SUPERCRITICAL GASIFICATION BIOMASS HYDROGEN PRODUCTION

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I certify that in my opinion the thesis submitted by YAHYA OMAR MOUSSA titled “SUPERCRITICAL GASIFICATION BIOMASS HYDROGEN PRODUCTION” is fully adequate in scope and quality as a thesis for the degree of Master of Science.

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“I declare that all the information within this thesis has been gathered and presented in accordance with academic regulations and ethical principles and I have according to the requirements of these regulations and principles cited all those which do not originate in this work as well.”

Yahya Omar MOUSSA

ABSTRACT

Master's Thesis

SUPERCRITICAL GASIFICATION BIOMASS HYDROGEN PRODUCTION

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Unlocking the hydrogen potential of biomass through supercritical gasification, this thesis delves into innovative methods for sustainable energy production. The study explores the supercritical gasification of coal, almond shell, and a mixed sample to evaluate hydrogen production efficiency. Results indicate that almond shell, with a hydrogen yield of 5.88% in dry conditions, outperforms coal, which achieved 3.71%. The mixed sample showed an intermediate yield of 4.76%. Key operational parameters, such as temperature, pressure, and residence time, were found to significantly influence gasification performance, with higher settings generally enhancing outcomes. Compared to conventional methods, supercritical gasification demonstrated higher hydrogen yields and lower tar formation, leading to reduced emissions of sulfur and other pollutants. Despite the high initial investment required for supercritical equipment, the process's increased efficiency and lower tar production offer potential economic benefits. The research contributes to the field by identifying optimal conditions for hydrogen production and highlighting almond shell as a superior feedstock. Future research should focus on scaling up the process, exploring a wider range of biomass types, and conducting detailed economic and environmental assessments. In order to further improve hydrogen yield and process efficiency, catalysts should also be used in supercritical gasification. This lays the groundwork for subsequent developments in biomass to hydrogen conversion technology.

Key Words : Supercritical, gasification, biomass, hydrogen production.
Science Code : 92801

ÖZET

Yüksek Lisans Tezi

SÜPERKRİTİK GAZLAŞTIRMA BİYOKÜTLE HİDROJEN ÜRETİMİ

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Süperkritik gazlaştırma yoluyla biyokütlenin hidrojen potansiyelini açığa çıkaran bu tez, sürdürülebilir enerji üretimi için yenilikçi yöntemleri araştırıyor. Çalışma, hidrojen üretim verimliliğini değerlendirmek için kömürün, badem kabuğunun ve karışık bir numunenin süperkritik gazlaştırılmasını araştırıyor. Sonuçlar, kuru koşullarda %5,88'lik hidrojen verimiyle badem kabuğunun, %3,71'e ulaşan kömürden daha iyi performans gösterdiğini göstermektedir. Karışık numune %4,76'lık bir ara verim gösterdi. Sıcaklık, basınç ve kalma süresi gibi temel operasyonel parametrelerin gazlaştırma performansını önemli ölçüde etkilediği ve daha yüksek ayarların genellikle sonuçları iyileştirdiği bulundu. Geleneksel yöntemlerle karşılaştırıldığında süperkritik gazlaştırma, daha yüksek hidrojen verimi ve daha düşük katran oluşumu göstererek kükürt ve diğer kirletici emisyonların azalmasına yol açtı. Süperkritik ekipman için gereken yüksek başlangıç yatırımına rağmen, prosesin artan verimliliği ve daha düşük katran üretimi potansiyel ekonomik faydalar sunmaktadır. Araştırma, hidrojen üretimi için en uygun koşulları belirleyerek ve badem kabuğunun üstün bir hammadde olduğunu vurgulayarak alana katkıda bulunuyor. Gelecekteki araştırmalar, süreci büyütmeye, daha geniş bir yelpazedeki biyokütle türlerini keşfetmeye ve ayrıntılı ekonomik ve çevresel değerlendirmeler yapmaya odaklanmalıdır. Hidrojen verimini ve proses verimliliğini daha da artırmak için, süperkritik gazlaştırmada da katalizörlerin kullanılması gerekir. Bu, biyokütleden hidrojene dönüşüm teknolojisindeki sonraki gelişmelerin temelini oluşturuyor.

Anahtar Kelimeler **:** Süperkritik gazlaştırma, biyokütle, hidrojen üretimi.
Bilim Kodu **:** 92801

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LIST OF SYMBOLS AND ABREVIATIONS

SYMBOLS

q : Heat flux (W/m2)
Q : Heat transfer (W)
m : Mass, (kg)
$\dot{m}$: Mass flow rate, (kg/s)
c : Heat capacity, (kJ/kgK)
ρ : Density, (kg/m3)
$C_{p,nf}$: Specific heat of nanofluid, (kJ/kgK)
ρ_{nf} : Nanoparticle density, (kg/m3)
k_{nf} : Heat transfer coefficient of nanofluid, (W/mK)
$T_{ç}$: The exit temperature of the nanofluid from the pipe, (K)
T_w : Channel wall temperature, (K)
T_b : Average fluid temperature, (K)
T_o : The outlet temperature of the fluid from the channel, (K)
A : Heat transfer surface area, (m2)
A_s : Surface area, (m2)
v : Fluid velocity (m/s)
f : Friction factor
Nu : Nusselt number
Pr : Prandtl number
Pe : Peclet number
Re : Reynolds number
ΔP : Pressure loss (Pa)
μ : Dynamic viscosity, (Pa)
Φ : Nanoparticle volumetric concentration (%)
FT-IR : Fourier Transform Infrared
PL : Photoluminescence

λ : wavelength

ABREVIATIONS

CFD : Computational Fluid Dynamics
HAD : Hesaplamalı Akışkanlar Dinamiği
SHY : Sonlu Hacimler Yöntemi
SEM : Scanning electron microscope
XRD : X-ray diffraction
UV : Ultraviolet
SCWG : Supercritical water gasification
EDX : Energy dispersive X-ray spectroscopy
SCF : Supercritical fluids
EP : Enterormorpha prolifera
PEC : Photo-electrochemical
SMR : Steam methane reforming
TGA : Thermogravimetric analyses
FTIR : Fourier Transform infrared spectroscopy
GC-MS : Gas chromatography mass spectrometry
DSC : Differential Scanning colorimetry
TEM : Transmission electron microscopy
IMO : International Maritime Organisation
GHG : Green House Gas emission
OCs : Oxygen carriers
CLG : Chemical looping gasification

PART 1

INTRODUCTION

Men used wood for fire in the prehistoric era so they could light themselves, prepare their food, and protect themselves from wild creatures. This was a significant step forward in the development of humanity (MacGillivray & Thomson, 1910). Global urbanization, population growth, and industrialization are all contributing to an ever-increasing need for energy. The discovery and use of alternative energy sources has been motivated by the depletion, exhaustibility, and effects of the most commonly utilized energy sources (fossil fuels) on the environment. It is crucial to consider renewable energy sources as a solution to these issues in order to meet the demand associated with human activities and reduce pollution. There are several types of renewable energy, including solar, geothermal, wind, biomass, etc. Utilizing biomass is becoming more popular as a means of lowering CO_2 emissions and fossil fuel usage.

Biomass, also known as biogenic leftovers or energy plants, has a water content of at least 50% and typically higher than 80%. These residues are the end product of processes used in the production of bioenergy, such as biochemically based procedures that do not utilize the entire plant, as well as industries including agriculture, the food and beverage industry, and the production of bioenergy. For thermochemical biomass processes utilizing dry biomass, for example pyrolysis or gasification, mostly dry wood is used. The procedures rely on coal conversion methods that necessitate a water content of less than 10%. It is possible to process "green" biomass in its original state, that is, with its natural water content, using a hydrothermal method, which involves processing an excess of water under high pressure and temperature (Lebuhn et al., 2014). This biomass does not need to be dried at great cost in hydrothermal gasification. During the procedure, water is required both as a reactant and as a reaction medium. Because of the rapid hydrolytic breakdown of carbohydrates and the high solubility of the intermediate products under reaction conditions, high gas yields are attained at relatively low temperatures with very little generation of undesired products such as tars and coke (Kruse, 2008). To produce chemicals with high added value and billions of tonnes of energy annually, lignocellulosic biomass can be used in bio-refineries by contributing lignocellulosic material (leaves, roots, stems, bark, bagasse, straw waste, seeds, pieces of wood, etc.) produced by the agro-food industries in their daily operations (Lachos-Perez et al., 2015). Figure 1.1 displays the lignocellulosic materials used in gasification and bio-refinery products.

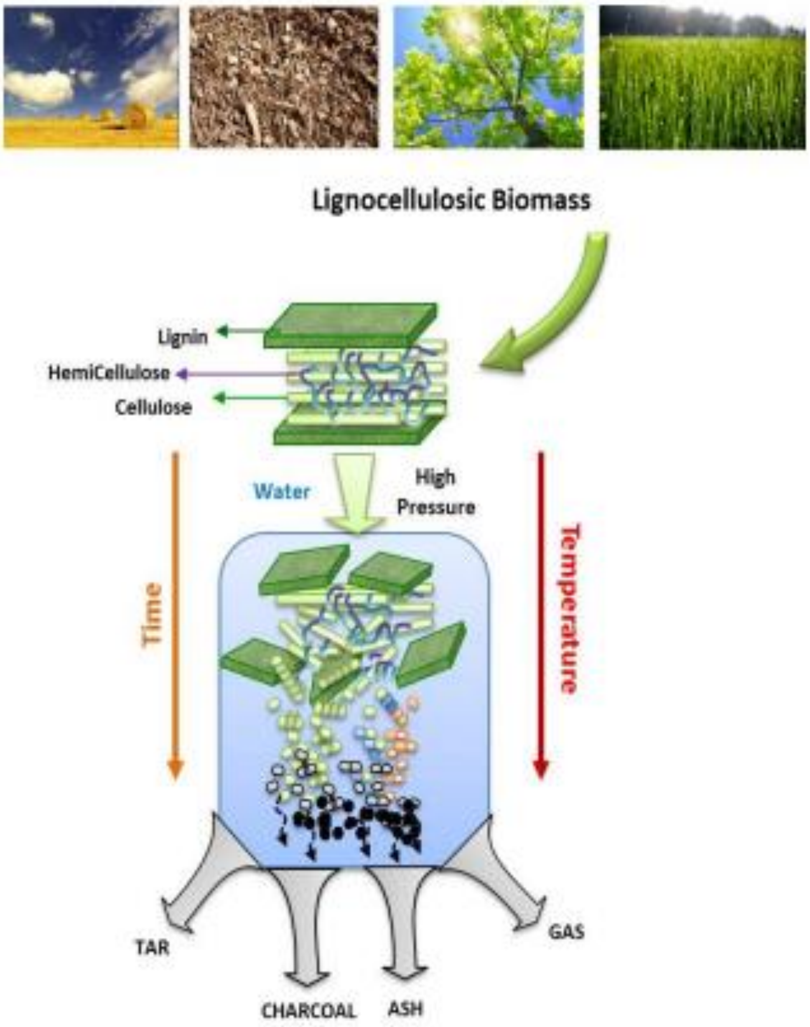


Figure 1.1. The lignocellulosic materials contribute to bio-refinery and gasification products. (Reddy et al., 2014).

