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**SIMULATION OF HYDROGEN PRODUCTION THROUGH THE
GASIFICATION OF PEANUT SHELLS UNDER SUPERCRITICAL
WATER CONDITIONS: INVESTIGATING EFFECTS OF $\text{Ca}(\text{OH})_2$
CATALYST, TEMPERATURE, PRESSURE, RESIDENCE TIME
AND ECONOMIC VIABILITY**

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Declaration

I hereby declare that I have completed the submitted thesis work and have solely utilised permissible reference sources and materials. All information presented in this document has been obtained adhering to academic ethics and guidelines. Furthermore, I attest that any materials and findings not originating from my authorship in this thesis are appropriately cited and referenced.

DEDICATION

This thesis is dedicated to my parents, brothers, sisters, teachers, professors, qur'anic masters, friends, and all the people who have supported me morally, emotionally, spiritually, and financially throughout my education. Thank you for guiding me through this adventure to its successful conclusion. I hope this achievement will fulfill the dream you envisioned for me.

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RÉSUMÉ

L'arachide (*Arachis hypogaea*) est une plante de la famille des Fabacées (légumineuses). L'arachide est l'un des principaux produits alimentaires cultivés dans les pays tropicaux comme le Sénégal et constitue une culture précieuse pour le secteur agro-industriel. Les arachides sont comestibles, mais leurs coques sont généralement jetées comme déchets après les étapes de récolte et de transformation. Cependant, la gestion des déchets générés par la récolte et la transformation des arachides représente un défi majeur dans le monde entier. Cette étude propose un schéma conceptuel pour la gazéification catalytique à l'eau supercritique des coques d'arachides. Un modèle détaillé de simulation cinétique de Power Law a été développé à l'aide du logiciel ASPEN Plus V14 afin d'analyser, d'optimiser et d'évaluer l'efficacité du processus de gazéification à l'eau supercritique des coques d'arachide. Le modèle développé comprend trois unités de traitement pour le prétraitement, la gazéification, la séparation et la purification. L'analyse économique du processus optimisé a été évaluée en utilisant l'hydrogène obtenu à partir de la gazéification de coques d'arachides, dans des conditions supercritiques, sur la base d'une analyse complète des flux de trésorerie actualisés (DCF). Les résultats de la simulation ont été validés en les comparant aux données expérimentales trouvées dans la littérature. La comparaison a montré que les résultats prédits par le modèle concordaient bien aux résultats rapportés dans la littérature. Les principaux effets ainsi que les effets d'interaction de quatre paramètres du processus, à savoir la température, la pression, la charge de catalyseur et le temps de séjour, sur le rendement du gaz de synthèse ont été étudiés à l'aide d'une analyse de sensibilité. Selon ces résultats, l'augmentation de la température de sous-critique (300 °C) à supercritique (1000 °C) a augmenté la production de H₂ et de CO, tout en réduisant la production de CH₄ et de CO₂. De plus, les rendements en H₂ et CO₂ se sont améliorés lorsque la pression a été augmentée de 220 à 350 bar, réduisant en même temps la production de CH₄ et de CO. Cependant, le changement de pression n'a pas montré d'effet significatif sur le rendement en hydrogène. Plus important encore, l'effet du catalyseur Ca(OH)₂ a été étudié et les résultats ont clairement démontré qu'il a une influence positive sur le rendement en H₂. Le catalyseur Ca(OH)₂ amplifie le rendement en hydrogène de 16,308 %. De plus, afin d'optimiser la production d'hydrogène du procédé, l'effet simultané des différents paramètres du procédé sur le rendement en hydrogène a été étudié à l'aide d'une analyse de sensibilité. Selon la meilleure prédiction du modèle, le rendement en hydrogène peut atteindre 193,993 kg/h lorsque les

conditions de réaction sont établis comme suit : la température = 750 °C, la pression = 220 bar, le rapport biomasse/eau de 1:4 et le temps de séjour d'une heure. Sur la base de l'analyse économique, le coût de l'hydrogène (LCOH) est estimé à 1,30 \$/kg, ce qui est relativement bas par rapport à l'hydrogène produit à partir d'autres procédés de conversion de la biomasse, en raison de la disponibilité de la matière première. En outre, un taux de rendement interne de 12%, une période de récupération de 4,6 ans et un retour sur investissement de 113,30% ont été obtenus avec une valeur actuelle nette de 11 839 892,99 \$. Les résultats de l'analyse de rentabilité indiquent que le projet SCWG de production d'hydrogène est viable d'un point de vue économique.

Mots-clés : Simulation de processus, Coques d'arachides, Hydrogène, Gazéification à l'eau supercritique, Aspen Plus ®, Analyse économique.

ABSTRACT

Peanut (*Arachis hypogaea*) is a plant from the Fabaceae family (legumes). Peanut is one of the most important food products grown in countries with tropical climates like Senegal and is a valuable crop for the agro-industrial sector. Peanuts are edible, but their shells are generally discarded as waste after the harvesting and processing stages. However, the management of waste generated by the harvesting and processing of peanuts represents a major challenge worldwide. This study proposes a conceptual design for the catalytic supercritical water gasification of peanut shells. A detailed Power Law kinetic simulation model was developed using ASPEN Plus V14 software to analyse, optimise, and evaluate the efficiency of the peanut shell supercritical water gasification process. The developed model comprises three process units for pretreatment, gasification, separation and purification. The economic analysis of the optimised process was evaluated using hydrogen obtained from the gasification of peanut shells, under supercritical conditions, based on a comprehensive discounted cash flow analysis (DCF). The simulation results were validated by comparing them with experimental data found in the existing literature. The comparison showed that the results predicted by the model agreed well with those reported in the literature. The main effects, as well as interaction effects of four process parameters, including temperature, pressure, catalyst loading, and residence time, on the yield of syngas, were investigated using a sensitivity analysis. According to these results, increasing the temperature from subcritical (300 °C) to supercritical (1000 °C) increased the production of H₂ and CO while reducing the production of CH₄ and CO₂. Furthermore, H₂ and CO₂ yields improved when the pressure was increased from 220 to 350 bar, reducing the production of CH₄ and CO at the same time. However, the change in pressure did not show a significant effect on hydrogen yield. More importantly, the effect of Ca(OH)₂ catalyst was investigated, and the findings demonstrated that it has a positive influence on H₂ yield. The Ca(OH)₂ catalyst amplifies the yield of hydrogen by 16.308 %. Moreover, to optimise the hydrogen production of the process, the simultaneous effect of different process parameters on the hydrogen yield was studied using a sensitivity analysis. According to the model's best prediction, the hydrogen yield can reach 193.993 kg/h when the reaction conditions are temperature = 750 °C, pressure = 220 bar, biomass to water of 1:4, and residence time of one hour. Based on the economic analysis, the Levelized cost of hydrogen (LCOH) is estimated at \$ 1.30/kg, which is relatively low compared to hydrogen produced from other biomass conversion processes due to the ready

availability of the feedstock. In addition, an internal rate of return of 12%, a payback period of 4.6 years, and a return on investment of 113.30% were obtained with a net present value of \$ 11,839,892.99. The results from the profitability analysis indicate that the SCWG project for hydrogen production is viable from an economic standpoint.

Keywords: Process simulation, Peanut shell, Hydrogen, Supercritical water gasification, Aspen Plus®, Economic Analysis.

ACRONYMS AND ABBREVIATIONS

ACAPEX: Annualized Capital Expenditure

ASPEN: Advanced System for Process Engineering

E_a: Activation Energy

BMC: Bare Module Cost

Ca(HCO₃)₂: Calcium Bicarbonate

CaCO₃: Calcium Carbonate

CAPEX: Capital Expenditure

Ca(OH)₂: Calcium Hydroxide

CH₄: Methane

CO₂: Carbon Dioxide

CO: Carbon Monoxide

CRF: Capital Recovery Factor

CSTR: Continuous Stirred Tank Reactor

EA: Economic Analysis

FCI: Fixed Capital Investment

GHG: Greenhouse gases

H: hour

H₂: Hydrogen

(HCOO)₂Ca: Calcium Formate

IRR: Internal Rate of Return

K: Pre-exponential Factor

Kg: Kilogram

kWh: kilowatt-hour

LCOH: Levelized Cost of Hydrogen

NPV: Net Present Value

OPEX: Operating Expenditure

PP: Payback Period

PL: Power Law

PR-BM: Peng-Robinson with Boston-Mathias function

ROI: Return on Investment

SMR: Steam Methane Reforming

SCW: Supercritical Water

SCWG: Supercritical Water Gasification

Syngas: Synthetic Gas

TEA: Techno-Economic Analysis

TCI: Total Capital Investment

WGS: Water Gas Shift

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1 Introduction

1.1 Background

Energy is a necessary component of human society and is required to drive global economic growth [1]. Global energy demand is expected to almost triple between 2000 and 2050 [2]. The negative environmental effects of increasing greenhouse gas emissions and associated anthropogenic climate change have pushed the world to look for new solutions to develop a fully decarbonised and more sustainable energy system. The feasibility and sustainability of many renewable energy sources, including biomass, solar energy, wind energy, etc., are currently being examined [3]. Moreover, they are environmentally benign and effective in reducing problems such as acid rain, climate change, and global warming caused by greenhouse gases (GHG) and carbon dioxide, among others [4]. Indeed, biomass can play a crucial role in this energy transition. More importantly, in addition to being clean, reliable, and environmentally friendly, biomass sources are widely available from all around the world.

Biomass refers to all organic matter, including plant and animal waste, and their by-products resulting from natural or induced transformations [5]. As a clean and renewable energy source, biomass can be converted into heat, electricity, and various fuels, including hydrogen. This makes it one of the most promising renewable energy sources, as it is widely available worldwide and does not emit carbon. Biomass can come from a variety of sources, such as forest residues, industrial and municipal waste, agricultural and agro-industrial waste, and be converted through biochemical and thermochemical processes to produce value-added products and more environmentally friendly energy fuels. The energy delivery in the form of hydrogen is referring to the “hydrogen economy”.

The "hydrogen economy" was first proposed by John Brockris in 1970 to describe the transition from hydrocarbons to hydrogen as an energy carrier. This transition should lead to a carbon-free energy system with broad technological application, economic performance, and social acceptance. The use of biomass and solid organic waste for hydrogen production is expected to support the realisation of the hydrogen economy while promoting energy decentralisation and resilience. It should be noted that hydrogen produced from biomass is a carbon-free process, as it maintains a natural cycle in which plants extract carbon from the atmosphere through

photosynthesis for growth and release it during the production of hydrogen, resulting in virtually no greenhouse gas emissions. Therefore, hydrogen-based biomass is highly regarded as a promising energy carrier necessary for achieving a fully decarbonized energy system. Additionally, it provides a powerful means of utilizing agricultural residues such as peanut waste.

The important oilseed crop known as groundnut or peanut (*Arachis hypogaea* L.) is grown worldwide (Figure 1 [6]). It is a 30-50 cm long herbaceous plant that can grow upright or prostrate. It has a well-developed taproot with numerous lateral roots and nodules. The underground pods of the peanut usually contain one to four seeds and are between 3 to 7 cm long. From planting a seed to its maturity, peanuts generally take 100 to 150 days, depending on the cultivar and the weather conditions. As a major crop, peanuts are now grown in the tropical, subtropical, and warm temperate regions of Asia, Africa, Europe, Oceania, North America, and South America [1].



Figure 1. Peanut (*Arachis hypogaea* L.) [6]

In the 19th century, West Africa was the main location for peanut production. For instance, in Senegal, the selling and exporting of peanuts accounts for about 20% of the country's GDP (Gross Domestic Products) [7]. As the world's ninth-largest exporter of groundnuts, Senegal generates over \$22 million in foreign exchange [8]. The main producing regions are Kaolack, Fatick, and Kaffrine (Figure 3), which all together form the peanut basin. Peanut farming employs around 70% of the local population and accounts for more than 35% of their household revenue [9]. However, the world faces many challenges related to managing the waste from peanut processing and harvesting. To address this issue, specific technologies such as thermochemical and biological processes have been developed to convert agro-industrial waste into useful energy.

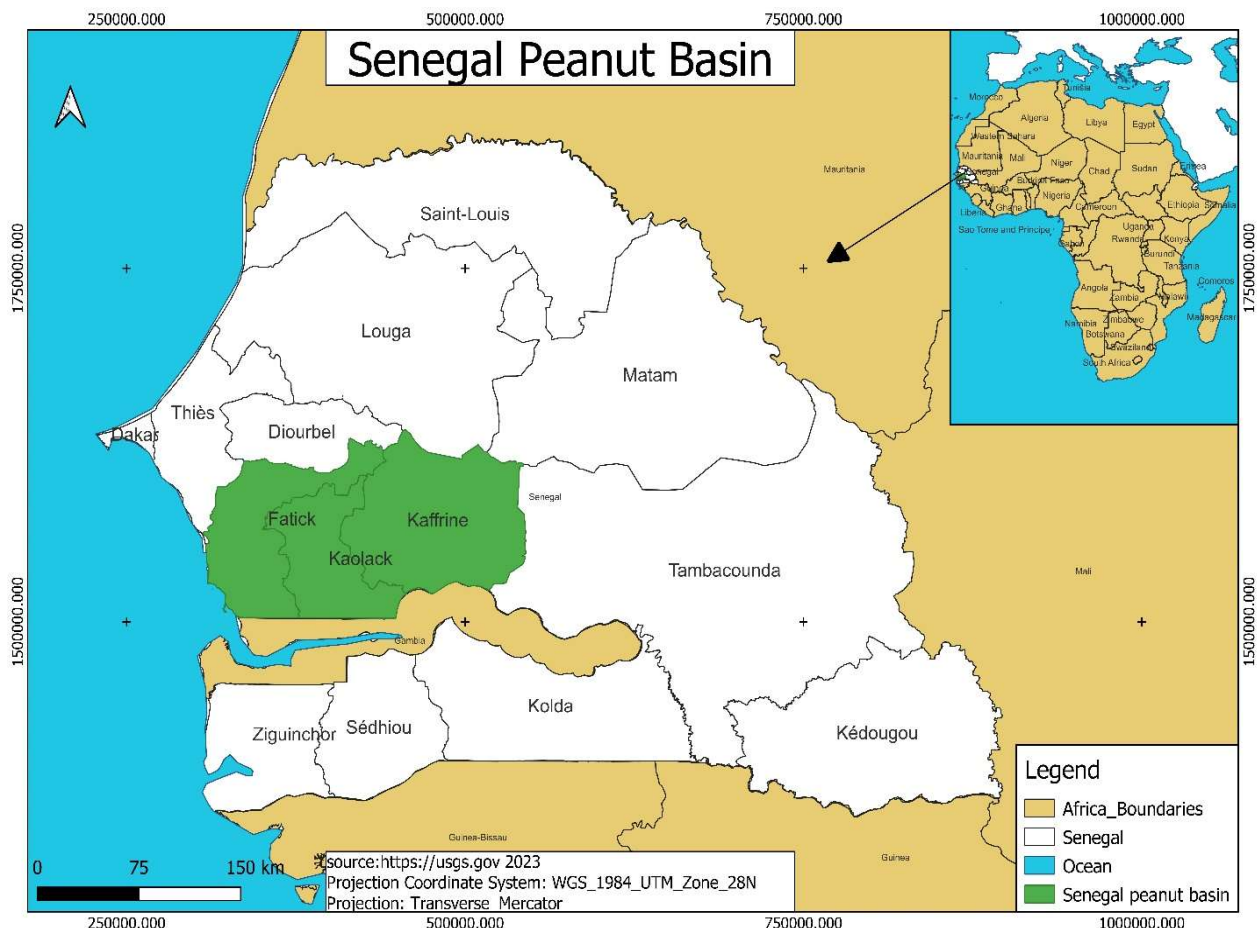


Figure 2. Peanut basin of Senegal in green (source: <https://usgs.gov> 2023)

To convert biomass into energy, different techniques such as thermal, biological, or mechanical techniques are used. However, given their ability to depolymerise the majority of organic components, thermochemical techniques seem to be the most promising for transforming them into low-value biowaste [10]. In addition, lower reaction times are required for the reactions. Since the main components of peanut shells are cellulose, hemicellulose, and lignin [10], SCWG (supercritical water gasification) seems to be the recommended technique for these lignin-rich materials from thermal options (combustion, pyrolysis, gasification and liquefaction). Furthermore, water is used as a gasification agent in the supercritical water gasification (SCWG) process, which is carried out at a temperature above 374 °C and a pressure of about 220 bar (22 MPa). A state of water that is above its critical temperature and pressure is called supercritical water. Biomass can be gasified with a high conversion rate using Supercritical Water Gasification (SCWG), and the resulting gas is composed of CO₂ and H₂. The phase diagram below shows the supercritical zone (Figure 3[11]).

