of energy inserted into the plant (b)	$\Sigma_{\text{fuel}} + \Delta P (<0) $	1.29E+04	1.98E+04
Thermal efficiency (a/b)	η	0.49	0.32

Thermal efficiencies for the CSR and SESR processes were calculated, and the results are displayed in Table 8.5. In the SESR process, both heat demand and excess useful heat were higher than in the CSR process, as also noted by Singh et al [82]. In the present work, the thermal efficiency was calculated, revealing a lower value in SESR. The thermal regeneration of adsorbent materials demanded a large amount of heat, directly impacting overall energy consumption. Although the CO₂ capture process demonstrated notable advantages, the high energy demand for regeneration posed

challenges to the system's overall efficiency. More energy-efficient approaches existed that maintained the advantages of the process. Industrially, for instance, PSA (Pressure Swing Adsorption) had been applied. PSA is used for gas separation when the partial pressure of CO₂ is high, relying on pressure variation rather than heating for adsorbent material regeneration. This allowed for a continuous process, less dependent on heat and, consequently, with a lower energy penalty. Additionally, PSA had been simpler to operate on an industrial scale and required less maintenance [235].

To enhance the CO₂ capture process using adsorbents, several solutions can be explored. One approach involves the use of biomass with a higher calorific value, which reduces the quantity of biomass needed and improves the plant's energy balance. Optimising the regenerator through multi-stage regenerative processes is also considered to increase CO₂ removal efficiency. Energy-saving technologies, such as pinch technology and heat integration, are also good options. In summary, Pinch Analysis is a specific methodology used to optimise heat integration. Heat integration refers to the broader practice of improving energy efficiency by effectively using and reusing heat within a process. Pinch Analysis helps identify key points where heat transfer can be maximised and energy losses minimised. It focuses on using excess heat from one part of the process to reduce the need for external heat, thereby improving the overall heat balance of the plant. Heat integration involves implementing these findings by using heat generated at different stages to preheat materials or perform other functions, which reduces overall energy consumption. This can include utilising excess heat for auxiliary processes or steam generation. By combining these strategies with the selection of an appropriate secondary fuel, the overall efficiency could be improved [236].

This work is an initial study that aims to identify points for future optimisation efforts. In this context, the results were satisfactory, establishing a basis for further improvements in efficiency and energy use.

8.3. Conclusion

To compare the CSR and SESR processes in terms of CO₂ emissions, hydrogen yield, and thermal efficiency, reforming was conducted using a molar ethanol acid mixture of 0.25:0.75, with a steam-to-carbon (S/C) ratio twice the stoichiometric value. Biomass burning was used as the energy source. The simulation results explored CaO as a potential CO₂ sorbent, with the reformer reactor operating at 600 °C and 5 bar. Under these conditions, the SESR process showed lower CO₂ emissions in both the reforming process (10.34 kg CO₂/kg H₂) and the combined biomass burning and reforming process

(25.12 kg CO₂/kg H₂). SESR also demonstrated a higher hydrogen yield (0.70 and 0.43 mol H₂/mol bio-oil FA). For high-purity hydrogen production, SESR delivered superior results. Although thermal efficiency was impacted by the significant heat demand for adsorbent regeneration, the proposed SESR model provides a suitable basis for future optimisation. To enhance CO₂ capture and overall efficiency, strategies such as using higher-calorific biomass, optimising multi-stage regeneration, and implementing heat integration and pinch technology should be explored. While Pinch Analysis has not yet been conducted, it is suggested for future work to identify opportunities for maximising heat reuse and reducing energy losses, which could increase efficiency and lower biomass consumption. This study offers valuable insights into advancing sustainable energy research and developing future strategies for clean, efficient energy production.

Chapter 9 – SUGGESTIONS FOR FUTURE WORK

For Chapter 5:

- The presence of impurities in mining wastes can make it difficult and economically unfeasible to carry out in steam reforming process, unless adequate purification and treatment measures are applied to remove or reduce the presence of these impurities. In this sense, it is suggested that the mining waste be subjected to a leaching process to precipitate CaO. In this case, an important process parameter is pH control. This would not only simplify the process of separating the other components, but would also help improve the quality of the final product.

Commonly to chapters 6 and 7:

- Use of a new combination of model molecules for bio-oil, including other compounds that realistically reproduce its composition. Also, test each catalyst used in this work in this new composition. This way, will be possible to better understand the catalytic performance of these materials in different scenario.

For chapter 8:

- Apply Pinch Analysis to the simulation carried out, in order to minimize energy consumption and maximize the global efficiency of a system, taking into account the thermodynamic restrictions associated with the processes.
- A future direction could involve a Life Cycle Assessment (LCA) to evaluate the environmental impacts of the process, ensuring a comprehensive understanding of its sustainability.
- An economic analysis to assess the cost-effectiveness and scalability of the process, providing insights into its industrial viability.