Utilising biomass to produce hydrogen is a viable approach to supplying energy needs while lowering reliance on fossil fuels and cutting greenhouse gas emissions. Thermochemical conversion of biomass to hydrogen at high pressure and high temperature in the presence of supercritical gas is known as supercritical biomass gasification. Hydrogen can be produced from a variety of biomass sources, including wood, straw, agricultural waste, and forest wastes, using this technique. Thus, the main focus of this thesis is on producing hydrogen through the supercritical gasification of biomass, and it does so by analysing the key process variables, the outcomes, and the benefits of this technique. A promising technique for producing hydrogen is supercritical gasification. With this process, a gas is transformed into a liquid phase under supercritical conditions. Supercritical gasification lowers the amount of resources and energy needed to produce hydrogen, which lowers prices and boosts productivity. In this thesis, we'll talk about the supercritical gasification process for producing hydrogen.

The supercritical gasification method involves the design, optimization and characterization of a device used for hydrogen production. At the design stage, the requirements for the supercritical gasifier are determined. Device size, pressure, temperature, flow rate and other parameters affect hydrogen production efficiency and product quality. In the optimization phase, hydrogen production efficiency is increased by adjusting the parameters of the supercritical gasification process. In the characterization phase, supercritical gasifier performance, energy consumption, product quality, efficiency and other properties are examined (Kurnia et al., 2016).

Supercritical gasification is a process that produces hydrogen with great efficiency and at a low cost. The efficiency and product quality of hydrogen production are enhanced by the design and optimization of the supercritical gasifier. The characterization assesses the supercritical gasifier's efficiency and serves as a foundation for additional method applications. The process of producing hydrogen using supercritical gasification will be crucial in the development of hydrogen energy (Ragauskas et al., 2006).

Supercritical gasification is a novel technical approach that involves transforming biomass which comes from organic resources including forestry waste, energy crops, and agricultural residues under supercritical water conditions. High temperatures and pressures in this special environment make it easier to convert biomass into useful products, with hydrogen as a clean fuel being the main focus. Prized for its adaptability, high energy density, and zero emissions of greenhouse gases when burned, hydrogen has the potential to completely transform a number of industries and sectors, including power production, transportation, and industry (Rout et al., 2022).

The complex relationship between hydrogen generation and supercritical gasification becomes central to our investigation. Realising the full potential of biomass as a sustainable feedstock for hydrogen production requires an understanding of the underlying ideas, difficulties, and opportunities in this relationship. By shedding light on the workings, effectiveness, and ecological consequences of supercritical gasification for hydrogen produced from biomass, this study hopes to further the conversation around sustainable energy.

Against the backdrop of a rapidly evolving energy landscape, this thesis aims to unravel the intricacies of supercritical gasification, shedding light on its role in advancing the global transition towards a more sustainable, resilient, and hydrogen-centric energy future. Through a synthesis of scientific inquiry, technological innovation, and environmental consciousness, this work seeks to make a meaningful contribution to the ongoing dialogue on renewable energy solutions, with a specific emphasis on the symbiotic relationship between supercritical gasification, biomass utilization, and hydrogen production.

PART 2

LITERATURE REVIEW

The need for and use of energy are rising as society develops. The three main energy sources in the world today are still coal, natural gas, and oil. The most plentiful fossil fuel in the planet is coal. Fossil fuels, contributing 80% to global energy consumption, are depleting rapidly, causing harmful gases and negative effects like glacier receding, biodiversity loss, climate change, and rising sea levels (Escobar, 2009; Agarwal, 2007).

Within the current global energy transition framework, hydrogen is becoming more and more popular. In reality, there is a rising and widespread excitement for it, as seen by the present global political and economic initiatives that support a swift transition to clean energy sources and carbon neutrality by 2030. Green hydrogen can provide much-needed flexibility to power networks by acting as a buffer against renewable generation that cannot be shipped. This could trigger a positive feedback loop in future electrical networks fuelled by renewable energy sources. It is possible to store excess energy from renewable and conventional power plants as hydrogen, which can then be used to generate electricity or heat via fuel cells, power systems, or both (cogeneration), lowering greenhouse gas emissions into the atmosphere. It is critical to understand the potential benefits of using hydrogen in this scenario.

The study made by Capurso et al. (2022) discusses the role of hydrogen in the global energy transition. The authors discuss the growing enthusiasm towards hydrogen and its potential to contribute to renewable electricity grids. They explore the benefits and drawbacks of hydrogen in various sectors, such as transport, industry, and power generation. The authors emphasize the importance of sustainable hydrogen production through electrolysis powered by renewable energies. They compare the efficiency and environmental impact of fuel cells and Li-ion batteries for mobility applications. The article also examines the blending of hydrogen with fossil fuels as a near-term solution to reduce power generation emissions. The authors present a case study showing the potential reduction in CO_2 emissions through hydrogen blending. Furthermore, they discuss hydrogen policies across the world and the increasing interest and investment in hydrogen research. Overall, the review provides insights into the potential of hydrogen, its challenges, and the current policy landscape surrounding its use in the energy transition. Green hydrogen production from biomass gasification is becoming a more sustainable, economical, and environmentally friendly method (Moneti et al., 2016; Levin and Chahine, 2010).

Furthermore, biomass is an energy source that is renewable and sustainable (Caner Acar and Boke, 2018). Nevertheless, just around 5% of the biomass on Earth has the potential to be converted into energy, meeting roughly 26% of global energy requirements (Gonzalez-V ¨ azquez ´ et al., 2021). The high demand for fossil fuels is affecting global economic activities and increasing crude oil prices. Biofuels, produced from sustainable biomass, offer advantages such as easy extraction, sustainability, carbon-dioxide combustion, and environmental friendliness (Weldemichael & Assefa, 2016). The biofuel market is expected to grow rapidly in the next decade due to environmental benefits (Kim & Dale, 2005).

One coal use technology that demonstrated high efficiency was supercritical water gasification (Y. Wang et al., 2023 and Recalde et al., 2022). Complex organic feedstock, such as coals, degraded into H2, CO2, and other products, such as CH4, CO, oil, and ash, under high temperatures and pressures in a water environment (Chen et al., 2021). In addition to acting as a source of hydrogen and free radicals (Park & Tomiyasu, 2003).

Zhang et al. (2017) conducted a comprehensive review on the topic of hydrogen production through biomass gasification in supercritical water (SWG) from an exergy perspective.

The review begins by discussing the importance of hydrogen as an energy source and highlights biomass gasification as a favourable method due to its fast process, efficiency, and environmental friendliness. It introduces SWG as a promising approach, leveraging the unique properties of supercritical water to enhance gasification reactions and achieve high hydrogen yields. Exergy analysis is emphasized as a valuable tool for evaluating hydrogen production processes. Unlike energy analysis, exergy analysis considers the conservation of energy and entropy principles, providing a more comprehensive understanding of efficiency assessment. The review stresses the superiority of exergy analysis in evaluating hydrogen production processes. The parameters impacting hydrogen production efficiency in SWG of biomass are investigated. These variables include feedstock properties, biomass concentration, gasification temperature, residence duration, reaction catalyst, and reactor pressure. The review identifies how each aspect affects the exergy efficiencies of hydrogen production. For example, biomass feedstock parameters influence hydrogen production by affecting H2 yield and biomass heating value. Biomass concentration, gasification temperature, and residence time all have different effects on exergy efficiency. Previous reviews related to hydrogen production from SWG of biomass are acknowledged, emphasizing the research gap regarding the exergy analysis of this specific process. The review highlights the need for a comprehensive analysis of exergy aspects to optimize hydrogen production efficiency (Zhang et al, 2017).

Due to their high water content, microalgae cannot be used in normal gasification, but because of their propensity for rapid development, they are regarded viable feedstocks for hydrogen production. An alternative method such as supercritical water gasification is required to fully realise this promise. The application of supercritical fluids in biomass conversion procedures like gasification, pyrolysis, and liquefaction has been the subject of research in recent years.

High-value goods and biofuels can be produced by SCF by improving the extraction efficiency of useful chemicals from biomass, such as cellulose, hemicellulose, and lignin. Furthermore, during biomass conversion processes, the special qualities of supercritical fluids have demonstrated promise for enhancing mass transfer, catalyst performance, and reaction kinetics (Lee et al., 2019).

The study has explored the utilization of various supercritical fluids, such as water, ethanol, and carbon dioxide, for biomass conversion applications. The effects of numerous operational parameters on yield, selectivity, and product quality have been studied. These factors include temperature, pressure, and solvent composition. Furthermore, the development of novel catalysts and reactor designs has been a focus to enhance the efficiency and sustainability of biomass conversion using supercritical fluids.

Table 2.1. Applications of Supercritical Fluid Technology.

Application	Description
Pharmaceutical Processing	Supercritical fluids are used for drug particle formation, encapsulation, and extraction in pharmaceutical manufacturing (Deshpande et al., 2011).
Food and Beverage Extraction	Extraction of flavours, fragrances, and bioactive compounds from natural sources using supercritical fluids (Brunner, 2005).
Polymer Processing	Supercritical fluids are utilized for polymerization, polymer impregnation, and production of polymer-based materials (Knez et al., 2014).
Environmental Remediation	Supercritical water oxidation (SCWO) is applied for the treatment of hazardous waste and pollutants.
Nanostructure Synthesis	Supercritical fluid technology is employed for the synthesis of nanoparticles with controlled size and morphology (Rao & Geckeler, 2011).
Herbal Extraction	Extraction of bioactive compounds from herbs, botanicals, and natural products for use in herbal medicines and supplements (Knez et al., 2014)..
Carbon Capture and Storage (CCS)	Supercritical carbon dioxide is investigated for its potential in carbon capture and storage to mitigate greenhouse gas emissions. (Machado et al., 2013)
Aerospace and Precision Cleaning	Supercritical fluids are used as environmentally friendly solvents for precision cleaning in aerospace and electronics industries (Knez et al., 2014).
Energy Production	Supercritical fluids are explored for use in advanced power cycles and geothermal energy extraction (Machado et al., 2013).
Oil and Gas Extraction	Supercritical fluids, particularly CO2, are employed for enhanced oil recovery and extraction of oil and gas reserves (Machado et al., 2013)..

Ultimately it becomes clear that the exploration and exploitation of the unique properties of supercritical fluids are ongoing efforts within the scientific community.

Researchers continue to discover new applications, extending the reach of these fluids to diverse areas, including pharmaceuticals, food processing and environmental remediation. The promise of innovative and sustainable solutions for a myriad of industrial challenges highlights the enduring importance of supercritical fluids in contemporary scientific research and industrial practices.

Gong et al. (2023)'s study explores the use of Enteromorpha prolifera (EP), a marine green alga that is known to have detrimental effects on the environment when it is present in large enough quantities. The main goal of the research was to convert EP into hydrogen-rich syngas by Supercritical Water Gasification (SCWG). Within this paradigm, the researchers systematically examine the impact of important reaction parameters on the ultimate hydrogen yield, including temperature, reaction duration, and moisture content. In parallel, the SCWG approach closely examines the catalytic performance of four commercially available catalysts: KOH, Ni, K_2CO_3, and $AlCl_3$.

Furthermore, researchers have focused on developing and improving catalysts for biomass gasification through a range of techniques such as co-precipitation, impregnation, and precipitation. The composition, structure, and activity of catalysts have all been investigated utilising catalyst characterization techniques such as energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Catalyst promoters, such as alkali and alkaline-earth metals, have also been studied to enhance catalytic stability and performance.

The importance of a number of homogeneous and heterogeneous catalysts for methanation, water-gas exchange, and other secondary reactions is underlined. Discussions of the parametric implications and particular reactor configurations for maximizing hydrogen generation are also covered, in addition to discussions of the technical challenges of the hydrothermal gasification processes.