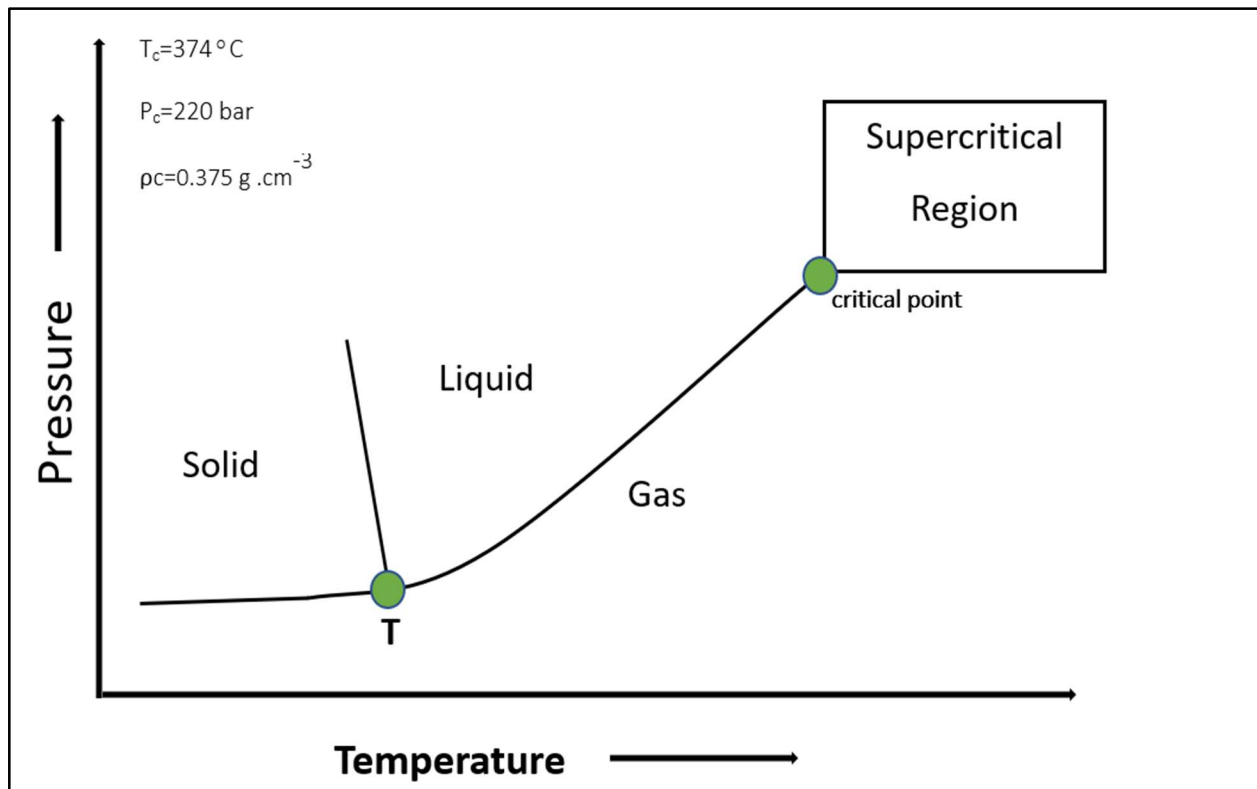


Figure 4. Phase diagram for water [11]

For this purpose, hydrogen is becoming increasingly popular as a recyclable or renewable energy source that can be used through combustion or fuel cells, producing water as a by-product. In biomass gasification, the catalyst plays an essential role, and different catalysts can have varying effects. Catalysts are substances that accelerate chemical reactions without being consumed themselves. A gasifier can increase the rate of the gas-producing reactions and improve the efficiency of the process by increasing the yield of gas per unit of feedstock.

Importantly, the production of high-quality gas requires the optimisation of complex processes such as SCWG. Recently, a variety of process simulation tools have been used to model, improve and simulate complex processes like biomass gasification. Some of these popular modelling software packages include ChemCAD, MATLAB, Aspen Plus, and computational fluid dynamics, including GAMBIT, FLUENT and OpenFOAM [12]. Aspen Plus is one of the most popular process simulation programs, both at the academic and commercial levels. Concepts such as pressurised anaerobic digestion and biogas upgrading, biomass oxy-combustion for near net zero emissions, and techno-economic evaluation of chemical manufacturing from biomass have all been studied using Aspen Plus [13] in the bioenergy sector.

Furthermore, over the last decade, there has been a considerable increase in the number of studies conducted on biomass gasification, and several review studies have addressed a range of issues [12]–[25]. In their review, Puig-Arnau et al [23] briefly explored the modelling of biomass gasification with Aspen Plus. The authors pointed out that while the modelling of biomass gasification was at the time limited and largely based on the equilibrium technique, there was considerable work on modelling coal gasification with Aspen Plus. The basic gasification reactions were included, but the hydrodynamic complexity of gasifiers and tar formation were not taken into account. As a result, Ahmed et al [16] worked on the modelling ideas for Aspen Plus biomass tars. Hantoko et al [22] investigated the modelling of solid waste gasification by Aspen Plus.

To the best of our knowledge, there is no study specifically focuses on the modelling and validation of biomass gasification of peanut shells in Aspen Plus under supercritical conditions, with a particular emphasis on the catalyst effect. In addition, there is no available study on the techno-economic analysis of hydrogen production from SCWG of peanut shells. Numerous

studies [12], [13], [16]–[18], [22]–[26] have addressed the modelling and simulation of Aspen Plus. Furthermore, no simulation using Aspen Plus in Senegal has yet been done to describe the interactions between peanut shell molecules and the $\text{Ca}(\text{OH})_2$ catalyst in supercritical water conditions. This thesis focuses on the economic analysis of the process as well as the description of the effects of $\text{Ca}(\text{OH})_2$ catalyst, temperature, pressure, and residence time for hydrogen production by gasification of peanut shells in supercritical water to fill these knowledge gaps.

1.2 Statement of the problem

One of the largest generators of agro-industrial waste (shells) is the peanut industry. It is interesting to study the high energy content of this residual biomass. Between 25 and 30% of the total weight of the legume is made up of the peanut shell, which is removed as waste in the final processing stages, either for the production of oil, and peanut butter or for direct consumption without the shell. This waste, produced worldwide by the peanut industry on an annual basis of over 11,000,000 tonnes [5], is still untapped. As a result, much of the waste from the peanut industry that could be used as biomass for energy purposes is disposed of. Many boilers in Mediterranean countries are currently fuelled by fossil fuels; however, if they were converted to burn other biomass materials, such as peanut shells, this would result in significant reductions in CO_2 emissions, leading to improved environmental sustainability [5]. Some production industries give their residues to others so that they can burn it to generate electricity. Due to the low density of peanut shells, large quantities of this waste have to be transported, which increases the cost of producing the legume.

Notably, peanut is an important cash crop in Senegal, where smallholders grow 250,000 tonnes per year [9]. Peanuts (*Arachis hypogaea*) are primarily harvested from the Senegal peanut basin, located in the centre of Senegal. This region produces an estimated 142,000 tonnes of peanut shells, which despite their light weight, have a density of 270 kg/m^3 and a low calorific value (LCV) of $16,704 \text{ kJ/kg}$ (4.64 kWh/kg) [27]. However, peanut waste, or shells, do not generally have value-added uses. For example, Georges et al., [9] and Tankari [28] noted that 47% of poverty and 57% of food insecurity among smallholder farmers in sub-Saharan Africa, including Senegal, was due to a lack of opportunities to acquire knowledge and develop value-added processing of peanuts. Many studies are currently investigating ways to add value to groundnut

shells [1], [5], [10], [14], [18] in the hope of reducing their environmental impact and attempting to make them into fuels or chemicals, through various processes such as SCWG.

The process of SCWG is a highly complex and interdisciplinary area of research, which involves intricate interactions between mass and heat transfer mechanisms and chemical processes. The operational performance and quality of the syngas can be influenced by a variety of factors, including feedstock type, gasifier configuration, gasification agent, catalyst used, temperature, and pressure [13]. Unfortunately, experimental process optimisation for a particular feedstock is time-consuming and expensive. In addition, there are still significant technological and financial barriers to evaluating and improving the performance of current processing plants.

1.3 Objectives

1.3.1 Main objectives

The main objectives of this Thesis are:

- To optimize the hydrogen yield in the process of supercritical water gasification (SCWG) of peanut shells using Aspen Plus V14.
- Perform Economic Analysis of the Process: conduct an economic analysis of the optimized SCWG process, considering factors such as costs, profitability, and feasibility.

1.3.1.1 Specific goals

More specifically, the objectives that this study aims to address are as follows:

- 1- Investigate the Effect of Process Parameters on H₂ Yield:
 - a- Analyse the effect of temperature on H₂ yield.
 - b- Study the influence of pressure on H₂ yield.
 - c- Evaluate the efficiency and performance of the Ca(OH)₂ catalyst for the supercritical water gasification (SCWG) of peanut shells, considering its influence on H₂ yield and relevant factors.
 - d- Investigate the simultaneous effect of temperature and pressure on H₂ yield.

- e- Study the simultaneous effect of temperature and residence time on H₂ yield.
- 2- Evaluate the economic viability of the optimized process.

1.4 Structure of the Thesis

This thesis begins with an overview of the research background, the problem and the objectives, including the main objective as well as the specific objectives of this chapter. Chapter 2 provides a comprehensive review of the catalytic supercritical water gasification (SCWG) of biomass. It covers the current state of SCWG process, including process scale, optimization, and catalysts (homogeneous and heterogeneous), as well as its applications for hydrogen production. In addition, it highlights the challenges, solutions, and prospects of producing hydrogen from waste.

Chapter 3 of this thesis deals with the materials and methods used. This section includes an in-depth explanation of the process model simulator, assumptions, model description, physical characteristics approach, and model sequence.

The modelling of peanut shell gasification in supercritical water for H₂ production in Aspen Plus is then the focus of Chapter 4, with particular attention given to model validation, H₂ yield optimization, and effects of temperature, pressure, residence time, and Ca(OH)₂ catalyst on H₂ yield by discussing various process configurations based on equilibrium and kinetic approaches. In the end, the conclusion and recommendations for future work are discussed in Chapter 5.

2 State of knowledge

2.1 Current status of SCWG process

The research on SCWG achieved a milestone in 1970 when Modell successfully gasified organics in supercritical water (SCW) for the first time and obtained hydrogen-rich products [29]. From then on, the use of SCW for biomass applications, such as electricity production, synthetic fuel creation, and hydrogen production, has sparked a research boom. There have been notable advancements in process scale, reactor types, and catalyst studies.

2.1.1 Process scale

Over the years, SCWG technology has been scaled up from laboratory to pilot scale [29]. Forschungszentrum Karlsruhe was the first to develop a pilot-scale SCWG system with a wet biomass capacity of 100 L/h, which operated stably for up to 10 hours. General Atomics followed suit by constructing a supercritical water partial oxidation system that could handle 200 kg/h of biomass slurry. In Enschede, a well-equipped SCWG system was built with a maximum output capacity of 30L/h [29]. In Japan, at Hiroshima University, a pilot-scale SCWG system with a capacity of 1 tonne/day was constructed. The State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF) in China developed the first pilot plant of SCWG-Solar, capable of producing an output of 1.03 tonne/h. With the continuous and stable operation of the demonstration plant, the feasibility of large-scale SCWG applications has been verified [30].

2.1.2 SCWG process optimization

The optimization of Supercritical Water Gasification (SCWG) has led to significant advancements in reactor configurations, resulting in a range of novel SCWG systems, including diamond anvil cell autoclaves, quartz capillaries, micro-tube reactors, tubular and hybrid reactors, Y-shape reactors, and bubbling fluidized bed SCWG reactors [29]. In addition, some studies have combined SCWG with other systems to improve performance, such as the thermodynamics cycle power generation system proposed by Guo and Jin [31], which combined SCWG of coal with a multi-stage steam turbine reheated by hydrogen combustion. The industrial prospects of coal and SCWG and the novel thermodynamics cycle power generation system were demonstrated. Cao et al. [32] proposed an innovative system that integrates pulping and SCWG of black liquor. This system fully utilizes the hydrogen, power, and steam generated by SCWG to meet the energy requirements of the pulping process. Darmawan et al. [33] integrated SCWG of black liquor with

syngas chemical looping and implemented the exergy-recovery technologies, creating an efficient and environmentally friendly black liquor utilization system. Albarelli et al. performed a SCWG process integrated with a sugarcane biorefinery system, and Aziz developed a microalgae SCWG process built on optimized process integration [29]. Finally, in a conceptual process that integrated SCWG and reforming process, Hankoto et al. [34] achieved a higher yield of syngas, producing 151.12 kg of syngas per 100 kg of feed compared to the conventional SCWG process which produced only 120.61 kg per 100 kg of feed.

2.2 SCWG catalysts

The production of H₂ through SCWG of biomass requires high temperatures and pressures. The addition of catalysts can reduce operating costs and improve H₂ selectivity, while also decreasing tar and char formation in the process [35]. The choice of catalyst for the gasification of biomass samples in SCWG depends on its ability to cleave C-C bonds, advance the WGS reaction, and minimize activity towards C-O bond cleavage. The role of catalysts in reducing the need for high operating conditions and increasing H₂ yields makes catalytic SCWG an attractive option [35]. This section provides an overview of current research on different homogeneous and heterogeneous catalysts that have been studied to enhance gas yields during SCWG.

2.2.1 Homogenous catalysts

SCWG is a high-energy-consuming process that operates at high temperatures and pressures, potentially leading to high processing costs. Catalysts are used in SCWG to enhance gas output while reducing heat requirements. Homogeneous catalysts, such as alkali and hydroxide catalysts (e.g., K₂CO₃, Na₂CO₃, KOH, KHCO₃, and NaOH), are effective for SCWG of biomass, as they are capable of breaking C-C bonds and improving product yield by accelerating the WGS reaction [36]. Homogeneous catalysts have advantages such as low cost, higher and rapid conversion rates, and flexibility for use in batch and continuous gasifiers [37]. Although homogeneous catalysts are more effective when compared to heterogeneous catalysts, they can also pose challenges, including reactor plugging and corrosion problems [38], and difficulty in recycling and reusing catalysts after an SCWG experiment. In contrast, heterogeneous catalysts allow a few ways for recovery and reuse at additional expenditures.

Nanda et al.[39] evaluated the efficiency of supercritical water gasification (SCWG) using timothy grass as an energy crop with four different homogeneous catalysts: especially hydroxides (NaOH and KOH) carbonate catalysts (Na_2CO_3 and K_2CO_3). The SCWG was conducted at a temperature of 650°C for 45 minutes with a biomass-to-water feed ratio of 1:8. The results showed high yields of H_2 (5.15 mol/kg) and overall gases (17.2 mol/kg). The presence of alkali catalysts improved the H_2 yields in the following order: KOH (8.91 mol/kg) > K_2CO_3 (7.84 mol/kg) > NaOH (6.68 mol/kg) > Na_2CO_3 (6.39 mol/kg) > no catalyst (5.15 mol/kg). It is proved that these alkali catalysts, especially KOH and K_2CO_3 aid in catalysing the water-gas shift (WGS) reaction, generating H_2 and CO_2 instead of CO. However, Na_2CO_3 promotes the decarboxylation of formic acid (HCOOH), an intermediate product of the WGS reaction, thereby increasing H_2 production [36]. Na_2CO_3 also produces precipitated particles in SCW that subsequently cause a larger surface area for many catalytic reactions. In contrast, NaOH promotes the yield of CH_4 by accelerating the methanation reaction even at subcritical conditions. The hydrolysis of biomass by NaOH generates sodium acetate (CH_3COONa) as an intermediate product, which further degrades to CH_4 and sodium bicarbonate (NaHCO_3) [36].

Chen et al. [40] studied the impact of different types of alkali salt catalysts on hydrogen generation from sewage sludge in SCW fluidized bed reactor, as a new reactor design. Their findings classified catalytic activity on SCWG of sewage sludge according to efficiency and H_2 selectivity as follows: KOH > K_2CO_3 > NaOH > Na_2CO_3 . The highest H_2 output of 15.49 mol/kg was obtained in the presence of KOH at 540°C . In another study, NaOH was examined as a catalyst for SCWG of glucose and other biomass materials in a batch reactor, which resulted in an 80% increase in H_2 yield at 450°C and 340 bar [41]. Zhang et al. [42] explored the effect of NaOH on the SCWG of sewage sludge and found that it increased the yield of H_2 . The application of NaOH on SCWG of sewage sludge not only improved the WGS reaction but also promoted CO_2 capture as stated by Gong et al. [43].

In a separate investigation, Aixia et al. [14] studied the catalytic mechanism of K_2CO_3 , ZnCl_2 , and Raney-Ni for H_2 production through the gasification of peanut shells in SCW. Their work showed that different catalysts had varying effects on hydrogen yields, with ZnCl_2 exhibiting the highest hydrogen selectivity, K_2CO_3 being lower, and Raney-Ni being the lowest. However, Raney-Ni was found to be the most suitable catalyst for gasifying biomass.

In conclusion, using stable and active catalysts for SCWG of biomass, including peanut shells, sewage sludge, and energy crops, can accelerate gasification reactions, resulting in high efficiency and reduced operational costs at lower reaction temperatures.

2.2.2 Heterogeneous catalysts

Heterogeneous catalysts can be classified into two types: metal oxides and transition metal catalysts. One of the primary advantages of heterogeneous catalysts is their ability to be recovered and reused, reducing the overall cost of catalyst development. However, their recovery requires additional costs. Heterogeneous catalysts are chosen for their selectivity and inertness to reside inside the reactor or on the support material. Nevertheless, the presence of Sulphur, nitrogen, coke, or any other heteroatom-containing compounds presents a significant challenge as it can cause deactivation, poisoning, and sintering of heterogeneous catalysts. Additionally, during SCWG, metal cations are converted into oxides and their corresponding salts, while elements such as S and Cl are easily oxidized into their corresponding organic acids, which remain in the aqueous phase after the reaction is complete[36].