Chapter 10 – REFERENCES

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APPENDIX – SUPPLEMENTARY INFORMATION

A. Flowsheet from simulation

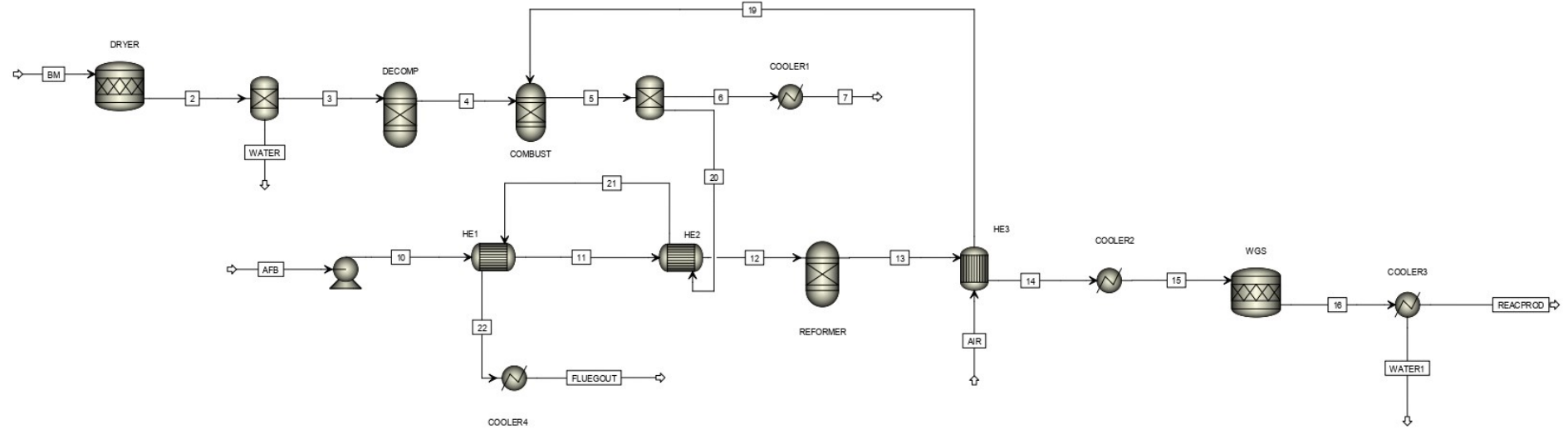


Figure A.1. Process model flow diagram for conventional steam reforming (CSR) (Figure 8.1)

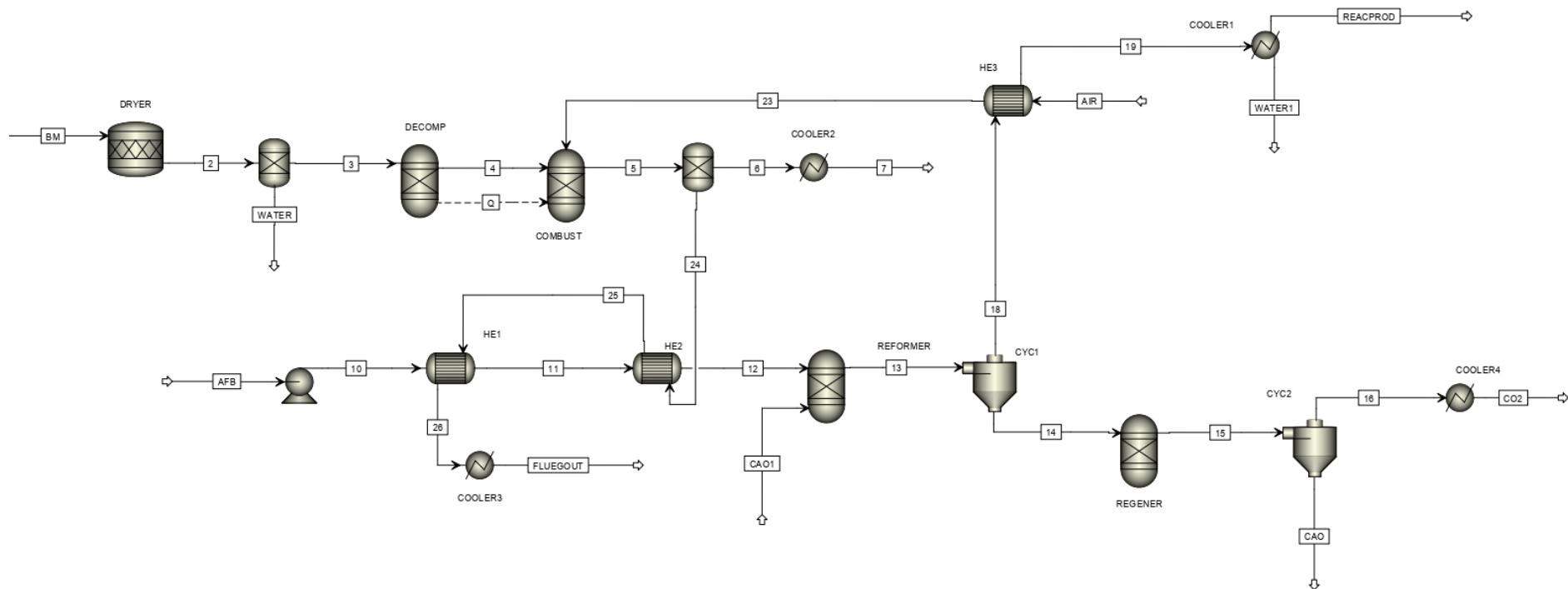


Figure A.2. Process model flow diagram for sorption enhanced steam reforming (SESR) (Figure 8.2)