The typical proportion of lignocellulosic biomass includes 30–60% cellulose, 20–40% hemicellulose, and 15–25% lignin. H_2, CO, CO_2, and CH_4 are produced during the gasification of biomass using high-temperature procedures with controlled oxygen and/or steam concentrations. Supercritical water is the preferred medium in the supercritical water gasification process, which is a way of gasifying biomass. Gasification of biomass uses supercritical water as a medium and reactant. Supercritical conditions are favourable for pyrolysis and hydrolysis reactions because they increase the formation of high density H^+ and OH^- ions.

Examining the various SCWG reactor configurations for the production of H_2 from biomass is another crucial aspect of our investigation. In a Lu and Al study, it is also noted that a number of process variables affect the H_2 yields of biomass during SCWG. Corn cob SCWG is affected by temperature, pressure, feedstock concentration, and residence time-related parameters. In order to help readers better grasp how temperature, pressure, feed concentration, catalyst type, and loading, along with reactor architecture, have an impact on overall reaction processes and H_2 yields, the following article provides a synopsis of important process parameters (Sivamohan et al, 2014).

Supercritical water gasification, while classified as a type of biomass gasification, is the process of reacting biomass at temperatures above 700°C with regulated amounts of oxygen and/or water vapour to create H2, CO, CO2, and CH4. The medium is supercritical water at 374 °C and 22.1 MPa. They came to the conclusion that the gasification medium is the only factor that separates SCWG from other thermochemical gasification methods. Another benefit, according to them, of SCWG biomass is that it produces H_2 at high pressure, which reduces the price of energy compression during storage it is crucial to research the SCWG of model compounds before trying to understand the mechanics, behaviour, and degradation of lignocellulosic biomass complexes under supercritical circumstances.
Glucose, glycerol, lignin, cellulose, phenolic chemicals, etc. (Milledge et al., 2014).

The following reactions take place when biomass is gasified in SCWG:

$$CH_x O_y + (2-y) H_2O = CO_2 + (2-y+x/2) H_2 \quad (2.1)$$

$$CH_x O_y + (1-y) H_2O = CO + (1-y+x/2) H_2 \quad (2.2)$$

Cellulose hydrolysis

(C6H10O6)n +nH2O = $nC_6H_{12}O_6$

Glucose reforming reaction

$nC_6H_{12}O_6 = 6CO + 6H_2$

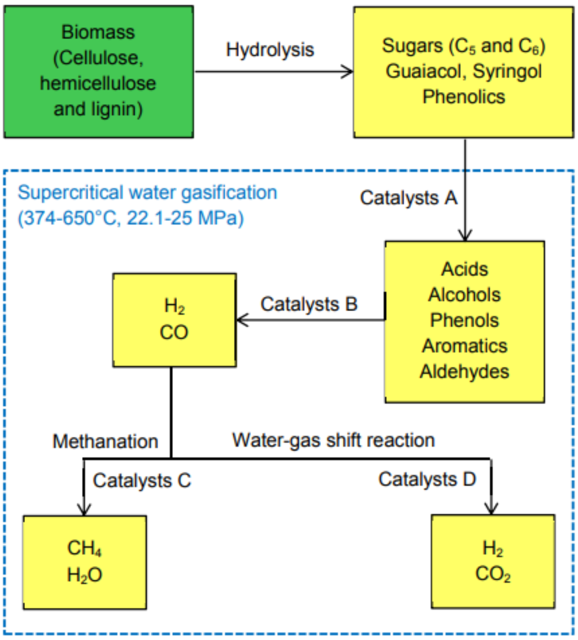


Figure 2.1. Typical reaction routes in supercritical water gasification of biomass Reddy et al. (2014).

Catalysts A (e.g., Ni, Ru, Rh, Pt, Pd, Ni/ Al_2O_3, Ni/C, Ru/Al_2O_3, Ru/C and Ru/TiO_2); Catalysts B (e.g., Ni, Ru, Pt and activated carbon); Catalysts C (e.g., Ni, Rh, Ru, Pt and activated carbon) and Catalysts D (e.g., Ni, Ru, NaOH, KOH, K_2CO_3 and Trona).

The review of Gong et al. indicates that higher temperatures, longer reaction times, and ideal moisture content all work together to produce higher hydrogen yields during the SCWG process. $AlCl_3$ stands out as the catalyst, notably with an emphasis on the significant work published in the article "Supercritical water gasification of biomass for hydrogen production" by Sivamohan N. Reddy et al. (2014), the significance of understanding the degradation mechanisms of biomass components, including cellulose, hemicellulose, and lignin, to optimize hydrogen production in high-pressure SCWG systems was underlined. Process conditions such as temperature, pressure, feed concentration, residence time, and catalysts are identified as critical factors influencing gasification. The unique properties of supercritical water, such as high kinetic energy and tuneable thermo-physical properties, are discussed as key contributors to efficient biomass gasification.

Supercritical water gasification, a revolutionary approach to biomass gasification for sustainable energy solutions. A variety of biomass gasification technologies, such as fluidized bed gasifiers, entrained flow gasifiers, and fixed bed gasifiers, have been developed. Fixed bed gasifiers are appropriate for smaller-scale applications since they operate at lower temperatures. Fluidized bed gasifiers, on the other hand, offer better heat transmission and can handle a variety of feedstock sources. Higher heating values are produced by entrained flow gasifiers because they run at higher pressures and temperatures.

The choice of catalyst has a significant impact on the efficiency and performance of this process. Dolomite, limestone, and olivine are common in-situ catalysts used in biomass gasification, which means that they are fed directly to the gasifier. These catalysts can improve the conversion of tar and lighter hydrocarbons to syngas (Sikarwar et al., 2017).

Nickel-based catalysts, such as Ni/Al2O3 or Ni/CeO2, are another type of catalyst utilised in biomass gasification. These catalysts are often used as ex-situ catalysts in a separate reactor or reformer located downstream of the gasifier. These catalysts have strong catalytic activity in tar cracking and reforming operations, resulting in better syngas quality (Nahar et al., 2017).

Furthermore, alkali and alkaline earth metal catalysts, as well as bimetallic catalysts, can be used to improve the gasification process by promoting the water-gas shift reaction, lowering tar formation, and increasing overall efficiency (Wang et al., 2019).

Pan et al. (2020) evaluate the usage of bimetallic Cu/Ni/olivine oxygen carriers (OCs) for chemical looping gasification (CLG) of cotton stalks. It was discovered that raising the Cu/Ni ratio improved OC sintering, and olivine was a suitable support material with an oxygen carrying capacity of 1.07%. The redox reactivity of the OCs remained constant during numerous cycles. The Cu9/Ni6/olivine OC had the greatest overall CLG performance in terms of gas yield, H_2+CO yield, and carbon conversion after optimising the Cu/Ni ratio, steam-to-biomass ratio, and OC-to-biomass ratio, owing to the synergistic effect of Cu and Ni. The OCs were able to give up to 65% of the lattice oxygen required during the CLG process, with the basic crystalline phase remaining stable during cycling, demonstrating the promise of these bimetallic Cu-Ni OCs supported on olivine for boosting biomass CLG efficiency.

Other scholars have examined the application of diverse catalysts to augment syngas quality, diminish tar production, and elevate overall process efficiency. Important factors to take into account are the type of catalyst used, how it is loaded, and if it can operate in supercritical circumstances (Sudarsanam et al., 2018).

Examined are the advantages and disadvantages of several reactor designs, including batch, tube, continuous stirred tank, and fluidized bed reactors in Al-Rumaihi et al.'s review (2022). Fluidized bed reactors operating under supercritical conditions are highlighted as having potential for overcoming technical challenges encountered in SCWG processes. The analysis also highlights how crucial catalysts and process variables are to maximising hydrogen production during SCWG. It investigates how the efficiency of hydrogen production is affected by temperature, pressure, feed concentration, type of catalyst, and loading.

The role of catalysts in water-gas shift reactions, methanation, and other sub-reactions during SCWG is discussed. Technical challenges associated with hydrothermal gasification processes, such as reactor design, catalyst selection, and process parameter optimization, are addressed. The review suggests future research directions, including the exploration of novel catalysts, reactor designs, and process optimization strategies to improve hydrogen production efficiency and scalability in SCWG processes. CO_2's low critical point, specific heat capacity, and non-supercritical transport history make it a promising candidate for supercritical water gasification systems to enhance gasification efficiency and reduce energy consumption.

The review of Wang et al. (2024) synthesizes the key findings and insights presented in the research paper, highlighting the significance of utilizing carbon dioxide (CO_2) as a transporting medium in the SCWG system to enhance gasification efficiency and mitigate energy consumption. The authors underscore the limitations of traditional SCWG systems that employ water as the transporting medium, emphasizing their elevated energy consumption and susceptibility to side reactions that compromise the gasification process. In response to these challenges, the authors propose the substitution of CO_2, citing its low critical point and low specific heat capacity as potentially advantageous for improving gasification effectiveness and diminishing energy requirements.

The study establishes a supercritical water coal gasification system employing lignite as the raw material, with a specific focus on exploring the production yields of gasification under varying conditions using CO_2 and H_2O as transporting media. The results reveal a nuanced trade-off: while the production of hydrogen (H_2) and carbon dioxide (CO_2) diminishes in the CO_2-transporting system compared to the H_2O-transporting system, there is a concomitant increase in the production of methane (CH_4) and carbon monoxide (CO). Notably, the energy and exergy efficiency of the CO_2-transporting system surpasses that of the H_2O-transporting system, underscoring the superiority of CO_2 as a transport medium in supercritical water gasification. The article positions this research within the broader context of coal utilization technologies, emphasizing the role of supercritical water gasification in ameliorating pollution and enhancing efficiency in coal-fired power generation. The transformative potential of SCWG is elucidated, as it can decompose complex organic feedstock into valuable products, including H_2, CO_2, CH_4, CO, oil, and ash. The distinctive properties of supercritical water, such as its role as a hydrogen and free radical source and catalytic behaviour, are expounded upon. Additionally, supercritical water's advantages, such as enhanced mass transfer, prevention of coke formation, and catalyst poisoning avoidance, are underscored.

The authors address the persistent challenges associated with side reactions and energy consumption in the gasification process, positing CO_2 as a viable solution to inhibit side reactions and reduce energy consumption. They draw attention to previous studies employing supercritical CO_2 as a particle transporting medium, highlighting its favourable characteristics in pneumatic conveying, including high feedstock conversion rates and side reaction inhibition at low temperatures. The research paper meticulously details the establishment of a supercritical gasification system, examining gas production under diverse temperature, pressure, and feedstock concentration conditions. The subsequent analysis of the impact of these factors on the system's energy and exergy further enriches the understanding of the proposed CO_2-transporting medium.

In summary, this review synthesizes the key findings of the research paper, offering insights into the utilization of CO_2 as a transporting medium in a coal supercritical water gasification system. The advantages of CO_2 over water are elucidated, experimental results comparing different transporting systems are presented, and the potential of CO_2 to enhance gasification efficiency and reduce energy consumption is underscored. The research contributes to the broader discourse on innovative approaches to coal utilization and sustainable energy production. And using CO2 to increase efficiency become a Breakthrough approaches to supercritical water gasification.

A comprehensive exploration conducted by Julian Dutzi et al. (2024) delves into the intricate dynamics of supercritical water gasification (SCWG) by screening ten diverse plants. The primary objective is to unravel the nuanced limitations and behaviours of various biomasses within this transformative conversion process. The investigation systematically assesses the gasification performance of a range of biomasses, encompassing dry and moist, woody and grassy varieties, all conducted under standardized conditions. In its conclusive insights, the study underscores that the SCWG process's efficacy in gasifying diverse biomasses is minimally influenced by macroscopic appearance or humidity levels. However, the criticality of meticulous feed preparation, encompassing size reduction and salt separation, emerges as a pivotal factor for ensuring the seamless and efficient operation of SCWG. These findings, therefore, offer invaluable insights into the potential use of various biomasses in precluding phytoremediation efforts, along with the associated challenges and considerations essential for optimizing SCWG processes in biomass gasification applications.