As previously mentioned, transition metal catalysts include nickel (Ni) and other novel metal catalysts such as Pb (Lead), Pt (Platinum), Rh (Rhodium), and Ru (Ruthenium), which have been utilized for SCWG to produce energy, synthetic fuels, hydrogen, etc. Among these, Ni-based catalysts are commonly used in SCWG due to their low cost compared to other novel metal catalysts. Although the use of nickel can potentially increase total gas production and enhance carbon gasification, the H₂ generation is reduced due to its consumption in the hydrogenation reaction. Moreover, nickel catalyses the methanation reaction, exhibiting high selectivity towards CH₄ in SCWG [44]. However, the primary issue with nickel is the inevitable problem of sintering and catalyst deactivation due to the formation of tar.

In SCWG, the metal catalyst can be either in the supported or unsupported form. The selection of suitable catalyst support is critical for improving catalytic activity and providing better stability, given the complex nature of the SCW environment. Commonly used catalyst supports in hydrothermal gasification include alumina, silica, molybdenum, olivine, metal oxides, activated carbon, carbon nanotubes, graphite, and more. Some studies have also explored the use of lignocellulosic biomass as a supported material and reactant in SCWG studies[36], [38], [44],

where catalytic metal nanoparticles were either impregnated or synthesized in the cell wall of the biomass by varying the metal concentrations and doping conditions (e.g., temperature, pH, agitation, duration, and additives).

Varying the supporting material is an alternative option for tailoring the catalyst and improving catalytic activity, stability, and gas yields. Several studies have investigated the use of different types of catalyst support to increase hydrogen production during the SCWG of both biomass models and real compounds. For example, Kang et al. [45] evaluated five different supports (Al_2O_3 (Aluminium oxide also known as Alumina), activated carbon or AC, TiO_2 (Titanium dioxide), ZrO_2 (Zirconium dioxide also known as Zirconia), and MgO (Magnesium oxide)) and three promoters (Co (cobalt), Cu (copper), and Ce (cerium)) for a Ni-based catalyst in the SCWG of lignin. The catalysts were synthesized and screened for their performance, with the results showing that Ni catalytic activity varied in the order of its supported materials ($\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{AC}$ (activated carbon) $> \text{ZrO}_2 > \text{MgO}$). Similarly, the catalytic activity of Ni-based catalysts for SCWG of lignin using different promoters was classified according to their performance ($\text{Ce} > \text{Co} > \text{Cu}$). The authors explained that Ce increased H_2 yield by elevating Ni dispersion, thereby weakening the Ni- Al_2O_3 interaction.

Resende et al. [46] evaluated the effects of different types of transmission metal catalysts (unsupported and supported), such as nickel, iron, copper, zinc, and zirconium wires, ruthenium powder, and Raney nickel slurry, on the SCWG of carbohydrate feedstocks (cellulose and lignin). They found that the presence of metals increased the yield of fuel gas production in general, particularly when the catalyst surface area-to-biomass weight ratio was $15 \text{ mm}^2/\text{mg}$. Among these catalysts, Ni and Cu supported the generation of higher syngas at a constant feed concentration of 0.8 wt% and residence time of 10 min, at two different reaction temperatures (500°C and 600°C). The highest yield of H_2 was estimated to be 16 mmol/g in the presence of Ni catalyst ($240 \text{ mm}^2/\text{mg}$) from cellulose at 500°C . However, the presence of metal catalysts had a relatively low effect on CH_4 output.

Hossain et al. [47] studied the deactivation and regeneration of AC catalyst during the SCWG of oleic acid. The deposition of impurities on the catalyst surface before decarboxylation and their participation in steam reforming, causes the deactivation of AC catalyst during SCWG. To regenerate the used catalyst, it was mixed with KOH and heated to 750°C at a rate of $0.5^\circ\text{C}/\text{min}$

for 3 hours under an inert atmosphere. The KOH was then neutralized with a diluted solution of nitric acid (HNO_3) and washed with water to remove the rest of the KOH before drying for 12 hours. Regenerated and fresh AC catalysts showed the same surface properties and product selectivity. Thermal treatments with KOH are considered a low-cost and effective approach for regenerating carbonaceous catalysts.

Heterogeneous catalyst recovery and reuse during SCWG is a significant problem that requires further research and development. Catalyst recovery and reuse are crucial from both environmental and economic perspectives. Catalyst deactivation during SCWG can occur mainly due to the deposition of carbon materials in the form of small particles of char, which block the active sites of the catalyst[36]. Therefore, even after the recovery of the catalyst during SCWG, effective regeneration is required to restore the catalyst's activity.

2.3 Applications of SCWG FOR H_2 production

The use of hydrogen as an energy carrier has the potential to address the global energy crisis, climate change, and pollution caused by the combustion of fossil fuels[38]. However, the sustainable production of hydrogen remains a major barrier to the broader implementation of this energy carrier. Supercritical water gasification is a potential method for efficiently converting various types of biomass, waste and fossil fuels into hydrogen-rich gas using water in a supercritical state. The major application of SCWG is the production of hydrogen gas through the gasification of waste biomass and organics[36]. In this section, we highlight some of the applications of SCWG for hydrogen production.

- ✓ **Biomass gasification:** Biomass gasification using Supercritical Water Gasification (SCWG) is a promising technology for generating hydrogen from various feedstocks. This process is particularly suitable for high-moisture feedstocks, such as agricultural residues and sewage sludge, which are difficult to gasify using traditional methods. With SCWG, wet biomass or organic waste can be efficiently converted into methane-rich or hydrogen-rich gaseous products without the need for prior drying. Methane-rich products are produced at relatively lower temperatures below 500°C , while hydrogen-rich products are generated at higher temperatures above 600°C [48].

- ✓ **Waste-to-energy/Waste-to-chemicals:** SCWG can also be used to transform waste materials, such as plastics and municipal solid waste, into hydrogen gas. This technology can help to reduce the environmental impact of waste disposal while producing a valuable source of renewable energy. Waste material such as plastic from packaging is nowadays one of the major environmental concerns due to its short usage time, low biodegradability in nature, strong resistance to ageing, and the big volume occupied by its relatively low bulk density [49]. The environmental impacts of plastic packaging are very alarming and concern air and water pollution. In recent years, there has been a greater awareness of waste management and its disposal in landfills. Several approaches were then studied, such as reuse to date, recycling, circular economy, and energy recovery. Recycling is a crucial path, as it offers a solution to the environmental and ecological damages associated with the consumption of fossil fuels, the CO₂ emissions, and the huge amounts of waste that require disposal. There are four distinct types of recycling: primary recycling, also known as re-extrusion, secondary recycling, which involves mechanical recycling and waste-to-materials processes, tertiary recycling, also referred to as Waste-to-energy/Waste-to-chemicals, and quaternary recycling, or energy recovery. Tertiary recycling, specifically Waste-to-energy/Waste-to-chemicals, involves the chemical or physical conversion of plastic waste into monomers, polymers, or other compounds [49]. Chemical recycling involves depolymerization of the polymers through chemical reactions, with resulting monomers being used for new polymerization reactions, regeneration of the original polymers, or production of other chemical products. Physical methods refer to the thermal decomposition of polymers, which can be conducted in the absence of oxygen through pyrolysis or in the presence of gasifying agents such as steam, oxygen, or air through gasification. Pyrolysis produces gas, oil, and char, while gasification produces mainly syngas as its primary product.
- ✓ **Fossil fuels:** Hydrogen can also be produced by gasifying fossil fuels such as coal and oil in supercritical water, a process that has the potential to be more efficient and environmentally friendly than traditional fossil fuel extraction and processing methods. In a recent review by Chen et al. [50], the process of coal supercritical water gasification (SCWG) was explored, revealing that it can occur through both heterogeneous (coal particles reacting with SCW) and homogeneous (dissolved coal molecules reacting with

SCW) pathways. The reaction temperature was found to be the most important factor for SCWG, with complete gasification of coal possible without catalysts at 900°C. Increasing the reaction time was found to increase H₂ yield and gasification efficiency, but it also led to the production of a lot of chars, which can plug the reactor. However, oxidation can be added to reduce char production. Figure 5 describes the pathway of coal conversion in SCW.

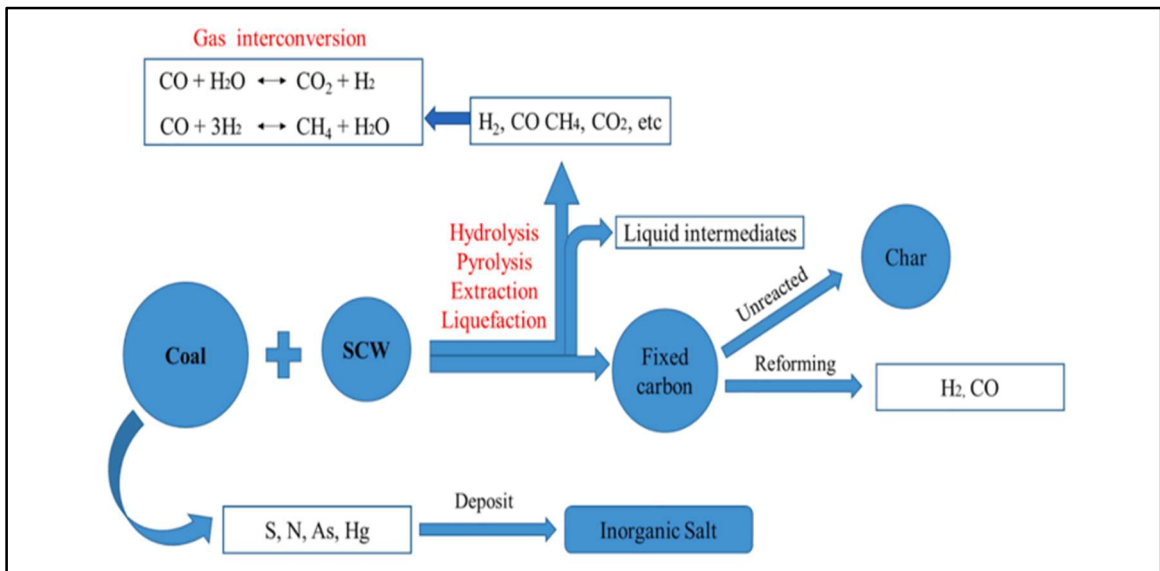


Figure 6. Coal conversion route in SCW [50]

- ✓ **Power generation:** SCWG technology offers the potential to produce hydrogen gas from various sources that can be used as a fuel for power generation. This technology can be a promising option as it has the potential to be more efficient and environmentally friendly than traditional fossil fuel-based power generation methods. Additionally, a wide range of chemicals can be obtained from biomass conversion, which is a value-added form of its use for power generation. However, utilizing available biomass resources for power generation requires addressing the challenges posed by their high moisture content and

low energy density in their as-received form, as well as ensuring their feasibility as clean and environmentally friendly energy sources [51]. Before introducing SCWG technology of biomass in the commercial stand for power generation, it is essential to resolve the issues related to the supply and availability of biomass in sufficient quantities.

we can conclude that supercritical water gasification (SCWG) is a promising technology for hydrogen production. It has the potential to reduce the environmental impact of energy generation and provide a valuable source of renewable energy. Furthermore, biomass, which has a relatively high heating value and is widely available, is a particularly promising feedstock for SCWG. Overall, the use of SCWG technology for hydrogen production holds significant promise and could play a crucial role in meeting the growing demand for clean and sustainable energy.

2.4 Challenges of H₂ production from waste, solutions and future prospective

Hydrogen is a valuable energy carrier, but it cannot be found in nature and must be synthesised from various renewable and non-renewable sources. Different methods are used to convert these sources of energy into hydrogen gas, such as electrolysis, gasification, hydrothermal liquefaction, SCWG, and Steam Methane Reforming (SMR). Unfortunately, the majority of hydrogen is produced from non-renewable sources such as oil, coal, and natural gas, leading to significant greenhouse gas emissions.

To overcome this issue, sophisticated technologies have been developed to convert renewable sources of energy such as solar, wind, and biomass into clean fuels. Moreover, to achieve a successful energy conversion, emission reduction, and development of the circular economy in the Supercritical Water Gasification (SCWG) process, the adoption of renewable energy is a promising option for the future. Thus, the conversion of biomass and organic solid waste to hydrogen gas is perceived as very promising. The development of supercritical water gasification (SCWG) technology has shown great potential for producing hydrogen gas from renewable sources. However, this technology is still under research and development, and there are many challenges, including technical and economic, that need to be addressed. The main barriers include reactor plugging, catalyst deactivation, and corrosion. The deposition of salt is a major problem causing catalyst deactivation and plugging in the SCWG process. However, this problem can be reduced by increasing the heating rate by mixing biomass with high-temperature preheated

water at the entrance of the reactor[29]. Several other solutions have been proposed to mitigate the plugging issue caused by char formation during the SCWG process. One such solution is the use of a fluidized bed reactor, which has been reported as an effective way to address this problem. However, this solution comes with high energy requirements, high operating costs, and a complex design, which are major obstacles to its adoption. Another solution is the continuous stirred tank reactor, which is an integrated technology of autoclave and tubular reactors that has been used successfully in the gasification of biomass and shown to reduce plugging issues[35]. Additionally, phenol and bimetallic catalysts have been proposed as a means to reduce char formation. Separating salts before the reactor or separating solids in a vertical reactor are other possible solutions to mitigate plugging issues by removing the inorganic salt deposition during the SCWG process.

Catalyst deactivation can be avoided by using catalyst support materials such as alumina, silica, activated carbon and magnesium and bimetallic catalysts (e.g., ruthenium (Ru) and cobalt (Co)). Corrosion can be avoided by selecting reactor materials that are resistant to corrosion (such as stainless steel and Nickel alloys) and maintaining high temperatures for instance at 600 °C or more[29]. In addition to the challenges previously mentioned, corrosion can also be caused by certain components in the biomass. For example, when a material contains both alkaline and sulphide, dealloying can occur, which is a process that selectively removes one of the metals in an alloy, leaving behind a porous structure. Then the Salt fouling can also lead to under-deposit corrosion[29]. To address these challenges, further high-quality environmental and techno-economic studies are necessary to improve the operational parameters and upgrade the SCWG processes. Breakthrough in material engineering is also essential for all SCWG technologies, including the materials used for the reactor, catalyst, oxygen carrier, and other apparatuses.

SCWG technology faces challenges in terms of competitiveness and complexity, which hinder its large-scale commercialization. Compared with other hydrogen production methods, it is not competitive. Additionally, SCWG experiments are expensive, time-consuming, and complex, making manual problem-solving difficult due to human error and time constraints. These challenges are addressed using Aspen Plus, a process modelling tool that solves critical engineering and operational problems, such as creating the process design, troubleshooting a unit operation and assessing overall process performance. Aspen Plus offers a comprehensive

database of property methods and physicochemical properties that can be used to design and observe an integrated and complex process system. That is why in this thesis, the main objectives are to use Aspen Plus to optimize the H₂ yield of peanut shell gasification in supercritical water and to study the economic viability of the optimized process. By addressing these challenges, the competitiveness of SCWG technology can be enhanced, leading to its large-scale commercialization.

3 Materials and Methodology

3.1 Biomass

Peanut shell is chosen as a typical real biomass substrate, which is a promising candidate for the SCWG (supercritical water gasification) process. Peanut is grown in large quantities every year in Senegal, particularly in the Senegalese groundnut basin. The proximate analysis and ultimate analysis values of the real biomass used to run the simulation are shown in Table 1.

Table 1. Ultimate and proximate analysis of peanut shell

biomass	Ultimate analysis (wt%)				Proximate analysis (wt%)				
	C	H	N	S	O	M	Ash	VM	FC
Peanut shell	43.80	4.92	1.52	0.17	34.10	7.99	7.50	65.85	18.66

Reference: Jin et al.[52]

3.2 Catalyst

$\text{Ca}(\text{OH})_2$ is used as a typical homogeneous catalyst. Homogeneous catalysts can be easily mixed with biomass materials and contribute to the efficient operation of the SCWG system.

The basic ideas behind selecting $\text{Ca}(\text{OH})_2$ as a catalyst are its ability to absorb carbon dioxide (CO_2) and its potential to integrate the water-gas shift reaction in a single reactor.

Furthermore, $\text{Ca}(\text{OH})_2$ acts as an alkaline catalyst and is used to further enhance syngas production. It plays a crucial role in affecting the steam reforming reaction, the conversion of water-to-gas, the partial oxidation of methane, and the water-gas shift reaction.

3.3 Kinetic models analysis

3.3.1 kinetics modeling

One of the objectives of this study is to design a simple process for producing H_2 from peanut shells using the SCWG process. The theoretical values derived from the kinetic modelling will be compared with other models. This will help us to assess the extent to which these values deviate from those of other models, particularly in terms of H_2 yield.

The process flow is intentionally designed to be as simple as possible so that it can be easily modified in the future and allow the process to be scaled up. In addition, the process is designed to be self-sustainable and energy-efficient.

Given that SCWG involves a series of complex reactions with the formation of several intermediates, the kinetic modelling method was chosen. This method is the most appropriate option for simulating process parameters such as temperature, pressure and the effects of the catalyst used to optimize the process.

A kinetic model, which is a model describing the rates and mechanisms of chemical equations, requires equations for each of the elementary steps involved in converting biomass into the desired product(s). Currently, there is no formulation available in the open literature concerning the kinetic simulation (modelling) of the catalyst with the elementary steps under supercritical conditions. This study is an effort to present the effect of catalytic gasification of biomass under supercritical conditions.

Kinetic models are based on the determination of the kinetic constants $k(T)$ of the chemical reactions employed for modelling thermochemical conversion processes such as the SCWG of biomass.