In summary, this investigation provides a holistic understanding of the screening process applied to diverse plants in supercritical water gasification. It unveils crucial factors influencing gasification efficiency and underscores the potential implications for biomass utilization in both environmental and energy applications. Lachos-Perez et al.'s (2015b) study offers a thorough analysis of the potential of supercritical water gasification (SCWG) as a biomass-to-hydrogen generation technique. The paper methodically explains the benefits that come with SCWG technology, highlighting its ability to recycle a variety of biomass feedstocks. Notable features of the system include its higher conversion efficiency compared to conventional methods and its ability to produce cleaner biogas with a high hydrogen concentration.

Beyond these technological advantages, the paper provides a thorough analysis of the crucial characteristics of supercritical water that are crucial in affecting the SCWG process. This process's biomass kinetics are thoroughly investigated, and the many variables influencing the SCWG's overall efficiency are also thoroughly examined. The article by Panichkittikul et al. (2024) discusses the disadvantages of the commercial technologies now in use, including their high energy input and greenhouse gas emissions, and emphasizes the significance of looking for alternate approaches to produce hydrogen.

Bio-hydrogen is a promising green and renewable energy source that is produced from biomass. Because of its quantity and diversity, biomass plays an important role in the production of renewable energy. Compared to conventional fossil fuels, biomass has the distinct advantage of absorbing CO2 throughout its growth, which results in a relatively low net CO_2 impact. The paper explores several biomass-based hydrogen production techniques, such as electrolysis, bioprocessing, and thermochemical processes. Gasification and pyrolysis are the two most popular thermochemical processes; gasification has proven to be effective in producing syngas, a precursor combination of hydrogen and carbon monoxide. The article emphasizes the importance of the lower heating value (LHV) in syngas production, influencing product quality, energy efficiency, and economic viability, environmental sustainability is a critical aspect of hydrogen production systems, necessitating the integration of carbon dioxide (CO_2) capture technologies. In the context of biomass-based hydrogen production, carbon capture becomes imperative during biomass gasification to prevent the release of CO_2 into the atmosphere. The review underscores the significance of sorbent-enhanced reforming, particularly using calcium-based materials like CaO, for efficient hydrogen production and simultaneous carbon capture. CaO adsorption, sourced from the decomposition of $CaCO_3$ or natural minerals, emerges as a cost-effective and widely available method for CO_2 capture in biomass gasification. And finally the focal point of this review is on the integration of supercritical water gasification and steam gasification with CaO adsorption for bio-hydrogen production. Simulation results presented in the discussed article reveal that both steam gasification integrated with CaO adsorption (SG-CaO) and supercritical water gasification integrated with CaO adsorption (SCWG-CaO) yield high-purity hydrogen. Notably, SCWG-CaO outperforms SG-CaO in terms of hydrogen purity (99.99% vs. 99.95%), hydrogen yield (14.16% vs. 14.12%), and energy efficiency (42.32% vs. 40.26%).

Martins et al. (2023) conducted an in-depth analysis of three biomass gasification processes using Aspen Plus®: conventional gasification, plasma gasification, and supercritical water gasification. The primary objective was to identify the gasification process yielding the highest hydrogen production. The results of their parametric study revealed that supercritical water gasification exhibited the highest hydrogen yields at 0.844 Nm3/kg biomass, followed by conventional gasification (0.828 Nm3/kg biomass) and plasma gasification (0.758 Nm3/kg biomass).

In addition to assessing hydrogen yields, the study conducted an economic evaluation using indicators such as net present value and payback. Surprisingly, the results indicated that, under the determined optimal operating conditions, none of the gasification processes are currently economically viable. A subsequent sensitivity analysis identified that conventional gasification could achieve viability for steam-to-biomass ratios below 3. Process intensification techniques also demonstrated potential, suggesting that supercritical water gasification could be economically viable for feed concentrations between 15% and 25%. The study further determined the minimum selling prices of green hydrogen generated by each gasification process. Notably, conventional gasification exhibited the lowest minimum selling price at 7 €/kg, followed by supercritical water gasification at 10 €/kg and plasma gasification at 13 €/kg.

Martins et al.'s findings hold significant implications for the burgeoning hydrogen economy. While the study underscores the potential of biomass gasification, it also highlights the current economic challenges associated with the examined processes. The minimum selling prices, though informative, indicate that further research and improvements in gasification processes are essential to enhance the competitiveness of green hydrogen in the market.

Finally the study highlights the potential of biomass gasification for green hydrogen production, emphasizing the need for further research and advancements to reduce costs and ensure commercial viability. The challenges and opportunities associated with scaling up supercritical gasification for industrial hydrogen production from biomass must be staged to transition to green energy in the decades we live in. In this regard, many recent studies have been carried out. A study by Nguyen et al. (2024) identifies key technical problems and challenges in biomass pyrolysis and gasification for hydrogen production. These challenges include achieving high process efficiency, addressing feedstock variability, minimizing tar formation, optimizing catalyst selection, overcoming scale-up and commercialization obstacles, and mitigating environmental impact.

The International Maritime Organisation (IMO) has sought to strengthen restrictions in response to concerns about greenhouse gas (GHG) emissions from international ocean transport. The purpose of these initiatives is to increase the sustainability of the maritime industry. These rules include the International Convention for the Prevention of Pollution from Ships, the Ship Energy Efficiency Management Plan, and the Energy Efficiency Design Index, which aim to improve marine vessel energy efficiency while lowering pollution (Yalama et al., 2022). These rules are essential tools for lowering the use of fossil fuels and emissions from global maritime operations, since over 95% of commercial ships run on fossil diesel fuel (Geertsma et al., 2017; Nguyen et al., 2023). They do this by imposing stricter emission restrictions and greater energy efficiency standards (Geng et al., 2017).

In their research, Hoang et al. (2023) draw attention to the mounting worry about greenhouse gas (GHG) emissions from international maritime commerce and the necessity of lowering these emissions. They talk about the most recent rules that the International marine Organisation (IMO) has put in place to try and lower greenhouse gas emissions from marine operations. One prospective substitute fuel for the shipping industry's decarbonisation efforts is hydrogen.

Although hydrogen has been researched and developed in a number of industries, the assessment notes that there have been few studies examining its viability for use in ocean freight.

The authors provide a review of existing information in the topic, with a focus on hydrogen synthesis, storage, and energy generation on ships.

Several difficulties to the development of hydrogen-based energy for the maritime industry have been recognised. These challenges include ship space constraints, hydrogen storage difficulties, underdeveloped infrastructure at hydrogen-bunkering ports, high retrofitting, maintenance, and operating costs, and a lack of comprehensive guidelines and international rules for integrating hydrogen into global shipping. In addition, the report notes that the availability of cheaper conventional fuels contributes to the reluctance of industry participants to convert to hydrogen.

The review concludes with concepts and recommendations for encouraging the green transition of hydrogen-powered maritime industries. These ideas address technology and policy implications for cleaner, more sustainable global trade. Overall, the essay provides an overview of the current state of hydrogen utilisation in the maritime industry, stressing barriers and potential solutions for fulfilling its decarbonisation potential (Hoang et al., 2023).

PART 3

BACKGROUND

3.1. HYDROGEN PRODUCTION

Hydrogen production is the process of generating hydrogen gas from various energy sources or feedstocks. Fuel cells, transportation, industrial operations, and energy storage are just a few of the many uses for hydrogen, an adaptable energy source. Hydrogen can be produced via a variety of techniques, each with unique benefits and drawbacks. Thermochemical water splitting, photo-electrochemical (PEC) water splitting, biomass gasification, partial oxidation, coal gasification, electrolysis, and steam methane reforming (SMR) are the techniques that are frequently employed. Hydrogen is produced chemically via SMR and Partial Oxidation using hydrocarbon feedstocks such as methane or petrol. Coal is gasified to produce a hydrogen-containing gaseous mixture. Using an electric current, electrolysis separates water into hydrogen and oxygen. Gasification of biomass refers to the conversion of biomass feedstocks into hydrogen and other gases. Thermochemical Water Splitting employs heat and chemical reactions to split water into hydrogen and oxygen. PEC Water Splitting uses semiconductor materials to turn sunlight directly into hydrogen. The environmental impact and energy efficiency of different methods vary, with developments being made continuously to improve efficiency and lower costs (Turner, 2004).

3.2. BIOMASS TECHNOLOGY

Biomass is a sustainable biological resource obtained from plant and animal waste. In many nations, especially developing ones, biomass is a common fuel for heating and cooking. The technology for biomass is being used more often in industrialised nations.

Generating electricity and moving people using biomass fuels in an effort to reduce the amount of carbon dioxide produced when fossil fuels are used. According to one source, biomass energy, which currently provides 10% to 14% of the world's primary energy, including roughly 3% for transportation, has the potential to contribute up to 30% to 40% of the world's energy by 2050 (Energy Information Administration, 2022).

3.2.1. Biomass a Promoted Renewable Energy Source

Biomass is one of the most promising, widely used, and well-supported renewable energy sources. Biomass is one of the most fascinating, and popular renewable energy sources. They have the potential to relocate regions with significant fossil fuel resources, boost the availability of liquid fuels for transportation, lower net carbon emissions into the environment per unit of energy produced, and improve energy security (Meadowcroft, 2009). Risks linked to increased biomass energy use include turning natural areas into monocultures, putting agricultural waste in waterways, threatening food supplies or farm lifestyles because of land competition, and raising net carbon emissions to the atmosphere from increased deforestation or energy-intensive manufacturing processes.

For its extensive use in an environmentally sustainable way, hydrogen can be produced from raw materials such as biomass, fossil fuels, and water electrolysis.

Because of its simple and clean structure, biomass is a renewable and environmentally benign energy source. Different types of biomass have different ash and moisture contents as well as chemical compositions (Tan et al, 2021).

Due to their simplicity of use and ability to quickly and cost-effectively create hydrogen, thermo-chemical approaches have attracted a lot of attention in recent years. Biomass gasification technologies have gained significant attention as a sustainable and renewable energy production method.

The process of converting solid biomass into synthesis gas, also known as syngas, is known as gasification. This process offers several advantages, including high energy efficiency, flexibility in feedstock utilization, and reduced greenhouse gas emissions compared to conventional fossil fuel combustion (Zhao, 2017).

3.2.2. Different Biomass Types

Different biomass kinds are depicted in Figure 3.1 All plants and substances generated from plants, including livestock waste, fall under these categories.

Primary biomass, commonly referred to as virgin biomass, comes exclusively from plants or animals. Various biomass-derived products yield waste or derived biomass. (For example, agricultural waste, energy crops, and herbaceous and woody biomass, Waste from forests, industry, and municipalities) (Basu, 2010).

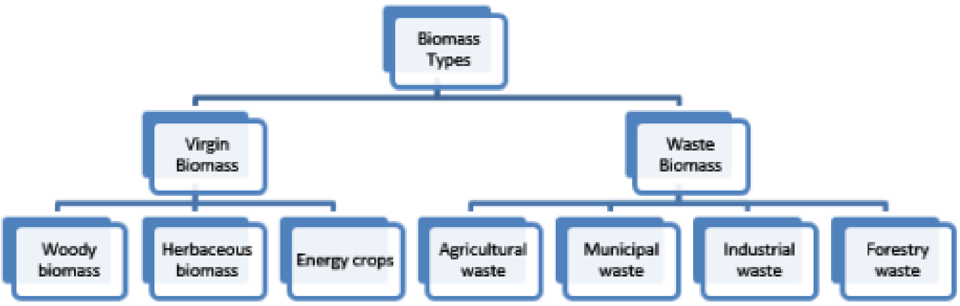


Figure 3.1. Biomass Types (Basu, 2010).