An analytical technique known as thermogravimetric (TG) analysis is used to calculate these kinetic constants. This technique is used to evaluate the Arrhenius kinetic parameters[53]. The Arrhenius kinetic parameters are the activation energy (E_a) and the pre-exponential factor (A). These parameters are crucial for determining the kinetic constant of the rate of a chemical reaction using the Arrhenius mathematical expression:

$$k(T) = A * \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

Where R is the universal constant for ideal gases and T is the absolute temperature.

Thermogravimetric (TG) analysis determines the loss of mass caused by volatilization, as a function of temperature or time.

The first derivative of the thermogravimetric curve, known as the DTG (derivative thermogravimetry), is used to calculate the maximum reaction rate and to select the appropriate temperature/conversion ranges for calculating the kinetic parameters[53]. These kinetic parameters are crucial and must be inserted as input data into the kinetic models.

In particular, non-isothermal methods are very reliable for assessing kinetic parameters. These methods are based on multiple heating rates. Non-isothermal methods include iso-conversional methods. In iso-conversional methods, the degree of conversion is assumed to be constant, so the reaction rate depends exclusively on the reaction temperature[53].

The kinetic model parameters found in online literature articles were adjusted to find the best values to fit the simulation results to the experimental data in the existing literature.

A continuous stirred tank reactor (CSTR) kinetic model that assumes perfect mixing of Homogeneous phases (vapor or liquid) was used. Thus, the composition and temperature are assumed to be uniform throughout the reactor volume and equal to the composition and temperature of the reactor effluent. In the CSTR model, the reactions were assumed to take place under isothermal conditions. In this reactor, the reaction kinetics were specified and, in the current modelling, a Power-Law (PL) rate model for peanut shells conversion in SCW was used to model the rate behavior.

The kinetic modelling was carried out using Aspen Plus *V14* software (AspenTech, Bedford, USA). Aspen Plus, which stands for Advanced System for Process Engineering, is a widely used commercial chemical process simulation software. It is renowned for its ability to simulate, model and optimise chemical processes and plants. Aspen Plus is a steady-state program with an integrated set of databases, including the physical properties database, the components database and the reaction kinetics database. These databases are essential for kinetic and thermodynamic calculations. In Aspen Plus, it is possible to develop a flowsheet using unit operation blocks, allowing each component present in the reaction to be specified, along with the kinetic data for each equation.

A general Power-Law (PL) representation is given as follows:

$$r_k = kT^n \exp - \left(\frac{E_a}{RT} \right) \prod_{i=1}^N C_i^{\alpha_i} \quad r_j = \nu_j * r_k \quad (2)$$

Where ν_j is the stoichiometric coefficient of component j , R is the universal constant C_i is the concentration of component i (*unit in Aspen plus* : molarity ($Kmol/m^3$); mole fraction; mass fraction; partial pressure (P_a); mass concentration (Kg/m^3), k is the pre-exponential factor, α_i is the order of reaction concerning component i , E_a is the activation energy unit in Aspen Plus ($KJ/kmol$; J/mol etc.), N is the number of components, and T is the reaction temperature (*unit in*

Aspen Plus: Kelvin), r_j is the rate of production of component j (unit in Aspen Plus: $\text{Kmol}/\text{m}^3 \cdot \text{s}$ or $\text{Kmol}/\text{Kg cat. s}$).

On the other hand, thermodynamic equilibrium model analysis is faster, more cost-effective and can be used to determine the optimum experimental operating conditions with high accuracy.

Furthermore, thermodynamic equilibrium is also crucial in energy evaluations as well as in determining whether a particular chemical process is sustainable from an energy point of view.

There are two approaches to thermodynamic modelling: the stoichiometric approach, which requires the identification of the different reactions taking place in the process, and the non-stoichiometric approach, which does not[54].

In the literature, there are also examples of modeling of the biomass thermochemical conversion processes that used both approaches at the same time, an equilibrium approach and a kinetic approach for different zones of the reactor[53].

3.4 Aspen Plus ® process description

In the Aspen Plus program, there is no readymade model relating to SCWG of biomass. That is why it is fundamental to simulate the entire process flow into different unit operations. The flowsheet of the SCWG process design developed using Aspen Plus is shown in Figure 5. As mentioned above, the process flow is kept as simple as possible to make provisions for modification and scale-up in the future.

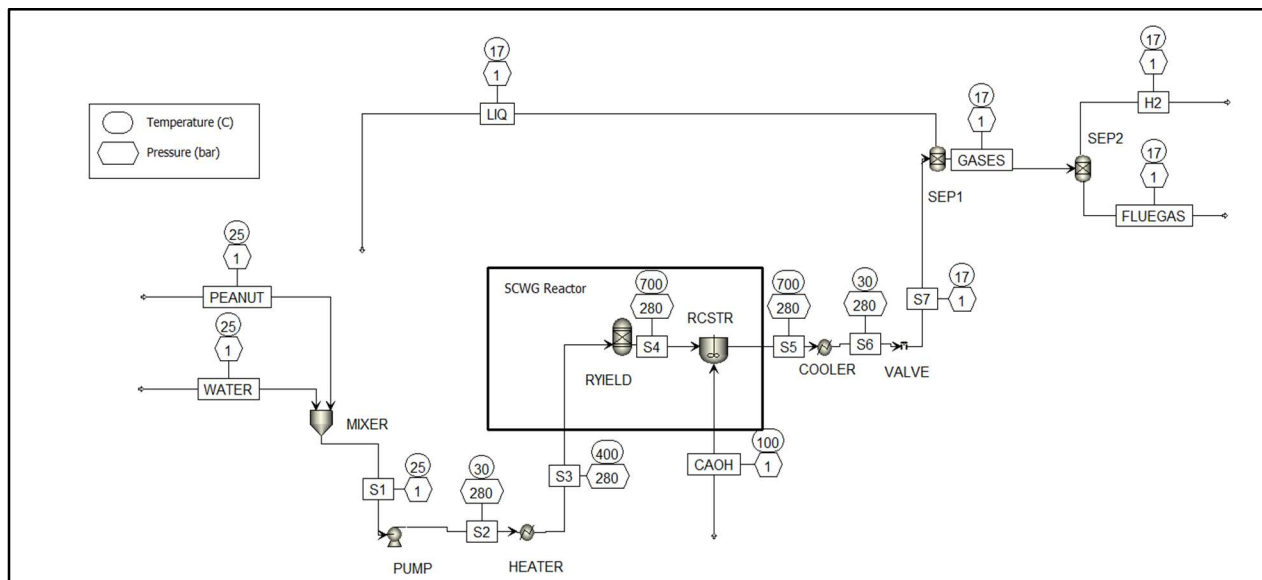


Figure 7. Aspen Plus ® flowsheet simulation of the SCWG model.

To provide a better understanding of the process, a description of the blocks included in the flowsheet, their block IDs, as well as their operating conditions, will be presented. The process type was chosen as COMMON, which allocated a generic industry type to the simulation, in contrast to chemical, petrochemical, pharmaceutical, refinery etc. The RYield and RCSTR blocks are used to simulate the Supercritical water gasification reactor as shown in Figure 5. It is worth noting that the reactor was kept at constant pressure (280 bar) and temperature (700 °C) during the entire process.

The components used in the Aspen Plus Program include: water (H₂O), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), biomass (peanut shell), oxygen (O₂), hydrogen (H₂), sulfur (S), nitrogen (N₂), ash, calcium hydroxide (Ca(OH)₂), calcium Formate ((HCOO)₂Ca), calcium hydrogen carbonate also called calcium bicarbonate (Ca(HCO₃)₂) and calcium carbonate (CaCO₃). The compounds H₂, H₂O, CO, O₂, CH₄, N₂, S, C, Ca(OH)₂, CaCO₃ and ((HCOO)₂Ca) were defined as conventional components, which have their thermophysical data stored in Aspen Plus ® databanks. As a result, no data input was required for these components. Ca(HCO₃)₂ was defined as a pseudo-component as this component is not available in the Aspen Plus ® databanks. Therefore, it requires data input such as its average Normal Boiling Point (NBP) (above 50 °C), density ($2.711 \cdot 10^6 \text{ g/m}^3$) and molecular weight (162.11 g/mol).

In the simulation, the Biomass and ash were defined as non-conventional components. Aspen Plus defines lignocellulosic biomass as a non-conventional stream containing heterogeneous solid components. Additionally, biomass does not have a defined molecular weight. For Aspen Plus ® to incorporate such a stream, the RYield block is used to degrade the biomass into the gaseous components (CO, CO₂, H₂ and CH₄), ash and residue (solid carbon). The non-conventional components are modelled by their ultimate and proximate analyses, specifically in ULTANAL, PROXANAL and SULFANAL models.

The ratio of biomass-to-water in the process is selected as 1:4. Therefore, the input consists of two flows: peanut, representing the biomass (100 kg/h) and water (400 kg/h) at standard conditions, i.e., 25 °C and 1 bar. A mixer (25 °C, 1 bar) is used to mix water with the biomass. The mixed solution is then pressurized from 1 bar to 280 bar using a pump (PUMP). A heat exchanger (HEATER) is used to heat the flow to 400 °C and then supply it to the RYield reactor

where the biomass is volatilized into the gas components (CO, CO₂, H₂, CH₄), H₂O and ash. The residue is considered as solid carbon.

A calculator block is included in the Ryield block for determining the composition of the products leaving the reactor. Furthermore, the yield distribution is estimated using an Excel sheet and then inputted into the Aspen Plus ® for modeling the SCW (supercritical water) gasifier.

The flow from the yield reactor is directed into a Continuous Stirred Tank Reactor (CSTR) where the SCW gasification and catalytic reactions take place.

Table 2 and Table 3 summarize the input and operating conditions of all feed streams and block units, together with their descriptions:

Table 2. Feed stream input conditions

Feed Stream	component	Temperature (°C)	Pressure (bar)	Flowrate (kg/h)
Water	H ₂ O (conventional)	25	1	400
Peanut	Biomass (non-conventional)	25	1	100
CA(OH)	Ca(OH) ₂ (conventional)	100	1	5

Table 3. Description of the Block units and their operating conditions

Block Information		Operating conditions		Description
Default ID in Aspen Plus	Assigned unit Operations for Block ID in the flowsheet	Temperature (°C)	Pressure (Bar)	Unit operation description
Mixer	MIXER	25	1	Mixes water with the biomass.
Pump	PUMP	30	280	Pressurizer: increases the pressure of the mixed solution stream from the Mixer from 1 to 280 bar.
Heater	HEATER	400	280	Heats the mixed solution stream coming from the pump from 30 °C to 400 °C.
RYield	RYIELD	700	280	It facilitates the thermal decomposition of biomass into gaseous components (CO, CO ₂ , H ₂ and CH ₄), as well as H ₂ O and Ash. The remaining residue is considered as solid carbon. A calculator block is used to determine the composition of the products exiting the reactor. This type of reactor is employed when the reaction stoichiometry is unknown or irrelevant, the reactions kinetics are unknown or unimportant but the yield distribution is known. additionally, the product yield distribution is estimated using an Excel sheet.

RCSTR	RCSTR	700	280	The Aspen plus CSTR reactor, RCSTR performs the SCWG and catalytic reactions by using reaction kinetics. RCSTR assumes perfect mixing in the reactor, meaning that the reactor contents have the same properties and composition as the outlet stream. RCSTR manages kinetic and equilibrium reactions as well as reactions involving solids.
cooler	COOLER	30	280	Reduces the temperature of the hot gases leaving the CSTR reactor from 700 °C to 30 °C and removes any moisture present.
valve	VALVE	30	1	Pressure reducer: reduces pressure of the incoming cold gas leaving the cooler from 280 bar to 1 bar.
Sep1	SEPARAT OR	30	1	It separates liquid H ₂ O from the gaseous components (CO, O ₂ , CO ₂ , H ₂ , CH ₄), along with ash, unconverted carbon (C) and intermediates formed during catalytic reactions (CaCO ₃ , (HCOO) ₂ Ca and Ca(HCO ₃) ₂).
Sep2	SEPARAT OR	30	1	It separates H ₂ gas from the components present in flue gas, including CO, O ₂ , CO ₂ , CH ₄ , ash, unconverted carbon (C) and intermediates formed during catalytic reactions such as CaCO ₃ , (HCOO) ₂ Ca and Ca(HCO ₃) ₂ .

The resulting stream (S5) leaving the RCSTR was Syngas, ash, unconverted carbon (C) and intermediates formed during catalytic reactions, which passed through the heat exchanger (COOLER) for cooling to ambient temperature, after which the pressure is reduced to atmospheric pressure in an expansion valve (VALVE). The gas-liquid separator (SEP1) is used to separate the liquid H₂O (LIQ) from the gaseous products, ash, unconverted carbon (C) and catalytic reaction intermediates (GASES). Another separator (SEP2) helps to separate the hydrogen gas (H₂) from the flue gas and residues (FLUEGAS).

For optimum efficiency, both the heat exchangers (HEATER and COOLER) are interconnected, in the process flow system. There is no depiction or visual representation of a connection in the system for additional cooling or heating fluid from an external source. The HEATER uses the heat recovered from the hot gases at the COOLER to preheat the mixed solution stream that goes to the RYIELD reactor. The liquid H₂O (LIQ) from Sep1 is being recycled and reused in the MIXER, for sustainable reasons. In this unit, the amount of water recovered was 16.7354 *kg/h*, which means an amount of 383.2646 *Kg/h* is consumed during the process. This excess of water (LIQ) recovered from the separator (SEP1) is recirculated into the process to reduce the water consumption.

The Peng-Robinson with Boston-Mathias function (PR-BM) property method was considered in this study for the kinetic modelling. Most importantly, (PR-BM) provides good accuracy for gasification simulations[55] and is the most appropriate for high-temperature gasification processes[56].

HCOALGEN and DCOALIGT models were selected to determine the enthalpy and density, respectively, of non-conventional components such as biomass and ash. HCOALGEN incorporates various correlations for calculating heat capacity, heat of combustion and heat of formation. The heat of formation is derived from the heat of formation of the products and the heat of combustion of the biomass. HCOALGEN uses a proximate and ultimate composition of the biomass, along with different correlations available in the Aspen Plus ® program, to determine the heat of combustion[56]. On the other hand, the DCOALIGT model is based on the IGT (Institute of Gas Technology) correlation and requires ULTANAL. As mentioned earlier, ash is considered a non-conventional component, and its proximate and ultimate analysis are defined as 100%.

The property packages used in the kinetic model are summarized in Table 4.

Table 4. Property packages used in this simulation

Attributes	specifications
Fluid-dynamic package	Peng-Robinson with Boston-Mathias function (PR-BM)
Stream class	MIXCINC
Enthalpy mode	HCOALGEN
Density mode	DCOALIGT
Biomass	Specified using its proximate and ultimate analysis

The main assumptions considered in this simulation were as follows:

1. The ash produced from the biomass was inert and assumed not to react with any other component.
2. The process was in a steady-state;
3. The pressure was uniform inside the reactor;
4. The reactor was operating isothermally,
5. Tar formation was not considered;
6. Arrhenius kinetics were considered for each reaction;
7. No heat and pressure losses occurred in the reactor;
8. NH_3 AND H_2S were not considered;
9. All gaseous compounds have ideal gas behavior;
10. Biomass particle size effects were negligible;
11. Unconverted solid carbon was present in the products.

3.5 Kinetic data collection

The data used to carry out the kinetic modelling was obtained from articles published in the literature. It should be noted that the kinetic model parameters used in this simulation were adjusted to find the best values fitting the simulation results with experimental data.

The SCWG and catalytic chemical reactions and their respective kinetic parameters considered in the SCWG model are shown in Table 5.

Table 5. Kinetic parameters of the main chemical reactions considered in the SCWG model.

Reaction	K	E_a (KJ/kmol)
Partial oxidation of CH ₄ : $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$	$2.4 \cdot 10^8$	126000
Water gas: $C + H_2O \rightarrow CO + H_2$	200	49900
Steam reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$	300000	125000
Boudouard: $C + CO_2 \rightarrow 2CO$	178000	180000
Water-gas shift: $CO + H_2O \rightarrow CO_2 + H_2$	2.78	12600
$Ca(OH)_2 + 2CO \rightarrow (HCOO)_2Ca$	124	15000
$(HCOO)_2Ca + 2H_2O \rightarrow Ca(HCO_3)_2 + 2H_2$	1204	150000
$Ca(HCO_3)_2 \rightarrow CO_2 + CaCO_3 + H_2O$	1250	125933

Reference: Puig-Gamero et al.[56]

3.6 Sensitivity Analysis

One of the most important and useful features of the Aspen Plus process simulator is its ability to manipulate and analyse the various design parameters to find the required value or investigate their impact on the process. Furthermore, conversion and yield calculations of the process might sometimes be important even though the results are not included in the simulation output. It is typically essential to optimize a process according to specific criteria, which is another important feature. Features such as sensitivity analysis and optimisation are available in Aspen Plus under the **Flowsheeting Options** and **Model Analysis Tools**. These functionalities can be utilized to evaluate and optimize the process output by altering the input variables.

consequently, a sensitivity analysis is conducted on the RCSTR block unit, where the SCWG and catalytic reactions occur (Table 5). The analysis aims to investigate the relative influence of various process parameters, including temperature, pressure, residence time and the presence of Ca(OH)₂ catalyst, on the composition of syngas, with a primary focus on evaluating their effects on the yield of hydrogen (H₂).

The range of operating conditions are chosen between the lower and upper limits used by researchers. In the existing literature, the highest temperature recorded to date is 800 °C, and the highest pressure is 680 bar in an autoclave reactor.