3.2.3. Biomass to Hydrogen Pathways

There are several methods for converting biomass into usable energy. The conversion process selection is influenced by the type and amount of biomass feedstock used, the amount of energy required for the project, end-use requirements, environmental constraints, financial situations, and project-specific considerations. The process path is frequently determined by the type and quantity of biomass available, as well as the form in which the energy is required.

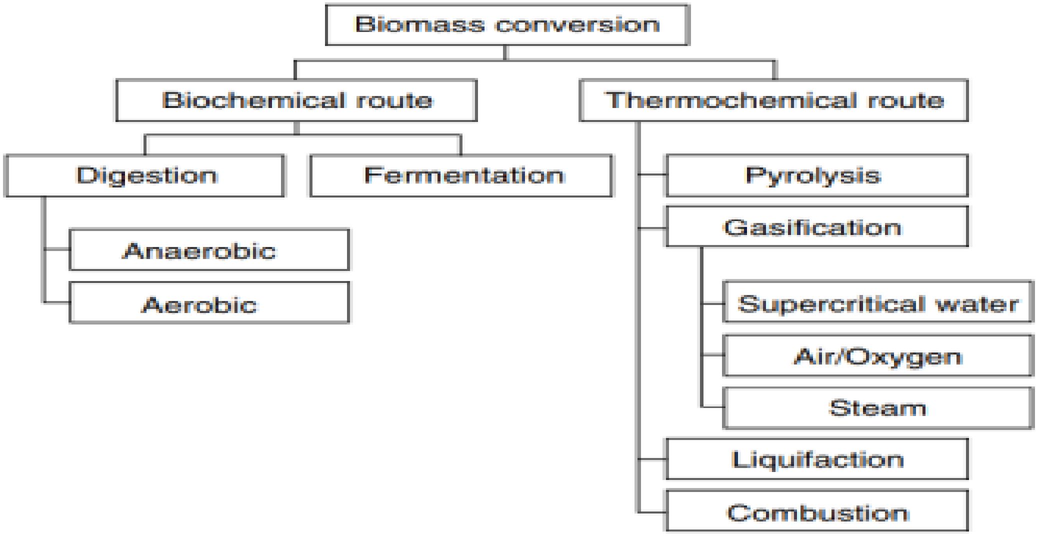


Figure 3.2. Biomass conversion methods (Basu, 2010).

The two main process technologies used to convert biomass to energy are thermo-chemical and bio-chemical/biological, as illustrated in Figure 3-2 for thermo-chemical conversion, there are four possible processes: liquefaction, gasification, pyrolysis, and combustion. Two processes are involved in biochemical conversion: fermentation, which produces ethanol, and digestion, which produces biogas, which is mostly composed of methane and carbon dioxide (McKendry, 2002).

The conversion of biomass to hydrogen gas has been found to be an effective way for producing sustainable hydrogen. Thermochemical or biochemical processes such as gasification, reformation, water-gas shift reaction, and hydrogen purification are some of the ones frequently used to convert biomass to hydrogen. (Brandt et al 2013).

Biomass gasification and pyrolysis are two well-studied thermochemical processes for converting biomass to hydrogen. Gasification has the advantage of producing a syngas rich in hydrogen, which may then be processed to create high-purity hydrogen. In contrast, oxygen is absent during the thermal degradation of biomass during pyrolysis, which results in a mixture of gases, liquids, and solids that can be reformed to produce hydrogen (Zhao et al. 2017b).

Anaerobic fermentation procedures using microorganisms are used in biochemical pathways, such as dark fermentation and photo-fermentation, to generate hydrogen from biomass. Some bacteria use a process known as "dark fermentation" to break down organic molecules into carbon dioxide and hydrogen, while bacteria that are photosynthetic use a process known as "photo fermentation" to manufacture hydrogen when light is present.

3.3. GASIFICATION

The thermochemical process which is gasification converts materials derived from organic matter or fossil fuels into syngas, a gaseous product mostly consisting of carbon monoxide, hydrogen, and methane. This unique technique provides a versatile and effective method of extracting energy from a wide range of feedstocks, including coal, biomass, and waste materials. During gasification, these feedstocks are treated to high temperatures and controlled amounts of oxygen or steam in a low-oxygen environment, causing complex hydrocarbons to break down into simpler gases. Syngas can be used for a variety of purposes, including electricity generation, chemical synthesis, and the manufacturing of liquid fuels. Gasification is viewed as a promising and environmentally sustainable alternative to classic combustion processes because it allows for the more regulated capture and potential utilisation of by-products such as carbon dioxide. As the global energy landscape evolves, gasification has enormous potential for improving energy security, lowering greenhouse gas emissions, and encouraging a more circular economy.

Gasification is a four-step process that includes partial combustion, pyrolysis, drying and gasification of degraded products. Figure 3.3 and figure 3.4 provide a summary of these processes. The fuel's moisture content drops during the drying process. In the absence of oxygen, pyrolysis converts heat into chemicals such as carbon, H_2, CO, and CH_4. The burning or oxidation of coal and other combustible materials produces burnt gases. These high-temperature gases supply the heat required for the subsequent procedures. The gasification reactions that result in syngas are produced during the reduction stage (Basu, 2010).

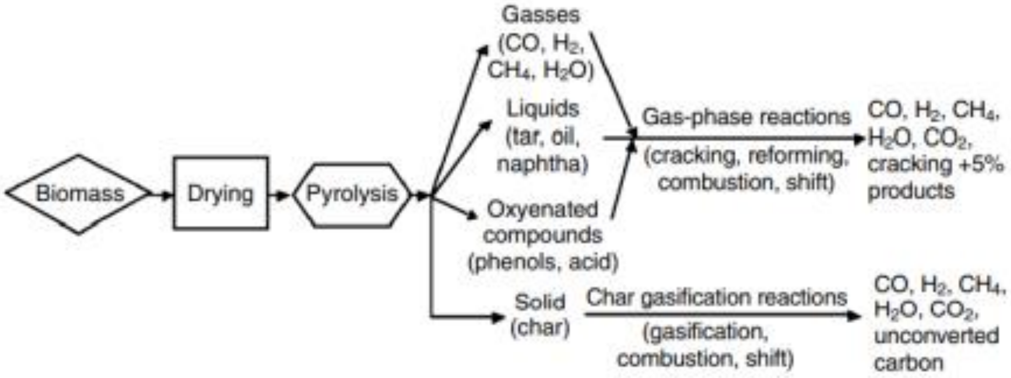


Figure 3.3. Gasification process (Basu, 2010).

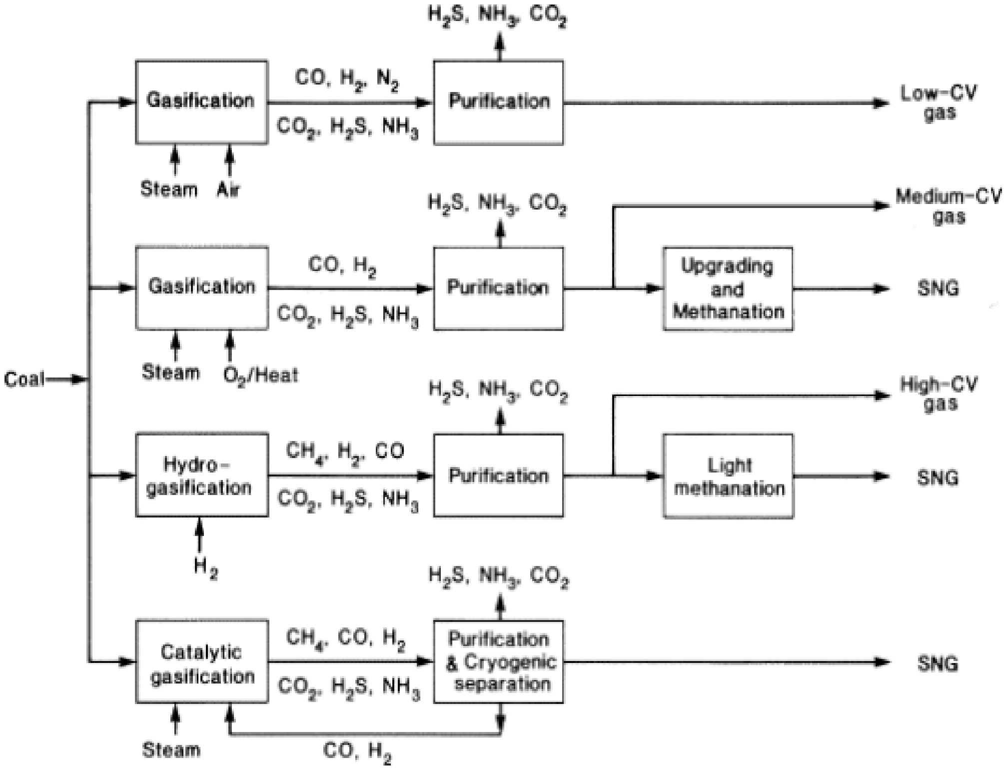


Figure 3.4. Main chemical reactions of the gasification process (Martins et al., 2023).

Table 3.1. Main chemical reactions of the gasification process (Martins et al., 2023).

Reaction ID	Reaction	Chemical reaction
R1	Char combustion	$C + O_2 \rightarrow CO_2$ (− 394 kJ/mol)
R2	Partial oxidation	$C + 0.5O_2 \rightarrow CO$ (− 111 kJ/mol)
R3	Boudouard reaction	$H_2 + 0.5O_2 \rightarrow H_2O$ − 242 kJ/mol
R4	Char reforming	$C + CO_2 \leftrightarrow 2CO$ (+ 172kJ/mol
R5	Char reforming	$C + H_2O \leftrightarrow CO + H_2$ + 131 kJ/mol)
R6	Methane reforming	$CH_4 + H2O \leftrightarrow CO + 3H_2$ (+ 206 kJ/mol)
R7	Water-gas-shift reaction	$CO + H_2O \leftrightarrow CO_2 + H2$ (− 41 kJ/mol)
R8,R9	Methanation	$C + 2H_2 \leftrightarrow CH_4$ (− 75 kJ/mol) $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ (− 165 kJ/mol)
R10	Dry reforming	$2CO + 2H_2 \leftrightarrow CH_4 + CO_2$ (− 247 kJ/mo)

3.4. GASIFIER REACTOR TYPES

According to how they interact gas and solids, gasifiers can be divided into three categories: entrained-flow bed gasifiers, fluidized bed gasifiers, and fixed or moving bed gasifiers (Basu, 2010).

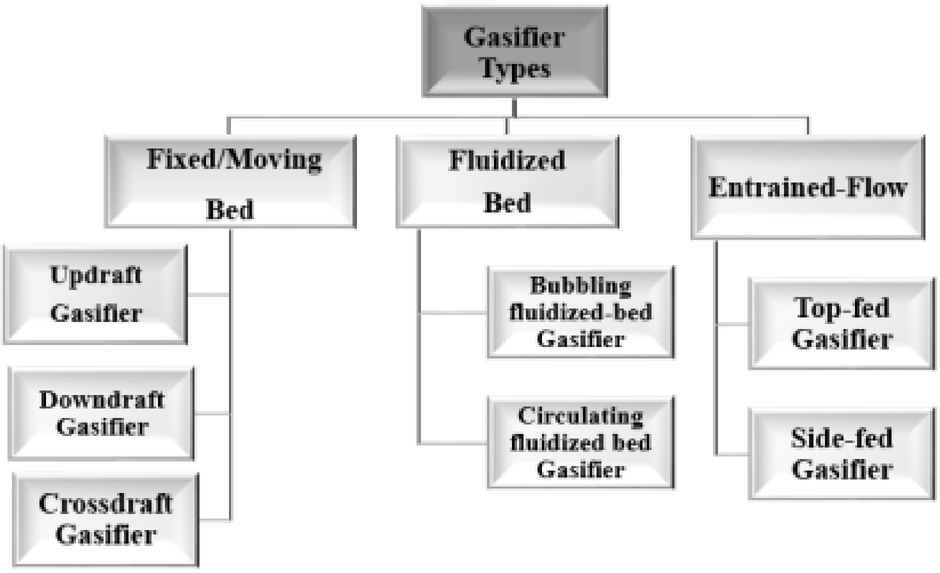


Figure 3.5. Gasifier Type (Basu, 2010).

3.4.1. Fixed-Bed/Moving Bed Gasifiers

Fixed-bed or moving-bed gasifiers are the most used types of gasifiers for producing synthesis gases. This kind of gasifier is easy to build and operate. Moreover, fixed-bed gasifiers can be made in small quantities. These advantages lead to their widespread use in industry, a stream of hot gas or sand suspends and fluidizes biomass particles in a fluidized-bed reactor. Better heat transmission and mixing are provided by this arrangement, which leads to faster heat transfer rates and shorter residence times. It does, however, necessitate close attention to the particle size distribution and fluidization velocity.

3.4.2. Downdraft Gasifiers

Biomass is fed into a downdraft gasifier from above, and as air and biomass flow downstream, syngas is produced at the bottom. A downdraft gasifier's schematic is displayed in Figure 3.6 (a). There are typically 12 phases in the gasification process. The evaporation process lowers the fuel's moisture content during the drying phase of a standard downdraft gasifier (>150°C). The heat it absorbs during pyrolysis (between 200°C and 500°C) forms products like coal and Burned gases are released during the combustion or oxidation of coal and other combustible materials, which occurs between 700°C and 1500°C. These high-temperature gases supply the heat required for the subsequent stages. The gasification reactions take place in the reduction phase (between 650°C and 900°C) (Basu, 2010).

3.4.3. Updraft Gasifier

Figure 3.6 (b) shows the updraft gasifier in action. These gasifiers have a grate at the bottom that feeds the air, and a top that delivers the feed. Feed and air move counter now in the gasifier. The gasifier's lowermost portion is essentially the "Combustion" zone, which is the place where the char that is produced as biomass dries and devolatilizes is burned. This causes the temperature of the gasifier's bottom section to rise to about 727 °C. Hot gases passing through the bed of down flowing biomass are reduced in the region directly above the combustion zone. The biomass is pyrolysed and dried by the hot gases higher up in the gasifier.

The temperature of the gases is lowered by these processes to between 200 and 300. (Choudhury et al., 2015).

3.4.4. Crossdraft Gasifier

The cross-draft gasifier, depicted in Figure 3.6(c), is a co-current moving-bed reactor where fuel is supplied from above and air is injected from the side via a nozzle. Its main application is in low-ash charcoal gasification. A nozzle positioned a predetermined distance above the grates allows high-velocity air to enter the gasifier. A highly hot zone (>1500 °C) is created in front of the nozzles due to the increased oxygen, which promotes oxidation and char combustion. The remaining char is gasified into CO in the next zone. On the other side of the gasifier, the product gas emerges. As the biomass moves through the pyrolysis zone, heat 13 from the combustion zone is directed around it, pyrolyzing the biomass (Basu, 2010).

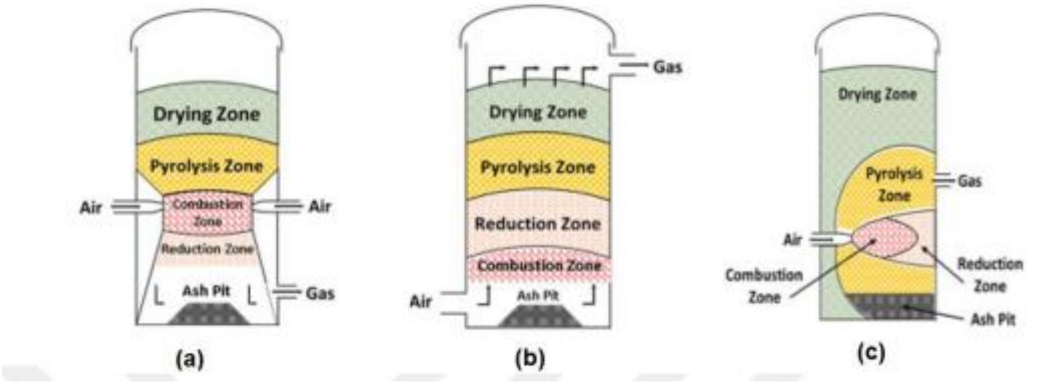


Figure 3.6. Schematic of (a) downdraft gasifier (b) updraft gasifier (c) cross-draft gasifier (Kumari & Karmee, 2022).

3.5. CONCEPT OF SUPERCRITICAL GASIFICATION

Supercritical gasification is the process of using supercritical fluids (water or steam) under supercritical conditions to turn a material, usually biomass or waste, into syngas (synthesis gas). Above the substance's critical point, at high pressures and temperatures, supercritical conditions arise where the substance exhibits characteristics of both a liquid and a gas. With the help of this process, biomass and trash can be efficiently converted into syngas, which can be utilized to make a variety of useful chemicals and fuels. It has benefits like decreased tar accumulation, more efficiency, and the possibility of producing cleaner energy (Thiounn & Smith, 2020).

3.5.1. Supercritical Gasification Process and Its Unique Properties

In the supercritical gasification process, organic materials are subjected to high temperatures and pressures in the presence of a supercritical fluid, which acts as an oxidizing and gasifying agent. Organic materials decompose into combustible gases, primarily hydrogen, carbon monoxide and methane, along with other gases such as carbon dioxide and water (Kumar & Sharma, 2017).

Supercritical gasification involves operating the gasification process under supercritical water conditions (temperature above 374°C and pressure above 22.1 MPa). Supercritical water exhibits unique properties, such as high density, low viscosity, and enhanced solubility, which significantly influence the gasification reactions. This approach offers advantages over conventional gasification methods, including faster reaction rates, improved biomass conversion, and increased hydrogen yields (Lachos-Perez et al., 2017).

3.5.2. Advantage of Supercritical Water Gasification

Supercritical gasification is a promising alternative to conventional methods, combining the advantages of liquid and gas states. It offers increased efficiency, reduced tar production, and the ability to process diverse feedstocks. Its environmental footprint is lower, with reduced pollutant emissions and carbon capture opportunities. The technology can reduce feedstock pre-processing and plant size, leading to cost savings. However, initial capital costs, equipment complexity, and scaling challenges remain (Sikarwar et al., 2017).

3.6. PARAMETERS AFFECTING SUPERCRITICAL GASIFICATION

Supercritical gasification is a cutting-edge technology that holds immense promise for efficiently converting biomass and other carbonaceous materials into valuable syngas. Understanding the various parameters influencing the supercritical gasification process is crucial for optimizing its efficiency, enhancing product yields, and minimizing environmental impacts (Muhammed et al., 2023).

3.6.1. Temperature

One of the key parameters in supercritical gasification is temperature. Elevated temperatures in the supercritical range (above the critical temperature and pressure of the working fluid) have been shown to enhance reaction kinetics, leading to higher conversion rates and improved gasification efficiency. However, the particular feedstock and gasification conditions determine which temperature range is ideal (Chu & Majumdar, 2012).

3.6.2. Pressure

In supercritical gasification, pressure is essential because it affects how the reactants and products behave in phase. Increased pressures have an impact on mass transfer rates, reaction kinetics, and reactant solubility. High pressures under supercritical circumstances can improve feedstock component solvation, increasing reactivity and encouraging the synthesis of particular gasification products. Furthermore, pressure has an effect on the supercritical fluid's phase behaviour, modifying its density and viscosity, which can then have an impact on how reactants and products are transported. Thus, the effectiveness, selectivity, and general performance of supercritical gasification processes are all highly dependent on pressure (Sikarwar et al., 2017b).

Greater solubility of reactants in the supercritical fluid may be encouraged by higher pressures, which could improve mass transfer and reaction speeds. For practical applications, though, the trade-off between pressure and energy consumption must be carefully evaluated (Osman et al., 2020c).

Finaly due to the supercritical conditions in which the experiment is conducted, increasing pressure exactly the reactor pressure leads to a decrease in the amount of pure hydrogen produced but an increase in CH_4 (Withag et al., 2012b).

3.6.3. Feedstock composition

The kind and makeup of the feedstock have a big influence on supercritical gasification. Numerous investigations have looked into how coal, waste products, and various biomass sources gasify under supercritical circumstances. The feedstock's moisture content, ash content, and volatile matter content might affect the process's overall efficiency, product distribution, and gasification kinetics (Osman et al., 2020b). The reaction kinetics, gasification efficiency, and product composition are all influenced by the chemical and physical characteristics of the feedstock. For example, the quality of the gasification products and the reaction pathways might be impacted by the presence of specific organic molecules or contaminants. Understanding and adjusting the feedstock composition is essential for attaining efficient and selective supercritical gasification. In addition, the reactivity and ash content of the feedstock might affect the overall performance and selectivity of the gasification process.

3.6.4. Catalysts

Catalysts can play a crucial role in supercritical gasification by promoting desirable reactions and suppressing unwanted side reactions. Catalysts can affect the gasification processes' activation energy under supercritical circumstances, speeding up the conversion of feedstock into the intended products. Catalysts can also minimize undesirable by-products while selectively promoting the synthesis of specific gasification products. Their existence can make it possible to use lower pressures and temperatures, improving the selectivity and efficiency of the operation. As a result, catalysts are essential in determining the results of supercritical gasification since they affect the process's overall performance, efficiency, and reaction selectivity.

3.6.5. Residence Time

One important factor that affects the results of gasification is residence time, or the amount of time reactants spend in the supercritical state. Longer times enhance interaction between feedstock and fluid, leading to increased conversion and efficiency. Shorter times limit conversion and affect product selectivity. Optimizing residence time is crucial for achieving desired outcomes. (Antal et al., 2000).

3.6.6. Supercritical Fluid Properties

The choice of supercritical fluid, like CO_2 or water, can have a big impact on the results of gasification. Researchers have researched the thermophysical properties and solubility characteristics of different supercritical fluids to understand their impact on reaction kinetics and product dispersion. Research on the possibilities of new supercritical fluids is still under progress (Knez et al., 2019).

In conclusion this part provides a comprehensive overview of the key parameters affecting supercritical gasification. Although significant progress has been made, much remains to be done to further explore and optimize these parameters to unlock the full potential of supercritical gasification for sustainable and efficient energy production. Future research should focus on integrating experimental and computational approaches to advance our understanding and facilitate the practical implementation of this promising technology.

3.7. SUPERCRITICAL FLUIDS AND THEIR APPLICATIONS

The versatile and unique properties of supercritical fluids (SCF) have been a subject of considerable interest within the scientific community, prompting extensive exploration of their applications across diverse industrial processes. Supercritical fluids, often exemplified by carbon dioxide (CO_2) or water (H_2O) at critical temperature and pressure conditions, occupy a distinctive state between gas and liquid, rendering them particularly suitable for numerous applications. This review delves into the extensive body of literature surrounding the remarkable attributes of supercritical fluids and their implications across various industries.