To study the effect of temperature on syngas yield, the temperature of the RCSTR was defined as a block variable in 24-point increments, ranging from 300 to 1000 °C, while the other variables such as the pressure and the residence time remained unchanged at 280 bar and 1 hr, respectively.

The selected temperature range aligns with the research conducted by Tushar et al.[26]. To investigate the impact of pressure on the composition of syngas yield, the pressure was specified as a block variable in 5-point increments from 220 bar to 350 bar. At the same time, the operating temperature was maintained at 700 °C and the residence time at 1 hr.

To allow a better insight into the required catalyst loading of the RCSTR, the catalyst was implemented as a block variable, varying from 0 to 25 Kg, with a 36-point increment, while keeping the operating temperature and pressure constant at 700 °C and 280 bar, respectively.

Finally, the product distribution curves concerning different process parameters obtained from the sensitivity analysis will be plotted and discussed in the following chapter (Chapter 4).

3.7 Economic analysis

The Economic Analysis (EA) study is used to evaluate the economic feasibility of the process and to determine metrics such as the levelized cost of hydrogen (LCOH), Return on Investment (ROI), Net Present Value (NPV), and Internal Rate of Return (IRR). Economic feasibility is a crucial factor in determining the viability of any technology for practical applications. Unlike previous analyses on SCWG processes, this study's target product is hydrogen. The analysis consists of determining the levelized cost of hydrogen (LCOH) of the optimized SCWG process, which should be competitive in the market. The two essential parameters for calculating the levelized cost of hydrogen (LCOH) in the optimized process are Capital expenditure (CAPEX) and Operational Expenditure (OPEX).

The plant has a processing capacity of 2400 kg/day of peanut shells and is assumed to run 7800 hours per year, with the remaining time allocated to maintenance. In other words, the plant is designed to process approximately 780,000 kg of peanut shells per year. For the economic analysis, the operating conditions are set as follows: temperature of 750 °C, pressure of 22 bar, biomass-to-water ratio of 1:4, and residence time of 1 hour.

Table 6. summarizes the assumptions made during the economic analysis of the model.

Parameters	Assumptions
Hydrogen production plant capacity	2400 kg/day of peanut shells
Design period	1 year
Construction period	2 years
Plant start-up time	3 months
Operation time	7800 h/year
Plant lifespan	20 years
Depreciation period of the plant	10 years
Depreciation method	Straight line
Contractors' fees	3% of the total module cost
contingencies	7% of the total module cost
Land cost	2% of fixed capital investment
Working capital	5% of fixed capital investment
Auxiliary facilities	30% of Equipment Purchasing Cost (PC)
Interest rate	8%
Operating labour costs	\$ 20,000/year per operator, a total of 7 operators are required.
Direct supervisory and clerical labour cost	10% of the operating labour cost
Maintenance and repair costs	5% of fixed capital investment
Operating supplies	10% of maintenance and repair cost
Laboratory charges	10% operating labour cost
Plant-overhead	50% operating labour, supervision, and maintenance costs
Administrative costs	30% of plant-overhead costs
Electricity cost	\$ 0.172/kWh
Water cost	\$ 0.02/kg

References: Gebremariam and Marchetti [57], Salkuyeh et al.[58]; Okolie [54]

3.7.1 CAPEX

Total capital investment refers to the overall cost associated with the plant construction. It is calculated by summing the fixed capital investment (FCI), land cost (LC), and working capital investment (WCI) (equation 3)[54]. Total capital investment includes direct plant costs (equipment purchasing cost, installation, electrical systems, instrumentation, and control), indirect plant costs (such as engineering and construction expenses), working capital, contractors' fees, and contingency[57]. The direct cost encompasses all expenses directly related to the plant installation, whereas the indirect cost includes expenses that are not directly related to the installation.

$$TCI = FCI + LC + WCI \quad (3)$$

The contractor's fees and contingencies are estimated to be 3% and 7% of the total module cost, respectively. Additionally, working capital cost and land cost (LC) are assumed to be 5% and 2% of the fixed capital investment (FCI), respectively[54]. Based on the process flow diagram shown in Figure 5, the equipment cost has been estimated. FCI includes the cost of purchasing the equipment as well as any additional expenses involved in the construction of the plant. The equipment purchase cost, also known as the bar module cost (BMC), includes all direct and indirect costs associated with the purchase and installation of equipment[59]. Some expenditures related to indirect fixed capital investment were also evaluated. It is important to note that the BMC is estimated using available data from the literature[54]. Furthermore, the auxiliary facility fees are estimated to represent 30% of the BMC in this analysis[60].

3.7.2 OPEX

The literature and current market prices from different suppliers have been used as the main sources of cost estimation for operating costs. Operating cost is further divided into fixed operating cost and variable operating cost. The fixed operating cost comprises of:

- labor cost,
- operating supplies,
- overhead cost,

- maintenance and repair costs,
- supervision and other fixed costs.

The fixed operating cost is estimated as a percentage of the FCI using the assumptions suggested by Salkuyeh et al.[58] and Okolie [54]. The variable cost comprises raw materials cost and utilities. Raw materials include peanut shells, process water, and catalysts, while the utilities include the cost per kWh of cooling water and electricity. The cost of raw materials is evaluated by multiplying the specified annual feed rate of each raw material by its price per kg. The utility cost is associated with the annual energy consumption, which includes electricity and process water for heating and cooling purposes. The utilities were calculated by taking into account the energy price per unit of each piece of equipment.

The operating labour cost is calculated by multiplying the number of operators per shift by their hourly salary and the total operating hours per year. The SCWG plant has a processing capacity of 780,000 kg/year of peanut shells and is assumed to require 7 operators to manage its operation. The average annual salary of operators is assumed to be \$ 20,000/year per operator. It is important to note that the number of operators is evaluated based on the information provided by Okolie [54].

The overall yearly production cost calculated in this thesis takes into account the fixed and variable operating costs, as well as the bare module cost, and the remainder of the investment cost is related to additional expenses.

3.7.3 Economic assessment and profitability index

The economic evaluation is performed to determine the fixed capital investment, total capital investment, and operating expenditure. Furthermore, the estimated operating and capital costs can be used, with additional financial assumptions, to 1) calculate the Levelized Cost of Hydrogen (LCOH) and 2) carry out a discounted cash flow (DCF) analysis. Key financial inputs include assumptions on plant financing, such as the interest rate.

The purpose of optimizing the process is to make it commercially competitive. The DCF analysis uses projected expenses and revenues together with the discount rate and plant lifetime to estimate a net present value (NPV), return on investment (ROI), and internal rate of return

(IRR) for the SCWG project. It is an approach for evaluating the financial value of the project, considering the time value of money[61]. In this scenario, the “project” refers to the investment in constructing and starting a new production plant for hydrogen, as well as the estimated profits based on projected future sales throughout the overall lifetime.

The DCF estimates the NPV given a specific lifetime period and discount rate. Most importantly the NPV can be used to calculate the ROI, IRR and the payback period. NPV estimates the profit of the project for a particular period, taking into account the time value of money. It indicates the sum of the present values of all cash flows, which includes the initial investment. NPV can be calculated by considering the total sum of the current cash flow in a particular year over the total number of years[54]. Therefore, NPV must be positive to consider the project profitable. The equation for the NPV is:

$$NPV = \sum_{n=1}^{20} \frac{\text{cash flows}}{(1+i)^n} - \text{initial investment} \quad (4)$$

$$\text{initial investment} = TCI + OPEX \quad (5)$$

$$ROI(\%) = \frac{NPV}{\text{initial investment}} * 100 \quad (6)$$

The capital recovery factor (CRF) is a ratio that is used to compute Annualised CAPEX (ACAPEX). ACAPEX is obtained by multiplying the value of the TCI with CRF. The equation for the capital recovery factor is:

$$CRF(i, n) = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (7)$$

where i is the interest rate (%) and n is the lifetime of the project (number of years)

$$\text{Annualized CAPEX} = \text{ACAPEX} = CRF * \text{CAPEX} \quad (8)$$

it is worth mentioning that to evaluate the profitability criteria for the SCWG of biomass, it is advised that the project lifetime should be more than 15 years but not too long. This is mainly due to the harsh operating conditions of the SCWG process[59]. Therefore, the project lifetime is set at 20 years, and the interest rate is set at 8%.

The levelized cost of hydrogen (LCOH) is defined as the average cost/kg of hydrogen produced by the SCWG plant. Therefore, this cost should be competitive in the market. The levelized cost is calculated by dividing the total annual cost by the yearly hydrogen (H₂) yield in kg, as shown in equations [62] (8) and (9).

$$LCOH(\$ /kg) = \frac{ACAPEX+OPE}{\text{average annual H2 yield in kg}} \quad (9)$$

The PP refers to the time it takes to pay off the initial investment with incomes generated from the start of the project.

$$PP = \frac{\text{initial investment}}{\text{annual cash flow}} \quad (10)$$

IRR is defined as the annual rate of growth an investment is expected to generate. IRR is estimated using the same concept as NPV, except it sets the NPV equal to zero[61].

These indicators are crucial in assessing the economic viability of the SCWG process with a capacity of 780,000 kg/year of peanut shells for hydrogen production.

4 Results and Discussion

4.1 Model validation

Model validation is the process of confirming whether the model accurately represents the system's behaviour and achieves its intended purpose. After calibrating the kinetic model with experimental results, the simulation model was evaluated and validated by using experimental data from Jin et al.

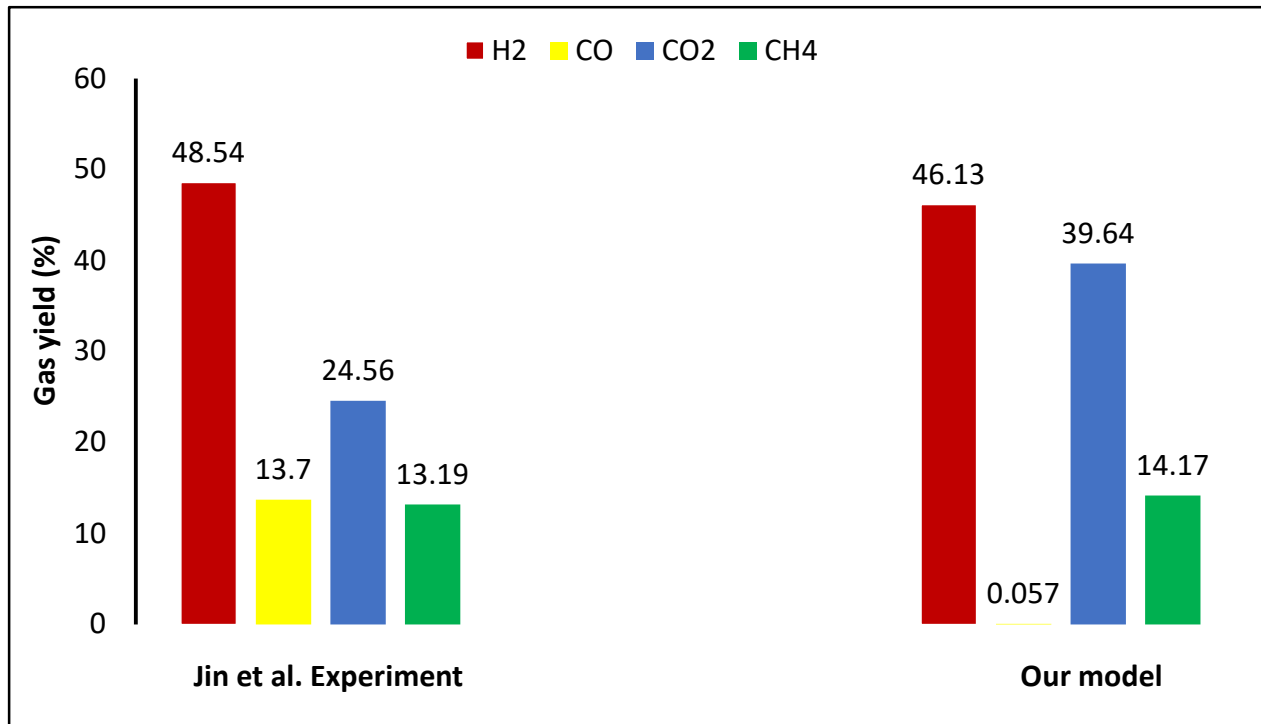


Figure 6. Experimental Results vs. Model Prediction for Hydrogen Production from Peanut Shell Gasification under Supercritical Water Conditions with $\text{Ca}(\text{OH})_2$ Catalyst [52].

In Jin's experiment, Peanut shell was used as typical real biomass to study the catalytic gasification result of biomass in supercritical water. The gasification process was carried out in a 140 mL, 316 L stainless-steel, high-pressure autoclave at a temperature of 400 °C, pressure ranging from 220 to 240 bar, and a residence time of 20 minutes. $\text{Ca}(\text{OH})_2$ was one of the various homogeneous and heterogeneous catalysts selected during the study. Most importantly, the ultimate and proximate analyses obtained from Jin's experiment were used to run this simulation. It is worth noting that in the simulation, the initial temperature and pressure of the reactor were

set at 700 °C and 280 bar, respectively. However, to ensure a more accurate comparison, a temperature closely matching the experimental setup, which was 400 °C, was chosen. During the sensitivity analysis, the temperature range was varied from 300 to 1000 °C, and the average temperature between 396.55 °C and 420.62 °C was calculated. The objective was to find the most suitable for comparison with the experimental temperature of 400 °C. The resulting average temperature was determined to be 408.62 °C. The same methodology was applied to obtain the values of CO, CO₂, CH₄ and H₂ at this temperature. The comparison between the experimental investigation and the simulation study of the composition of syngas produced from the gasification of peanut shells under supercritical water conditions at 400 °C is summarized in Figure 6.

The difference in the composition of the produced syngas (Experimental data and Model Predictions) is used to evaluate the extent to which the Aspen Plus findings deviate from the literature values.

It is observed that the model predicted H₂, CH₄ with higher accuracy compared to CO and CO₂. These variations can be attributed to the water-gas shift and Ca(OH)₂ catalytic reactions since they were considered the more influential reactions. Ca(OH)₂ was used to absorb CO₂ and to integrate water-gas shift reaction and CO₂ absorption in a single reactor. moreover, it can be seen that the presence of Ca(OH)₂ catalyst increases the yield of H₂ while enhancing carbon gasification efficiency. Indeed, the basic catalyst has a catalytic effect on the water-gas shift reaction[52]. On the other hand, the variations could also be attributed to either adjusting the kinetic parameter values of the reactions (Table 5) to improve the model prediction accuracy or considering the presence of O₂ in the model.

For the H₂, and CH₄ yield, the difference between the experimental data and Model predictions is found to be around ± 2%. Therefore, it can be concluded that a comparable product syngas composition has been demonstrated through the comparison of the simulated results and the literature values.

4.2 Effect of supercritical water gasification process parameters

To gain a deeper understanding of the effects of process parameters, a sensitivity analysis was conducted to investigate the impact of temperature, pressure, residence time and Ca(OH)₂

catalyst on the yield of syngas and hydrogen produced during gasification of peanut shells under supercritical water conditions.

4.2.1 Effect of temperature on syngas (H₂, CO₂, CO, CH₄) yield

Figure 7 shows the effect of temperature on the amounts of produced syngas obtained from the supercritical water gasification of peanut shell. The temperature range investigated was from 300 °C to 1000 °C, while maintaining a pressure of 280 bar. As depicted in Figure 7, the amounts of H₂ and CO increased while the CH₄ yield decreased as the temperature was increased from 300 °C to 1000 °C. In contrast, the yield of CO₂ exhibited a significant increase with temperature from 300 °C to 950 °C. However, beyond 950 °C, the sensitivity analysis results revealed a slight reduction in CO₂ yield, indicating a decrease starting at 951 °C.

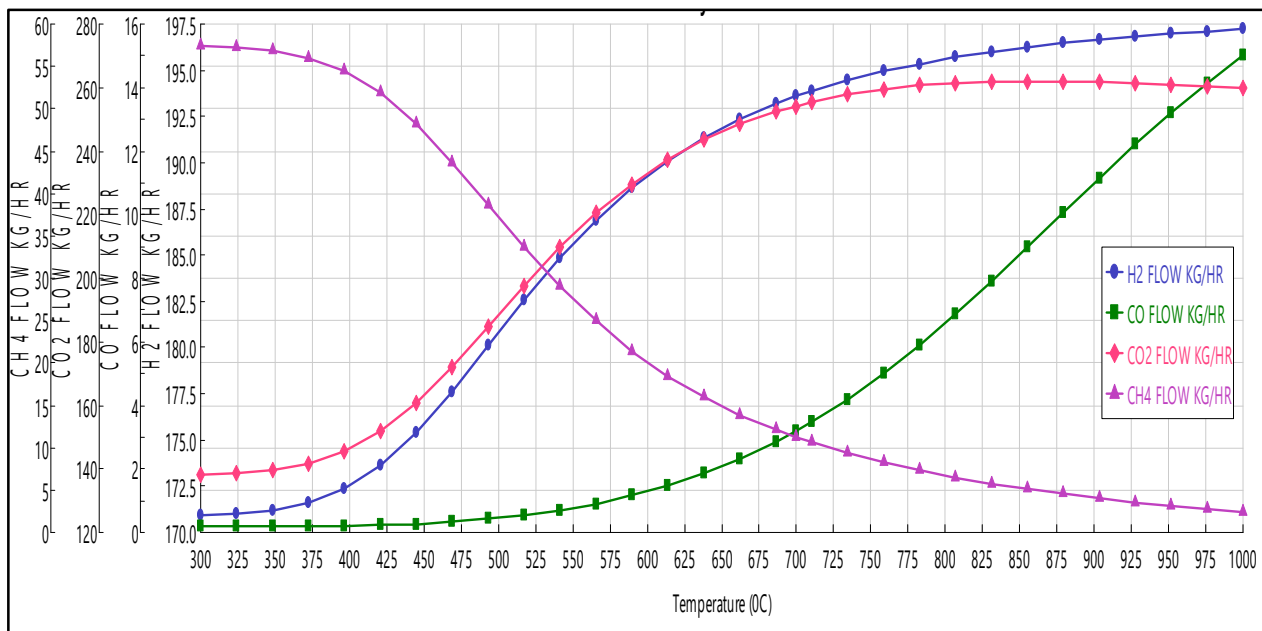


Figure 7. Effect of temperature on syngas yield produced during the catalytic gasification of peanut shell in supercritical water ($T=300 \sim 1000$ °C, $P=280$ bar, residence time = 1 hour).