Key among the notable characteristics is the high diffusivity exhibited by supercritical fluids. This property allows for efficient penetration into porous materials, facilitating enhanced mass transfer within complex structures. Additionally, the low viscosity of these fluids facilitates their seamless flow through intricate pathways, a feature that contributes to their applicability in a spectrum of industrial settings.

Another pivotal aspect of supercritical fluids is their tuneable solvation properties, offering researchers a versatile tool for selective extraction and separation processes. This versatility is exemplified in the realm of biomass conversion, where supercritical fluids, owing to their ability to selectively dissolve specific components, play a pivotal role in extracting valuable compounds from natural sources.

SCF, characterized by their unique properties between those of a gas and a liquid at critical temperature and pressure conditions, have emerged as versatile media for various applications. Supercritical fluids offer distinct advantages, including high diffusivity, low viscosity, and tuneable solvation properties, making them attractive for biomass conversion processes (Chémat et al., 2019b).

3.8. CATALYTS OF BIOMASS GASIFICATION

Catalysts in biomass gasification can significantly impact the gasification performance and product distribution. They promote the activation of biomass molecules, facilitate tar cracking and reforming, and improve the overall reaction kinetics. Metal catalysts, in particular, exhibit high catalytic activity and stability, enabling efficient tar reduction, enhanced hydrogen production, and lower carbon deposition rates. The addition of catalysts also aids in the control of gasification parameters, such as temperature and residence time, to optimize the gasification process (Ennaert et al. 2016b).

Table 3.2 lists a few biomass elements that have been continuously gasified for the production of H_2 in SCW. The incoming biomass slurry from one side of the T-junction, where SCW is being supplied.

Table 3.2. Studies on supercritical water gasification of biomass and its constituents in batch reactors Reddy et al. (2014).

Feedstock	**Operating conditions**[a]	**Catalyst**	**H_2 yields**
Glucose	400 °C, 24.5 MPa, 9.1 wt.%	–	1.3 mol/kg
		Ni/γ-Al_2O_3	10.5 mol/kg
		Ni/CeO_2-γ-Al_2O_3	12.7 mol/kg
	400 °C, 22.5–25 MPa, 20 min	Ni–Mg–Al	7.2–11.8 mol/kg
	400–600 °C, 25 MPa, 60 min, 5 wt.%	K_2CO_3	1.5 mol/mol
	550 °C, 36 MPa, 10 min, 6.7 wt.%	Ru/α-Al_2O_3	10.8 mol/kg
		Ru/α-Al_2O_3/NaOH	21.1 mol/kg
		Ru/α-Al_2O_3/CaO	14.7 mol/kg
	400–600 °C, 20–42.5 MPa, 60 min, 0.4 M	–	2.2 mol/mol
		K_2CO_3	3.9 mol/mol
Cellulose	550 °C, 36 MPa, 10 min, 6.7 wt.%	Ru/α-Al_2O_3/CaO	9.1 mol/kg
	500–600 °C, 0.05–0.2 g/cm^3, 10 min, 5–33 wt.%	Ni, Cu and Fe	0.3–2.2 mol/kg
	365–500 °C, 0.05–0.2 g/cm^3, 10–30 min, 1–33 wt.%	–	0.1–2.9 mol/kg
Xylan (Hemicellulose)	550 °C, 36 MPa, 10 min, 6.7 wt.%	Ru/α-Al_2O_3/CaO	10.7 mol/kg
Lignin	365–725 °C, 0.05–0.2 g/cm^3, 2.5–75 min, 1–33 wt.%	–	0.1–7.5 mol/kg

Feedstock	Operating conditions[a]	Catalyst	H_2 yields
	500–600 °C, 0.05–0.2 g/cm^3, 15 min, 5–33 wt.%	Ni, Cu and Fe	0.9–2.7 mol/kg
Sawdust	550 °C, 36 MPa, 10 min, 6.7 wt.%	$Ru/\alpha\text{-}Al_2O_3/CaO$	10.4 mol/kg
Sugarcane bagasse	400 °C, 0.3 g/cm^3, 15 min, 0.1 g	–	0.5 mol/kg
		Ru/TiO_2	3.2 mol/kg
	400 °C, 0.5 g/cm^3, 15 min, 0.1 g	Ru/AC	1.92 mol/kg
Sea weed	500 °C, 30.2–33.5 MPa, 60 min, 5 wt.%	–	11.8–16 g/kg
Hog manure	500 °C, 31 MPa, 30–90 min, 28–57 g/L	Pd/AC, Ru/Al_2O_3, Ru/AC, AC, NaOH	0.4–0.5 mol/kg

a Operating conditions (in the sequence) refers to temperature, pressure, residence time and feed concentration. AC: activated carbon.

Since hydrogen is not a naturally occurring source of energy, it must be created through a variety of processes from numerous sources. Large amounts of greenhouse gas emissions are produced during the production of H_2 from non-renewable energy sources such coal, natural gas, and oil. Modern technology is used to transform renewable energy sources like wind, sun, and biomass into fuels. The lack of net CO_2 emissions from biomass, lower operating costs, and improved efficiencies encourage us to consider SCWG as a suitable technology for handling a wide range of biomass.

In comparison to conventional gasification methods, which necessitate enormous quantities of energy for biomass pre-treatments such drying, SCWG of biomass has the benefit of direct utilisation of wet biomass. Another benefit of high pressure SCWG is the creation of H_2, which lowers the cost of gas compression and separates CO_2 from the final gases. Therefore, efforts are focused on producing H_2 from biomass in an environmentally acceptable manner to meet the current energy needs. High temperatures and pressure call for advanced materials that can withstand harsh circumstances as well as expensive operating expenses for high pressure processes. In SCWG of biomass, plugging and char development are major issues. Because inorganic salts are less soluble under SCW conditions, their precipitation during SCWG of biomass is more likely. Fluidized bed SCW gasification of biomass is used. The development of an effective SCWG system is still ongoing due to the complexity and interaction of the process elements.

Another obstacle to overcome is pumping biomass at increasing quantities. For the biomass to pump its slurry effectively, the biomass must be broken down into tiny particles. Equipment with high energy recovery efficiency is required to optimize the SCWG process. In order to efficiently hydrothermally degrade biomass into gases, water must be heated and mixed with the biomass.

The operating settings that produce the highest H_2 yields are decreased when catalysts are used in SCWG. Although Ni and Ru, in particular, are used in the SCWG of biomass to increase H_2 production, they are also discovered to be active in methanation processes that produce CH_4. Currently, the cost of producing hydrogen from biomass directly gasified is over three times greater than the cost of producing hydrogen from natural gas reforming. US$/kg, however it costs 10 to 14 US$/GJ to produce biomass. The low-cost lignocellulosic biomasses, on the other hand, provide benefits such as direct use, strong H_2 production, and no Sulphur removal from the product gases. Furthermore, the H_2 created by the gasification of biomass has a net increased heating value and an energy efficiency of 56 to 64% (Reddy, Nanda, Dalai, & Kozinski, 2014).

Although natural gas for SMR is more expensive than SCWG's feedstock, the operating and capital expenses for high-pressure SCW systems are considerable. The current commercial application of SMR from natural gas is constrained by a lack of technology that has been shown to produce H_2 on a wide scale from SCWG of biomass with net positive energy. Since drying is not necessary with the new supercritical water gasification (SCWG) technique, it has shown out to be more effective than traditional ones. SCWG can be utilized for biomass with high water content and substantially avoids drying issues. This results in generally better SCWG conversion efficiencies than those of traditional technologies, enabling the production of syngas with higher hydrogen concentration. Another study conducted by Lachos-Perez D., Juliana M. Prado, Torres-Mayanga P, Tânia Forster-Carneiro1, M. Angela A. Meireles in 2015 on 'Supercritical Water Gasification of Biomass for Hydrogen Production: Variable of the Process ' which reviews the main known and emerging properties of supercritical water that influence the SCWG of biomass (viscosity, density, dielectric constant and ion product), the advantages of SCWG over conventional gasification, the efficiency of the process. This article deals with the factors influencing the process (temperature, pressure, residence time, concentration, catalyst effect, effect of reactor geometry, reactor design, heating rate and type of biomass particles).

Particularly in the absence of a catalytic converter or in the presence of less efficient catalysts, temperature has a substantial impact on the SCWG of biomass. According to the main gasification product, pressurized water gasification may actually be separated into three classes (table 3.3).

Table 3.3. Division of hydrothermal reaction by temperature reaction Reddy et al. (2014).

Feedstock	Operating conditions[a]	Catalyst	H_2 yields
Glucose	550–650 °C, 23–27 MPa, 5–30 wt.%	–	2.5–7.7 mol/kg
Corn cob	550–650 °C, 23–27 MPa, 5–18 wt.%	–	2.6–12 mol/kg
Sewage sludge	480–540 °C, 25 MPa, 4–12 wt.%	KOH, K_2CO_3, NaOH, Na_2CO_3	1.9–15.5 mol/kg

Operating conditions (in the sequence) refers to temperature, pressure and feed concentration.

Finally, they concluded, "supercritical water gasification" technology has great potential to produce clean biogas with high hydrogen content in various types of biomass, thereby utilizing pollution and CO_2 emissions.

A key revelation from the experiments is the consistent carbon gasification efficiency of 60.3 ± 5.1% across the different biomasses, with gas compositions displaying remarkable similarities. Notably, the study introduces the influence of potassium hydroxide addition as a homogeneous catalyst, demonstrating its potential to enhance gasification efficiency. However, the concurrent risk of system plugging due to the formation of solid deposits is identified, particularly with the addition of potassium (Julian Dutzi et al,.2024).

PART 4

EXPERIMENTAL METHODOLGY

4.1. PRESENTATION OF THE SYSTEM

A fixed bed pyrolysis system has three types of reactors: fixed bed reactors, fluidized bed reactors, and entrained reactors. A variety of criteria influence reactor type selection, such as technological improvement, fuel type, product application, and installation size. Fixed bed reactors are appropriate for small, decentralized power plants (less than 5 MW) that are close to the biomass production facilities that supply the reactors with materials like agricultural and wood waste. Additionally, compared to fluidized bed reactors (0.1 to 0.6 mm) or nozzle reactors (0.01 to 0.03 mm), fixed bed reactors use significantly larger particle sizes (0.5 to 5 cm), which lowers the cost of grinding and processing biomass. Fixed bed processes are generally simpler and more robust in construction. In these processes, a dense bed is moved vertically inside a reactor (Karl and Pröll ,2018).

This section introduces the system used to produce supercritical hydrogen from biomass gasification. The Fischer reactor, the Moisture and Volatile Content Device, and the Sulphur Rate Determination Device (Leco SC-144DR) are the three main parts of the system. To ensure the effectiveness, dependability, and environmental friendliness of the biomass-to-hydrogen conversion process, each component is essential to the overall process of gasification of biomass and production of hydrogen. The goal of this section is to give a thorough understanding of these parts, their functions, and the importance of each to the system.

4.2. SYSTEM DESCRIPTION

4.2.1. Moisture and Volatile Content Device

One crucial part of the apparatus used to determine the moisture and volatile content of the biomass feedstock is the Moisture and Volatile Content Device. It guarantees that before the feedstock enters the Fischer reactor, it is appropriately conditioned. The apparatus employs many methodologies, including gas chromatography and thermogravimetry, to precisely ascertain the biomass's volatile composition and moisture content.