Temperature plays a crucial role in the catalytic gasification of biomass in SCW. Higher temperatures maximize the gasification efficiency and increase the yield of H₂ [35]. Some of the chemical reactions that occur inside the reactor are endothermic, such as the water-gas, Boudouard, and steam reforming reactions, while the water-gas shift reaction is exothermic. As a

result, the operating temperature would have a complex effect on the final composition of the product[18]. According to Le Chatelier's theory, higher temperatures favour the formation of products in endothermic reactions.

During the catalytic gasification process of biomass in supercritical water, the production of gaseous products is primarily attributed to key reactions such as steam reforming, water-gas shift, and catalytic reactions. Additionally, the presence of a $\text{Ca}(\text{OH})_2$ catalyst enhances the water-gas shift reaction through its catalytic effect.

The increase in H_2 and CO yield is a result of endothermic reactions namely the water-gas, steam reforming, and Boudouard reactions. The Water-gas shift reaction is exothermic usually favoured at low temperature, while the steam reforming reaction is endothermic that promotes the production of hydrogen at higher temperatures.

At $400\text{ }^\circ\text{C}$, the observed low H_2 yield can be primarily attributed to the water-gas shift reaction. However, as the temperature was increased from $300\text{ }^\circ\text{C}$ to $1000\text{ }^\circ\text{C}$, the H_2 yield increased significantly due to the steam reforming reaction, which is favoured at higher temperatures.

Furthermore, an inverse relationship was observed between the temperature and the yields of CO_2 and CH_4 , indicating a decrease as temperature increases. The decrease of CO_2 is attributed to an exothermic water-gas shift reaction that is favoured at low temperatures.

Similarly, the decline in CH_4 production could be a result of two chemical reactions: steam reforming and partial oxidation of methane. These reactions, typically favoured at higher temperatures, are likely responsible for the decrease in CH_4 amount. According to Ramzan et al.[63], higher temperatures are associated with increased CO production and decreased CO_2 production. A previous study conducted by Faraji and Saidi [18] reported that higher temperatures favour the production of H_2 and CO , whereas lower temperatures favour CH_4 and CO_2 production. Several SCWG studies have investigated the effect of increasing the temperature from subcritical to supercritical conditions on the yield of hydrogen. Raising the temperature from $300\text{ }^\circ\text{C}$ (subcritical) to $550\text{ }^\circ\text{C}$ (supercritical) in a gasification study of pinecone, the hydrogen yield improved from 0.02 to 0.8 mol/Kg biomass at 210-230 bar and 25 wt% for a half-hour reaction time [24]. A significant increase in hydrogen yields was observed from 0.7 to 13.8 mol/Kg biomass with the change in temperature from $300\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$ for the SCWG of nickel-impregnated sugarcane bagasse at 1:8 biomass-to-water ratio and 230-250 bar for 50 min reaction time [64].

As shown in Figure 7, increasing the reactor temperature from 300 °C to 1000 °C increased the H₂ and CO yield from 170.894 to 197.22 kg/h and 0.190 to 15.022 kg/h, respectively, while reducing the CH₄ yield from 57.358 to 2.329 kg/h.

however, the sensitivity analysis revealed that raising the temperature from 800 °C to 1000 °C did not significantly improve hydrogen production yield. The observed increase in hydrogen yield from 800 °C to 1000 °C is only 1.523 kg/h. consequently, increasing the operating temperature beyond 800 °C to generate additional hydrogen is not economically viable.

4.2.2 Effect of pressure on the syngas (H₂, CO₂, CO, CH₄) yield

A limited number of studies have investigated the influence of pressure on hydrogen yield in SCWG using real biomass feedstock, either through experiments or simulations. The influence of pressure on the catalytic gasification of biomass under supercritical conditions is quite complex. Pressure tends to be constant during the process while altering variables such as temperature, residence time, catalyst loading and feed concentration. Pressure has a direct effect on the process efficiency. SCW, when used as a medium for the reaction, tends to impede the progress of the reaction. However, raising the pressure in the gasifier to higher levels enhances the SCWG process by accelerating some specific reactions. High pressures have a restraining effect on reactions involving solutes like coking and polymerization, while simultaneously favouring reactions involving solute and solvent molecules such as reforming and water-gas shift reactions [65].

Figure 8 displays the influence of pressure on the yield of syngas generated during the catalytic gasification of peanut shells under supercritical water conditions. The pressure range investigated varied from 220 bar to 350 bar, while the temperature remained constant at 700 °C.

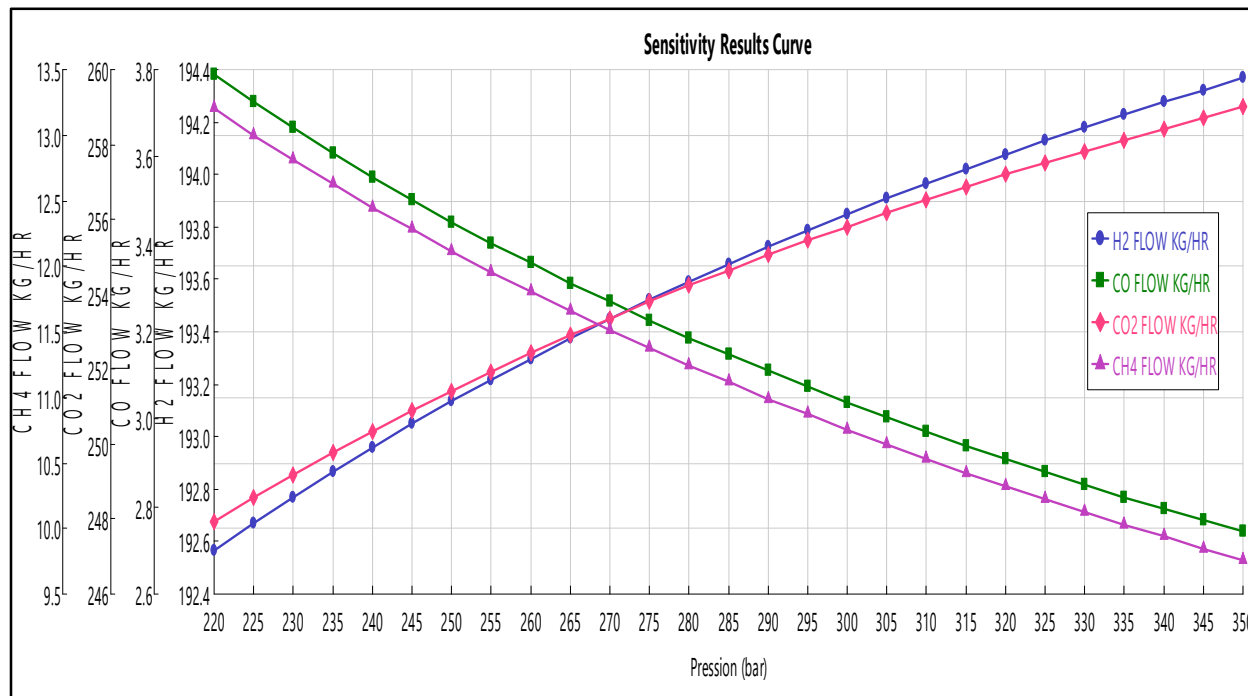


Figure 8. Effect of pressure on syngas yield produced during the catalytic gasification of peanut shell in supercritical water ($T=700\text{ }^{\circ}\text{C}$, $P=220\sim 350$ bar, residence time = 1 hour).

With increasing reactor pressure, the yields of CO_2 and H_2 increased, while the yields of CH_4 and CO decreased. The moderate increase in H_2 and CO_2 yield, as well as the slight decrease in CO yield, can be ascribed to the exothermic water-gas shift reaction and the catalytic effect of $\text{Ca}(\text{OH})_2$ on it. The decrease in the amount of CH_4 at higher pressure can be explained by its consumption as a reactant in the endothermic steam reforming reaction.

As the gasifier pressure was raised from 220 bar to 350 bar, the amounts of H_2 and CO_2 increased from 192.564 to 194.368 kg/h and 247.928 to 258.992 kg/h respectively. Conversely, the amounts of CO and CH_4 decreased from 3.787 to 2.741 kg/h and 13.202 to 9.759 kg/h, respectively. Consequently, modifications in the system pressure have no significant effect on the yield of syngas, especially on the formation of H_2 in the system.

Higher pressure enhances the operational efficiency of the process in terms of energy and exergy. Additionally, downstream operations often require gas with elevated pressure. However, the widespread commercial adoption of biomass-pressured reactors is hindered by the complexities associated with their high-pressure operations, construction, and management [18]. It is important

to note that the special physical and chemical properties of SCW are only present above the critical point. When the process pressure falls below this critical point, these unique properties disappear, potentially inhibiting the production of hydrogen.

The continuous SCWG of wood sawdust demonstrated an increase in H₂ yields from 15.2 to 17 mol/kg biomass when the pressure was raised from 170 to 300 bar. Simultaneously, there was a corresponding decrease in CH₄ and CO yields at a temperature of 650 °C [66]. The investigation carried out by researchers from the University of Twente on the effects of pressure (50-450 bar) on SCWG of glucose and glycerol revealed that the pressure had minimal impact on the yield of product gases within the studied pressure range [35]. A previous review conducted by Lee et al.[66] on the SCWG of real biomass reported an increase in H₂ yields obtained from cotton coconut shell, from 5.9 wt% to 12.6 wt%, when the pressure was increased from 230 to 480 bar. The process conditions, including a temperature of 477 °C, a feed concentration of 10 wt%, and a residence time of 1 hour, were kept constant. Tushar et al.[26], studied the effect of pressure on the yield of product gas. They performed simulations of SCWG for H₂ production using two types of model biomass: glucose and a mixture of phenol and HMF (hydroxymethyl furfural). The simulations were conducted using the Aspen Plus ® software. The pressure range investigated was 200 to 500 bar, while the temperature and biomass concentration were maintained at 700 °C and 5 wt%, respectively. The results of their simulations indicated that varying the reactor pressure did not have a significant effect on the SCWG of biomass, regardless of whether glucose or the mixture of phenol and HMF was used. Most reports suggest that increasing the pressure has a positive influence on hydrogen yield, although the effect is often not significant. Furthermore, challenges related to capital and operating expenditures (CAPEX and OPEX) arise when designing a system for safe operation at higher pressures. As a result, it is common practice to maintain the operating pressure below 300 bar for an SCWG process to balance the effects of pressure on hydrogen yield and operating costs [26].

4.2.3 Effect of Ca(OH)₂ catalyst on the H₂ yield

The use of catalyst has an undeniable importance in the efficient production of hydrogen during SCWG. Moreover, SCWG reactions have high activation energies. In this study, Ca(OH)₂ catalyst was chosen as the typical homogeneous catalyst due to its ability to integrate water-gas shift and CO₂ absorption in a single reactor. Figure 9 illustrates the influence of Ca(OH)₂ catalyst on hydrogen yield during gasification of peanut shell under supercritical water conditions. The operating conditions were fixed at 700 °C, 280 bar and 1 hour. Catalyst loadings ranging from 0 to 25 kg was investigated.

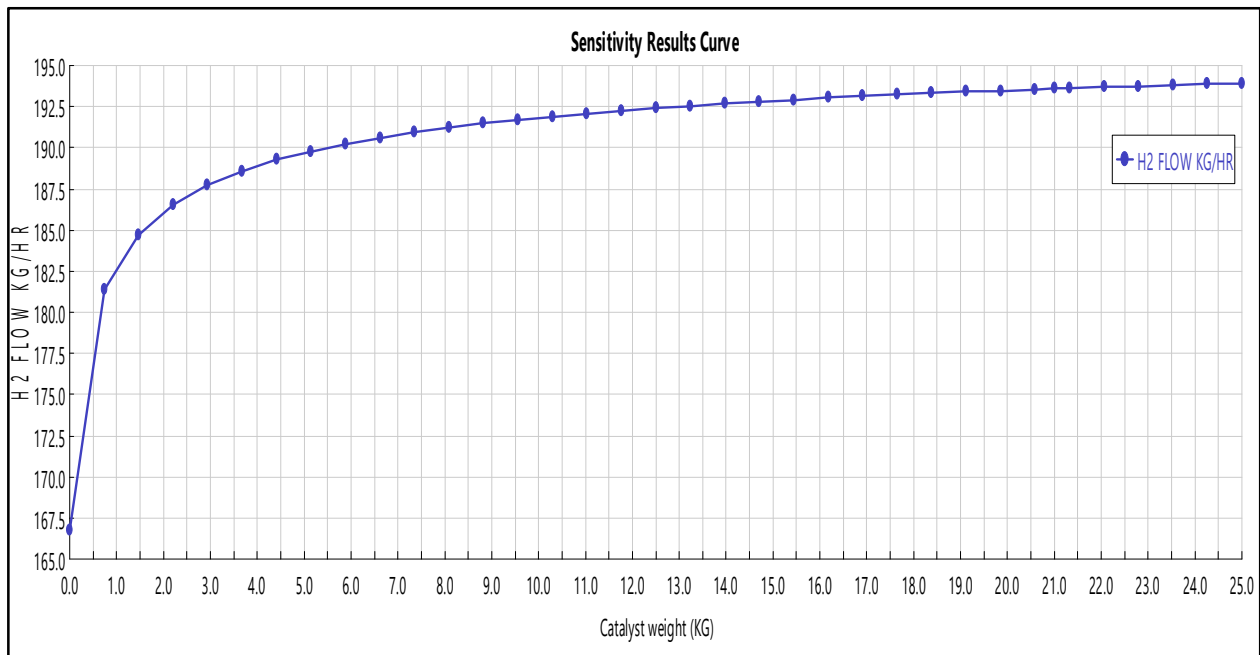


Figure 9. Effect of Ca(OH)₂ catalyst on H₂ yield produced during the catalytic gasification of peanut shell in supercritical water ($T=700\text{ }^{\circ}\text{C}$, $P=280\text{ bar}$, residence time = 1 hour).

The results demonstrate that the presence of the catalyst increased the yield of hydrogen. The amplification is 16.308 %. Without a catalyst, the yield of hydrogen was 166.738 kg/h. However, by increasing the catalyst loading from 0 to 25 kg in the CSTR reactor, the hydrogen yield improved from 166.738 to 193.931 kg/h. It is worth noting that increasing the Ca(OH)₂ loading from 5 to 25 kg has no significant effect on the hydrogen yield (from around 190 to 193.931

kg/h). The efficiency of the catalyst decreases when the catalyst loading in the reactor exceeds 5 kg, which subsequently impacts the overall process efficiency. To ensure cost-effectiveness, it is crucial to limit the catalyst loading to 5 kg or less. By reducing the amount of catalyst introduced into the reactor to 5 kg or less, both CAPEX and OPEX can be reduced.

Catalysts can decrease the reaction temperature and speed up the reaction to guarantee the technological and economic feasibility of the SCWG process[52]. Moreover, catalysts can significantly enhance the conversion of biomass at lower temperatures, thereby reducing the capital and operating costs of this process [66].

Several researchers have investigated various types of catalysts as well as the catalyst loading, process parameters, reactor configuration, and reaction environment in the context of SCWG of real biomass. The catalytic gasification of biomass in SCW has gained significant attention, and the catalysts investigated can be classified into homogeneous and heterogeneous catalysts. The purpose of using a catalyst in the process is to selectively enhance the hydrogen (H₂) gas yields, while lowering the reaction temperature. Furthermore, most of the catalysts investigated demonstrated the ability to enhance H₂ and CO₂ yields while reducing CO yields through the water-gas shift (WGS) reaction[24]. As mentioned previously, a homogeneous catalyst is simple to mix with feedstock and easy to operate for the gasification system. Alkali metal catalysts such as Ca(OH)₂, KOH, ZnCl₂, Na₂CO₃, LiOH, KHCO₃, K₂CO₃, and NaOH are common homogeneous catalysts that can promote hydrogen production by accelerating the water-gas shift (WGS) reaction[24]. The water-gas shift (WGS) reaction is accelerated by alkaline metals, leading to increased yields of H₂ and CO₂, and reduced CO production. Additionally, alkali catalysts reduce the starting reaction temperature required for cellulose degradation. They facilitate the breakage of C-C, C-O, C-H, and O-H bonds to yield a hydrogen-rich gas mixture[24]. As mentioned above, Ca(OH)₂ is used due to its ability to integrate the WGS reaction and CO₂ absorption in one reactor. In the reaction process, formic acid is assumed to be the intermediate product, which subsequently undergoes decomposition to yield H₂ and CO₂ (see the catalytic reactions). Additionally, Ca(OH)₂ absorbed the CO₂ produced during the process to form CaCO₃. However, the solubility of inorganic salt in SCW is significantly lower than the ambient condition. Additionally, the eutectic melting of inorganic salt is observed, which may cause issue in the continuous operation of the gasification system[52]. This effect may explain

the observed decrease in the efficiency of the $\text{Ca}(\text{OH})_2$ catalyst in hydrogen production when the catalyst loading in the reactor exceeds 5 kg.

According to Lin et al.[67], the formation of a eutectic mixture of calcium compounds significantly influences the behaviour of the solid material in the reactor. At a temperature of 700 °C, melted solids led to a blockage of the reactor. However, the occurrence of eutectic melting was successfully prevented at a relatively lower temperature of 650 °C. Jin et al.[52] investigated the effects of $\text{Ca}(\text{OH})_2$ catalyst on biomass gasification in SCW at a temperature of 400 °C, pressure ranging from 220 to 240 bar, and a residence time of 20 minutes. Peanut shell was selected as the typical biomass. In the absence of catalysts, the hydrogen yield was measured at 2.86 mmol/g. However, upon adding the $\text{Ca}(\text{OH})_2$ catalyst to the reactor, the hydrogen yield significantly increased from 2.86 to 6.66 mmol/g. In other words, the addition of $\text{Ca}(\text{OH})_2$ resulted in an increase in the hydrogen fraction from 21.60% to 48.54%. This value is close to the predicted percentage of hydrogen from our model at approximately 400 °C. Furthermore, their investigation revealed that among the various homogeneous catalysts tested, the catalytic effects on hydrogen fraction of biomass gasification of $\text{Ca}(\text{OH})_2$ were found to be higher than those of K_2CO_3 , KOH, NaOH, and Na_2CO_3 . However, the catalytic effects of $\text{Ca}(\text{OH})_2$ were still lower compared to LiOH.

While lowering the operating temperature is advantageous, recovering the homogeneous catalyst is difficult to achieve, therefore resulting in additional costs for the continuous addition of fresh catalyst. In addition, the liquid waste containing alkali metal catalyst generated after the SCWG is difficult to treat[66]. Because of these limitations, most researchers have turned their focus towards heterogeneous catalysts to achieve similar catalytic activity as well as high selectivity towards hydrogen production.

4.3 Hydrogen Production Optimization

Optimization of process parameters involves the selection of the optimal operating parameters that can maximize the production of the desired products and gasification efficiency during an SCWG process while minimizing the overall expenses. Generally, H_2 is the desired product from the SCWG process. Therefore, it is feasible to optimize the operating conditions in order to enhance H_2 production by combining various gasification variables such as pressure, temperature and residence time. To select the best combination of these parameters, a sensitivity analysis of

the H₂ yield generated during the catalytic gasification of peanut shell in supercritical water was used to investigate the simultaneous effect of various gasification parameters.

4.3.1 Simultaneous effect of temperature and pressure on H₂ yield

Figure 10 illustrates the combined effect of temperature and pressure on the H₂ yield generated during the catalytic gasification of peanut shells in supercritical water, with a residence time of 1 hour. Increasing the reactor temperature significantly enhances hydrogen yield, while increasing reactor pressure has a more moderate effect on increasing hydrogen yield.

The temperature range investigated varied from subcritical (300 °C) to supercritical (750 °C) in increments of 20 °C, while pressure ranged from 220 to 350 bar with a 30-point increment. The residence time was consistently set at 1 hour. Optimization results reveal that the maximum hydrogen yield of 195.355 kg/h is obtained at 750 °C and 350 bar, while the minimum yield of 170.867 kg/h is observed at 300 °C and 220 bar. Furthermore, the sensitivity analysis showed that setting the temperature to 750 °C and the pressure to 220 bar resulted in a hydrogen yield of 193.993 kg/h, which is near the maximum yield.

Moreover, operating at 750 °C, 220 bar, and 1 hour not only prevents the complexities associated with high-pressure operations and biomass-pressured reactor construction and management but also ensures high hydrogen production. However, it should be noted that operating at high temperatures and pressures necessitates higher CAPEX and OPEX costs. Considering cost-effectiveness, catalytic SCWG processes that achieve higher hydrogen yields at temperatures below 600 °C are desirable[66]. Therefore, to ensure cost-effectiveness, the process can be operated at 586 °C and 220 bar, resulting in a hydrogen production rate of 186.584 kg/h, as determined through the sensitivity analysis of the simultaneous effect of temperature and pressure. This approach allows for the reduction of both CAPEX and OPEX costs.

In a previous study conducted by Kang et al.[68], the non-catalytic SCWG of lignin was performed in a batch reactor with the specific focus on hydrogen yield optimization. The primary effects and interactions of three parameters, including temperature, pressure, and water-to-biomass ratio, were investigated using both experimental and statistical modelling across a wide range of 399-651 °C, 230-290 bar, and 3-8, respectively. Central Composite Design (CCD) methodology was used to optimize these parameters. It was found that up to 650 °C, higher

temperature is desirable for hydrogen production; however, a change of pressure from 230-290 bar did not show significant effect on hydrogen yield. According to the model, the maximum hydrogen yield of 1.60 mmol/g biomass is obtained when the reaction conditions are 651 °C, 250 bar, and water to biomass ratio of 3.9 in 50 min.

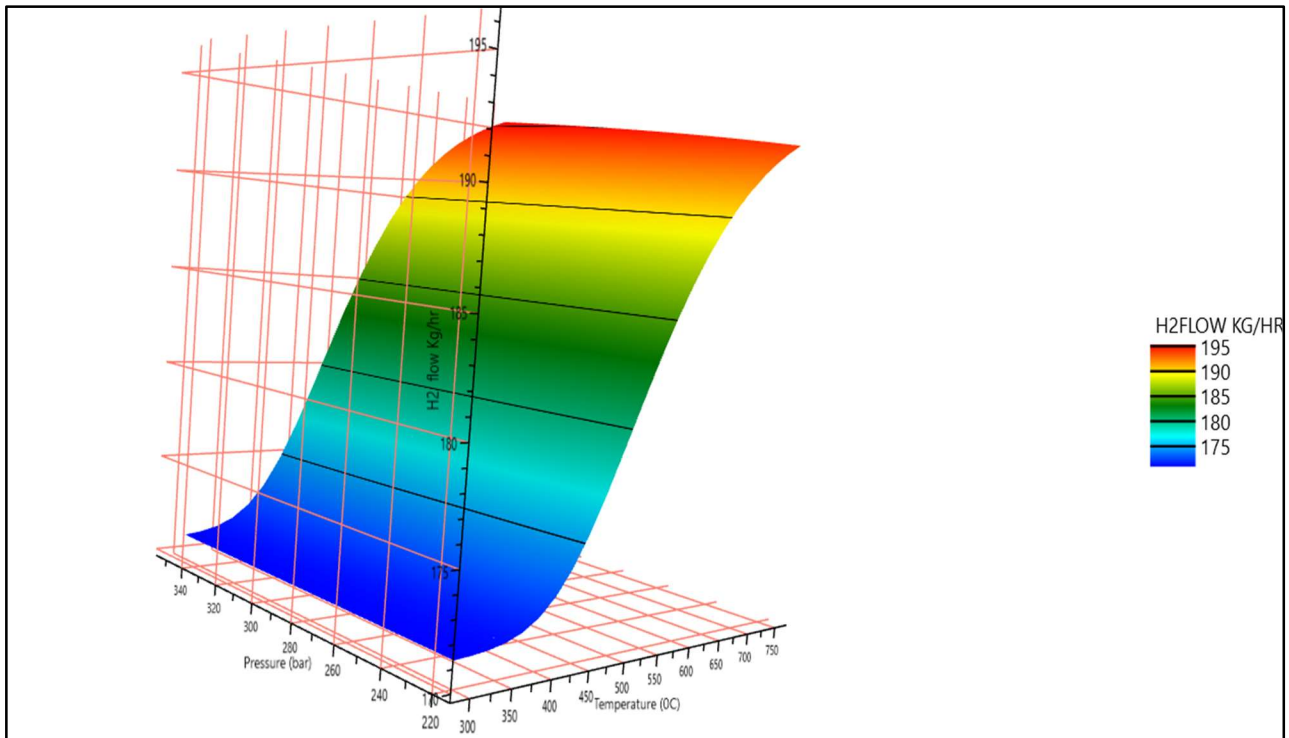


Figure 10. Simultaneous effect of temperature and pressure on H₂ yield.

4.3.2 Simultaneous effect of temperature and residence time on H₂ yield

Figure 11 illustrates the simultaneous effect of temperature and residence time on H₂ yield during the catalytic gasification of peanut shells in supercritical water at a constant pressure of 280 bar. The results show that increasing the reactor temperature leads to higher hydrogen yield, while variations in residence time have no significant influence on the hydrogen yield. Therefore, temperature is the primary factor affecting hydrogen yield. The findings reveal that, remarkably, the maximum hydrogen yield of 194.775 k/h can be achieved even at a residence time as low as 0.0625 hours, under reaction conditions of 750 °C temperature and 280 bar pressure. In contrast, the minimum yield of 170.894 kg/h is obtained at 300 °C temperature and the same residence time of 0.0625 hours. The temperature and residence time were investigated over a wide range of 300-750 °C and 0.0625-10 hours, respectively. The sensitivity analysis's results demonstrate that among the studied parameters, residence time has a lesser impact on hydrogen production. The relative importance of hydrogen production based on the investigated parameters can be classified as follows: temperature > catalyst loading > pressure > residence time.

Lu et al.[65], studied the influence of four parameters on H₂ yield during SCWG of corncob. They found that the factors affecting H₂ yield followed this order: temperature > pressure > feedstock concentration > residence time.

The limited effect of residence time on hydrogen yield could be attributed to several factors. Firstly, the reaction kinetics of hydrogen-producing reactions, such as water-gas shift, steam reforming, and catalytic reactions, may not be highly dependent on residence time. This suggests that the reaction reaches completion or equilibrium within a relatively short time, rendering further extension of residence time insignificant in influencing hydrogen yield. Secondly, the hydrogen-producing reactions may be more influenced by other process parameters, including temperature, catalyst loading, and pressure, making the residence time less influential. Finally, the design and configuration of the CSTR reactor are assumed to provide adequate mixing and sufficient reaction time, even at shorter residence times, minimizing the effect of residence time on hydrogen yield.

Interestingly, optimal conditions for achieving the highest hydrogen yield during catalytic gasification of peanut shell involve lower residence time along with higher temperature and lower pressure.

The maximum hydrogen yield was obtained when the reaction conditions were as follows: temperature = 750 °C, pressure = 350 bar, biomass-to-water = 1:4, and residence time = 1 hour.

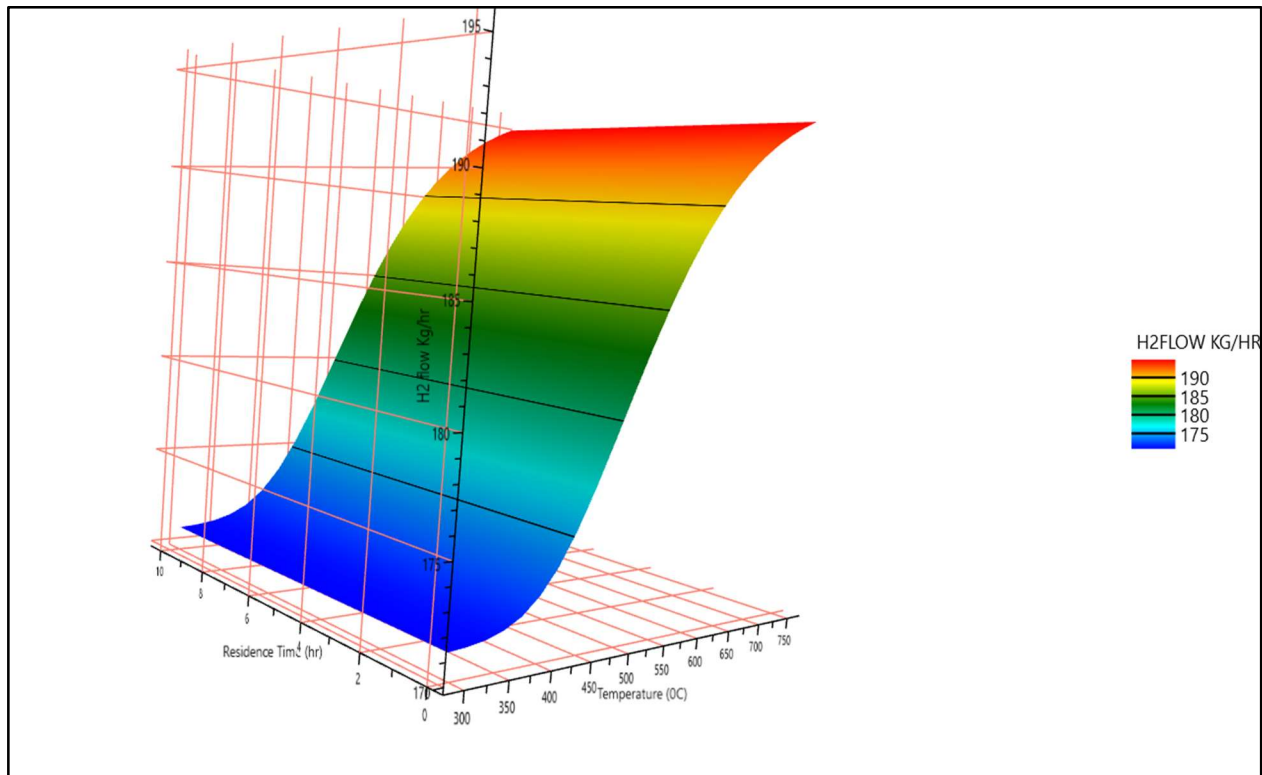


Figure 11. Simultaneous effect of temperature and residence time on H₂ yield.

4.4 Estimation of fixed capital investment

The fixed capital investment (FCI) associated with the procurement and installation of various equipment is presented in Table 7. As mentioned earlier, the FCI was evaluated based on data from the literature[54]. The gross root cost is calculated as the sum of the total module and auxiliary facilities costs, as shown in Table 7. To ensure the smooth and continuous operation of the plant, we opted for two SCWG reactors. As a result, the total gross root capital cost is twice as high as the cost of each process unit. Besides, the total module cost is estimated as the sum of the bare module cost (BMC), contingency and contractors fees[54]. The FCI obtained during the SCWG of peanut shells is reported as \$ 8.828 million based on the data from Table 7.

The dominant costs of the FCI are attributed to the gas-liquid separator (34.887%), heat exchanger (heater) (21.294%), Pressure Swing Adsorption (19.029%), and SCWG reactor (16.763%). conversely, the pump, mixer, cooler and valve represent 5.437%, 1.359%, 0.680% and 0.55% of FCI, respectively. These cost distributions agree well with most of the results of similar studies involving various processing capacities, catalysts and feedstocks[54], [60], [69].

Moreover, the heat exchangers are necessary for heat recovery and efficient heat integration in the process, which makes them relatively expensive. The yield product comprises a mixture of solid unconverted carbon (char), water, and hot syngas, and therefore requires a gas-liquid separator. As the SCWG reactions take place at temperatures and pressures above the critical point of water, it is crucial to choose a reactor material that can endure extreme conditions while being more resistant to corrosion[54]. This results in an expensive SCWG reactor such as the Inconel reactor, which is more expensive than stainless steel. Inconel reactor provides better corrosion resistance and offers the advantage of inhibiting the repolymerization reaction, which reduces tar and char formation while boosting hydrogen yields[54]. The process also uses pressure swing adsorption (PSA) for hydrogen gas recovery from the syngas mixture. The FCI added to the LC (land cost) and the WCI (working capital investment) gives the TCI, which is estimated at \$ 9.446 million.

Table 7. Estimation of the fixed capital investment

Process unit	Total module cost (\$ million)	Auxiliary facilities cost (\$ million)	Grass root capital cost (\$ million)	Total Grass root capital cost (\$ million)
Mixer	0.05	0.01	0.06	0.12
Pump	0.19	0.05	0.24	0.48
Heater	0.75	0.19	0.94	1.88
SCWG reactor	0.59	0.15	0.74	1.48
Cooler	0.02	0.01	0.03	0.06
Valve	0.0163	0.008	0.0243	0.0486
liquid-gas separator	1.23	0.31	1.54	3.08
Pressure swing adsorption (H ₂ separation)	0.67	0.17	0.84	1.68
Total	3.516	0.898	4.414	8.828

Reference: Okolie [54].

The percentage of equipment cost involved in the fixed capital investment (FCI) is broken down in Figure 12.

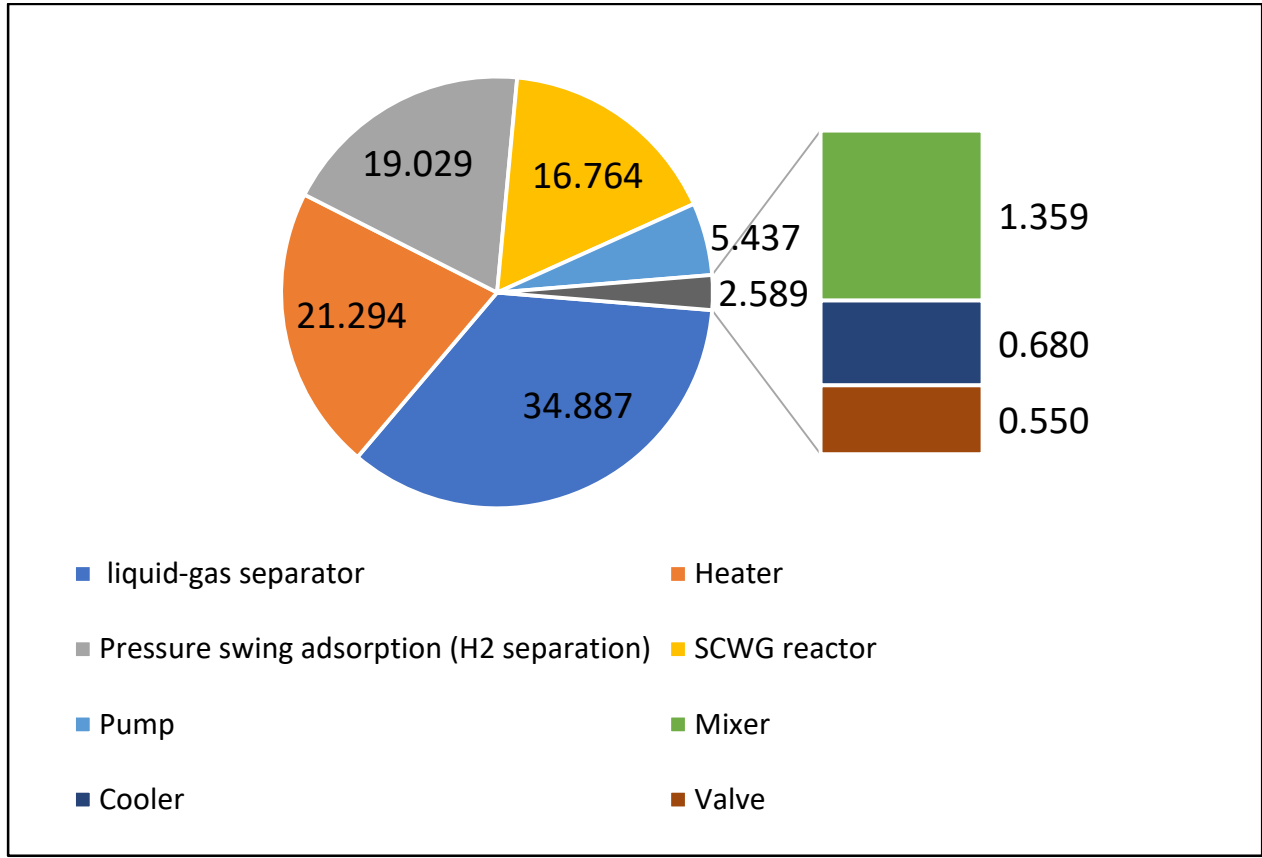


Figure 12. Percentage distribution of equipment costs involved in the Fixed Capital Investment (FCI).

4.5 Estimation of operating costs

Table 8 presents the operational expenditure of the optimized SCWG plant, including fixed and variable operating costs. The fixed operating cost is independent of the production rate. As a result, it is calculated as a fraction of the FCI. In contrast, the variable operating cost, which includes raw materials and utility costs, is evaluated using the production rate. Additionally, the variable operating cost includes the cost of electricity consumption for the heat exchanger, pump, mixer, and other utilities used. This cost is dependent on the additional cost of electricity consumption per hour during operation.

Based on the results in Table 8, the total operational expenditure for processing 780,000 kg/year of peanut shells for hydrogen production is projected to be \$ 1,003,201.44 . This cost includes fixed and variable operating costs, which amount to \$ 698,494.25 and \$ 304,707.19, respectively.

A significant portion of the plant's total operating cost is allocated to maintenance and reparation (22.001%), plant overhead (18.676%), operating labour and supervision (15.351%), raw materials (15.322%), and utility costs 15.052%. Furthermore, operating supplies, combined with laboratory charges and administrative costs, account for 9.198%, while the additional expenses represent 4.400% of the total operating cost.

The raw materials cost includes the cost of feedstock (peanut shells), process water, and catalysts (Ca(OH)₂) as well as their transport and storage costs.

Table 8. Summary of operating cost calculations for optimum hydrogen production using the process model (capacity: 780,000 kg per year of peanut shells).

Cost category	Per unit cost in \$	Total cost (\$)
Raw material		
Peanut shells (1)	\$ 0.077/kg	\$ 60,185.19
Catalyst (2)	\$ 0.798/kg	\$ 31,122.00
Water (3)	\$ 0.02/kg	\$ 62,400.00
Total material cost (4)	(4) = (1) + (2) +(3)	\$ 153,707.19
utilities		
Electricity (5)	\$ 0.172/kWh	\$ 150,000.00
Cooling water (6)	\$ 0.0011/kWh	\$ 1,000.00
Total utilities cost (7)	(7) = (5) + (6)	\$ 151,000.00
Variable operating cost (8)	(8) = (7) + (4)	\$ 304,707.19
Labor cost (9)	\$ 20,000/year per operator, a total of 7 operators required.	\$ 140,000.00
Direct supervisory and clerical labour cost (10)	(10) = 10% of operating labour cost	\$ 14,000.00
Maintenance and repair costs (11)	(11) = 5% of fixed capital investment	\$ 220,715.00

Operating supplies (12)	(12) = 10% of maintenance and repair cost	\$ 22,071.50
Laboratory charges (13)	(13) = 10% operating labour cost	\$ 14,000.00
Plant-overhead (14)	50% operating labour, supervision, and maintenance costs	\$ 187,357.50
Administrative costs (15)	30% plant-overhead costs	\$ 56,207.25
Additional expenses (e.g., marketing, logistics, operations services, etc) (16)	(16) = 1% of fixed capital investment	\$ 44,143.00
Fixed operating cost (17)	(17) = (9 + 10 + 11 + 12 + 13 + 14 + 15 + 16)	\$ 698,494.25
Total operating cost (18)	(18) = (8) + (17)	\$ 1,003,201.44

References: Okolie [54]; Gebremariam and Marchetti [57]; Salkuyeh [58]

A breakdown of the percentage of the fixed and variable operating costs included in the total operating cost is shown in Figure 13.

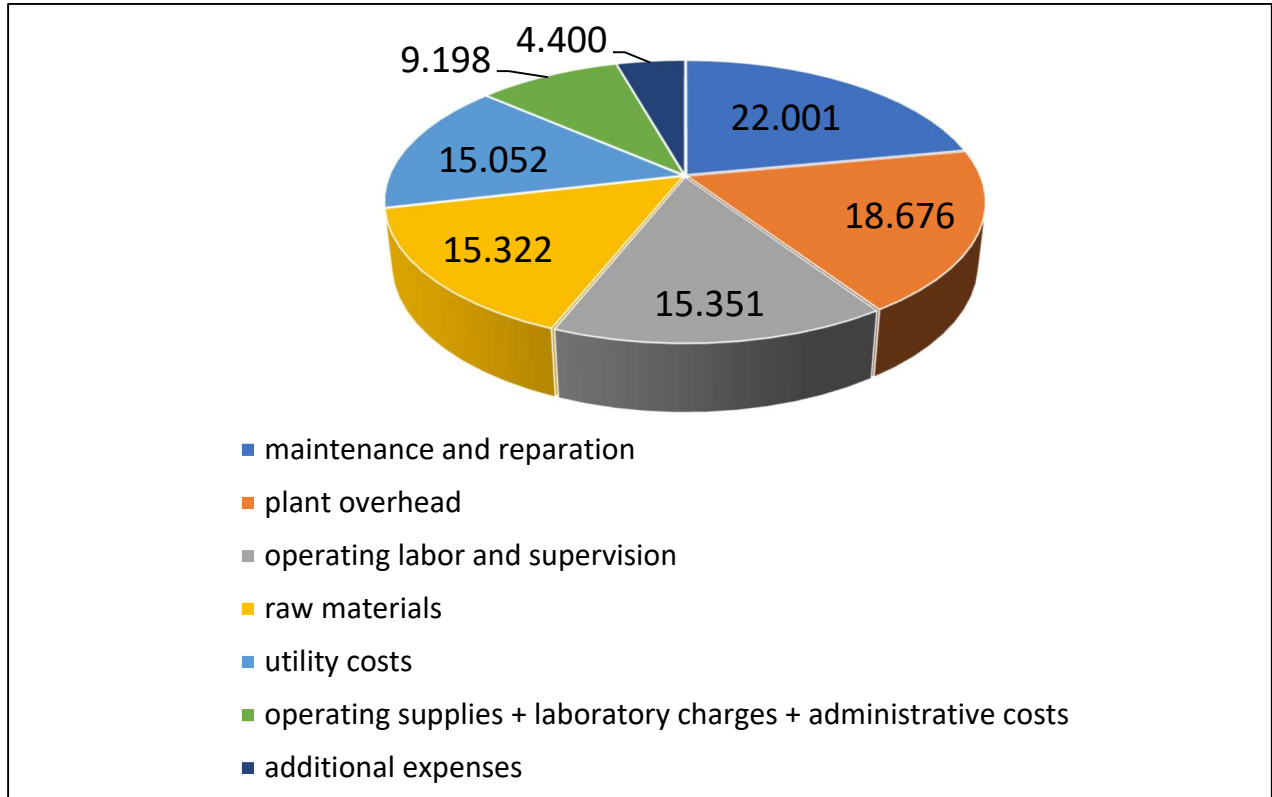


Figure 13. Percentage distribution of the fixed and variable operating costs included in the total operating cost.

4.6 Estimation of the total annual revenue

Table 9 presents the estimation of the total annual revenue, including the annual income from hydrogen and hydrochar. The calculation of the Levelized Cost of Hydrogen (LCOH) is based on Equations (8) and (9), considering annualized CAPEX, OPEX, and the plant's annual hydrogen yield. The LCOH is reported to be \$ 1.30/kg, representing the unit hydrogen production cost.

The key calculations are as follows:

- $CRF = 0.101$
- $ACAPEX = 0.101 * \$ 9,446,602 = \$ 962,157.28$
- $Annual\ Hydrogen\ yield = 1,513,145.4\ kg/year$
- $LCOH = \frac{(962,157.28 + 1,003,201.44)}{1,513,145.4} = \$ 1.30/kg$

Thus, the estimated annual revenue from hydrogen production amounts to \$ 2,269,718.10, while the income from hydrochar reaches \$ 536.71 . Combining these figures, the total annual revenue of the SCWG is \$ 2,270,254.81.

Table 9. *Estimated total annual costs for revenue generation.*

Unit H ₂ production cost (1)		\$ 1.5/kg
Hydrogen production rate (2)	(2) = 193.993 x 24	4,655.832 kg/day
Annual revenue from H ₂ (3)	(3) = (1) x (2) x 325 days	\$ 2,269,718.10
Hydrochar cost (4)		\$ 0.117/kg
Production rate of hydrochar (5)		14.114 kg/day
Annual revenue from Hydrochar (6)	(6) = (4) x (5) x 325 days	\$ 536.71
Total annual revenue (7)	(7) = (3) + (6)	\$ 2,270,254.81

4.7 Discounted Cash Flow and Profitability analyses

To ascertain the economic viability of the SCWG plant, the NPV, IRR, PP and ROI have been calculated. Return on investment is an important indicator of the profitability of a process, ROI of 113.30% indicates that the SCWG plant with a processing capacity of 2,400 kg/day of peanut shells for hydrogen production is highly profitable for the venture capital market. Right after the building of the facility and the start of hydrogen production, the income gained from sales and investments are recovered at an IRR of 12%. Similarly, the payback period (PP) is the duration in which the total capital investment is recovered through the normal operation of the plant. A minimum of 4.6 years is the estimated PP required to sum up the total capital investment for hydrogen production via SCWG of peanut shells. Additionally, for the project to be profitable,

the PP should always be less than the estimated project lifespan[54]. This indicates that the optimized SCWG plant for hydrogen production using peanut shells as feedstock is profitable from an economic standpoint. Although the payback period is a useful profitability index, it has the drawback of not explaining the project's performance after this period. The NPV of the discounted cash flow is estimated to be \$ 11,839,892.99 at an interest rate of 8%. Furthermore, when the unit H₂ production cost is set at \$ 1/kg, the NPV, ROI, IRR, and PP obtained are \$ 4,411,750.69, 42.21%, 5% and 6.9 years, respectively. To conclude, based on the results of the economic indicators, the project is considered profitable.

5 Conclusion

The implication of supercritical water gasification technology to produce hydrogen from biomass is growing over the years. This growth requires efforts to make the process economically viable, feasible, environmentally beneficial, and technologically competitive with other hydrogen production techniques. Operating conditions such as temperature, pressure, residence time, and catalyst play crucial roles in optimising H₂ production.

In this study, a conceptual design of the SCWG process was developed to produce hydrogen under supercritical conditions, utilizing 780,000 kg/year of peanut shells as feedstock. To simulate, optimize and analyse the supercritical water gasification process of peanut shells, a Power Law kinetic model was built using ASPEN Plus V14 software. The process was simulated based on the following operating conditions: temperature of 700 °C, pressure of 280 bar, biomass-to-water ratio of 1:4, and residence of 1 hour.

The model was validated by comparing the simulation with the experimental data. The comparison showed that the simulation results were in good agreement with the results in the literature.

To investigate the effects of process parameters such as temperature, pressure, residence time, and Ca(OH)₂ catalyst on the syngas yield (H₂, CO, CO₂, and CH₄), a sensitivity analysis was performed. Based on these results, increasing the temperature from subcritical (300 °C) to supercritical (1000 °C) boosts the hydrogen yield from 170.894 to 197.22 kg/h. Although an increase in temperature leads to an increase in H₂ yield, increasing the temperature from 800 °C to 1000 °C has no significant effect on H₂ yield. The observed increase in hydrogen yield from 800 °C to 1000 °C is only 1.523 kg/h. Furthermore, a slight increase in H₂ yield (from 192.564 to 194.368 kg/h) is observed when the pressure is increased from 220 to 350 bar.

Most importantly, the effect of the Ca(OH)₂ catalyst on H₂ yield was studied and the results demonstrated that it has a positive influence on hydrogen production. In other words, increasing the load of Ca(OH)₂ catalyst in the CSTR reactor from 0 to 25 kg results in an increase in hydrogen yield from 166.738 to 193.931 kg/h. however, it should be mentioned that increasing the Ca(OH)₂ loading from 5 to 25 kg has no significant effect on hydrogen production (from approximately 190 to 193.931 kg/h).

The simulation results show that, within the range of process parameters, the order of the effects of the factors on the H₂ yield of peanut shell gasification in supercritical water is as follows: temperature > catalyst loading > pressure > residence time. The results of the sensitivity analysis are in close agreement with the results reported in the literature, which have investigated the effect of these process parameters on hydrogen production from biomass, under supercritical conditions.

To find the optimum operating condition for hydrogen yield, a sensitivity analysis was carried out to investigate the simultaneous effects of different process parameters on H₂ yield during the catalytic gasification of peanut shells under supercritical conditions. Furthermore, according to the model's best prediction, taking into account cost-effectiveness, the hydrogen yield can reach 193.993 kg/h when the reaction conditions are set as follows: temperature of 750 °C, pressure of 220 bar, biomass to water ratio of 1:4, and residence time of 1 hour. These values were used to optimize the process. As a result, the model can accurately navigate the system for the optimum hydrogen yield under different operational conditions.

A detailed techno-economic analysis (TEA) assessment was performed to ascertain the economic viability of the optimized SCWG process. The simulated flowsheet was used to size the equipment, and it was determined that an initial investment of \$ 10,449,803.44 would be required to implement the optimized SCWG plant. The NPV value of \$ 11,839,892.99 was estimated, assuming that the plant operates for 20 years with an interest rate of 8%. In addition, the IRR was determined to be 12%, while the ROI is reported as 113.30%. Additionally, the PP was calculated to be 4.6 years, and the LCOH was determined to be \$ 1.30/kg. The relatively low LCOH, short PP, positive NPV, high ROI, and IRR values demonstrate that the optimized SCWG design for hydrogen production is profitable from an economic perspective.

The following points are the contributions of this thesis to the advancement of knowledge on biomass:

- In this study, peanut shell, as agro-industrial residue was proven to be a promising feedstock for the SCWG process.

- An overall idea is being developed for a better understanding of the Power Law Kinetic model for predicting syngas yield and the variation of the SCWG system with process parameters.
- The SCWG biomass model developed in this thesis could be used in future studies to achieve results similar to those obtained experimentally for various types of biomass.
- The detailed techno-economic evaluation and profitability analysis of the optimized SCWG process for hydrogen production indicates that the process is economically viable.

5.1 Future works and recommendations

This thesis has concluded that the implementation of an SCWG processing plant using peanut shells as feedstock is technologically feasible and economically viable, but there is still some work to be carried out in-depth in the future, including:

- Experimentally investigating kinetic parameters such as pre-exponential factor (k) and activation energy (E_a) for all reactions to be inputted into the simulation environment, especially for $\text{Ca}(\text{OH})_2$ catalytic reactions.
- A detailed kinetic model with a specific heterogeneous catalyst for biomass SCWG should be explored in the future. In addition, the performance of the heterogeneous catalyst should be compared with that of the best homogeneous catalysts in terms of hydrogen production.
- For the CSTR reactor, the effects of continuous stirring should be studied to see if they have an impact on hydrogen yield and selectivity, given that the presence of the stirrer allows perfect mixing of the biomass and water.
- A detailed techno-economic analysis should be combined with an appropriate Life Cycle Assessment (LCA) to determine the economic and environmental impacts of the SCWG process. However, high-quality data is needed to carry out a reliable LCA, which involves a significant amount of work and is time-consuming.
- The possibility of installing a CCUS (CO_2 Capture, utilization and Storage) System in the process should be considered in the future.

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