It is important to regulate the moisture content since too much moisture can cause poor gasification and more tar production. Analysing the biomass's energy content and reactivity is aided by the measurement of its volatile content. The system can improve the production of hydrogen and optimise the gasification process by closely monitoring and modifying these parameters.

Figure 4.1. Moisture and volatile content Device.

The moisture and volatile matter device, also known as a moisture analyzer or moisture balance, is a laboratory instrument used to measure the moisture content or volatile matter content of a sample. It works by heating the sample (almond shell or coal) and measuring the weight loss as moisture or volatile components evaporate. This information is important in industries such as food, pharmaceuticals, and agriculture for ensuring product quality and compliance with standards. The device provides quick and accurate results, making it a valuable tool for various applications.

4.2.2. Fischer Reactor

The Fischer reactor is the central component of the biomass hydrogen production system. It is named after Franz Fischer, who developed the Fischer-Tropsch process in the early 20th century. The reactor facilitates the conversion of biomass feedstock into a synthesis gas, commonly known as syngas, through a series of chemical reactions (Martín, 2016).

The Fischer reactor operates under supercritical conditions, where the reactants are exposed to high temperatures and pressures. This state allows for a more efficient conversion of biomass into syngas (Newman & Jensen, 2013). The reactor consists of a high-pressure vessel, a catalyst bed, and a heating system. The catalyst bed, typically composed of iron-based catalysts, promotes the desired reactions, such as carbon gasification and water-gas shift reactions, leading to the production of hydrogen-rich syngas as illustrated in Figure 4.2.

Figure 4.2. Fischer reactor.

4.2.3. Sulphur Rate Determination Device (Leco SC-144DR)

The Sulfur Rate Determination Device used in the system is the Leco SC-144DR. This device is specifically designed to measure the sulfur content in solid and liquid samples. It utilizes combustion techniques coupled with infrared detection to accurately quantify the sulfur present in the biomass feedstock.

The Leco SC-144DR employs a high-temperature furnace to combust the sample, converting sulfur compounds into sulfur dioxide (SO_2). The released SO_2 gas is then carried through a series of chemical reactions and analyzed using infrared detection methods. The device provides precise and reliable measurement of sulfur content, allowing for effective sulfur management in the biomass gasification process.

Accurate determination of sulfur content is essential as sulfur can have detrimental effects on the performance of catalysts (if catalyst is added) used in the Fischer reactor. High sulfur levels can lead to catalyst poisoning, reduced activity, and increased maintenance requirements. By utilizing the Leco SC-144DR, the system can monitor and control sulfur levels, enabling optimal operation and prolonged catalyst live.

Figure 4.3. Sulfur Rate Determination Device (Leco SC-144DR).

4.3. COMPONENTS

4.3.1. Almond Shell

As a kind of biomass nutshell, almonds are commonly grown in China, India, Pakistan, and Iran, among other parts of the world. Three million tons of almonds were produced annually worldwide as of 2014 (statistics). Since almond shells make up between 35 and 75 percent of the weight of the fruit overall, between 10.5 and 22.5 million tons of shells remained (Ebringero & Hromádková 2007). Almond shells have a well-developed pore structure as illustrated in figure 4.4 with large holes ranging in diameter from 300-500 µm. The area around these holes is dense but filled with small hollow balls. Under SEM, almond shells are tightly compacted with diameters of 40-60 µm and a visibly layered wall. These holes make the shell light and potentially absorbable (Li et al., 2018).

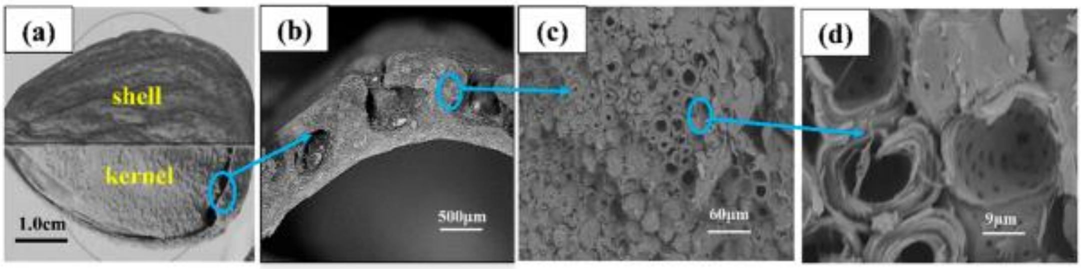
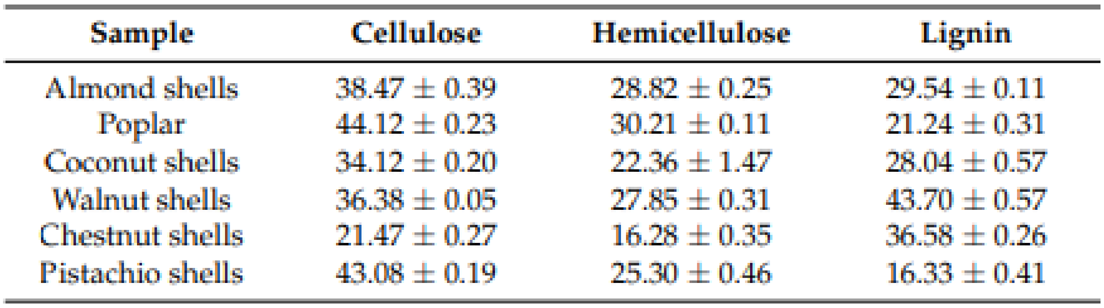


Figure 4.4. Almond shell micro-topography. (a) Overall view; (b) Cross-section of shell; (c) Dense part of almond shell; (d) Hollow ball in the almond shell.

Almond shells have a cellulose content of 38.475%; this is higher than other shells, with the exception of pistachio shells, which have a cellulose value of 44.12% (Table 4.1). This suggests that the mechanical qualities of the composite made from almond shells may be better than those of the majority of biomass-derived nut shells (Xinyuan et al., 2015).

Table 4.1. Proportion of cellulose, hemicellulose, lignin in six kinds of biomass (wt %).



Sample	Cellulose	Hemicellulose	Lignin
Almond shells	38.47 ± 0.39	28.82 ± 0.25	29.54 ± 0.11
Poplar	44.12 ± 0.23	30.21 ± 0.11	21.24 ± 0.31
Coconut shells	34.12 ± 0.20	22.36 ± 1.47	28.04 ± 0.57
Walnut shells	36.38 ± 0.05	27.85 ± 0.31	43.70 ± 0.57
Chestnut shells	21.47 ± 0.27	16.28 ± 0.35	36.58 ± 0.26
Pistachio shells	43.08 ± 0.19	25.30 ± 0.46	16.33 ± 0.41

The Fourier-transform infrared FTIR spectra of poplar and almond shells, as presented in the Table 4.1, indicate a high degree of similarity between their chemical composition, mostly consisting of cellulose, hemicellulose, and lignin. (Jian et al., 2003).

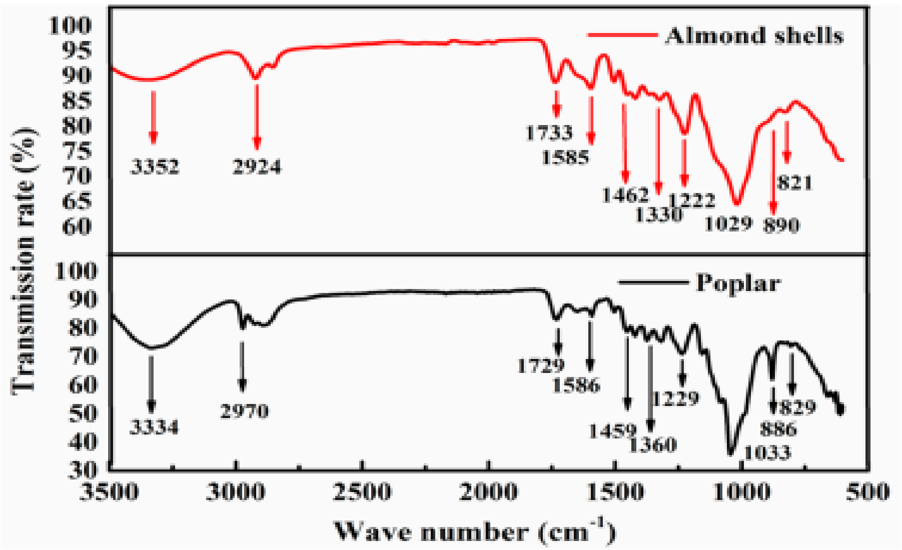
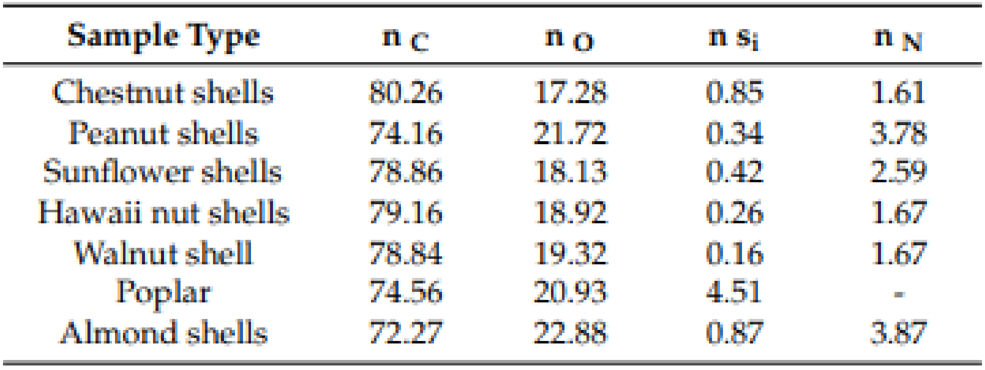


Figure 4.5. Infrared spectra of almond shells and polar.

The primary chemical components found in almond shells are largely the same as those found in other nuts, as Table 4.2 illustrates. Almond shells have a higher oxygen concentration and a lower carbon content than those of Chinese chestnut, peanut, sunflower, Hawaii nut, and walnut shells. Nut shells often have higher nitrogen content and lower silicon content as compared to poplar. Because nitrogen can be a flame-inhabitant, almond shells may consequently have an advantage in terms of fire resistance when creating composite materials (Li et al., 2018).

Table 4.2. Surface chemical composition and relative content of nut and poplar (wt. %).



Sample Type	n_C	n_O	n_{Si}	n_N
Chestnut shells	80.26	17.28	0.85	1.61
Peanut shells	74.16	21.72	0.34	3.78
Sunflower shells	78.86	18.13	0.42	2.59
Hawaii nut shells	79.16	18.92	0.26	1.67
Walnut shell	78.84	19.32	0.16	1.67
Poplar	74.56	20.93	4.51	-
Almond shells	72.27	22.88	0.87	3.87

4.3.2. Coal

Carbon makes up the majority of the complex biological sedimentary rock known as coal, although it also contains different proportions of hydrogen, oxygen, nitrogen, Sulphur, and other elements as illustrated in table 4.3. Four general categories can be used to group its constituent parts: ash, volatile matter, fixed carbon, and moisture. The term "moisture" describes the amount of water that is contained in coal, which can vary based on the type of coal and its geological past from a few percent to forty percent or more. The gases and vapours that are emitted when coal is heated, such as hydrocarbons, carbon dioxide, carbon monoxide, and other Sulphur and nitrogen compounds, are referred to as volatile matter. The solid residue that remains after volatile stuff has been removed is called fixed carbon, and it is mostly made up of carbon with lesser amounts of hydrogen, oxygen, and nitrogen. The inorganic mineral stuff known as ash is what's left over after coal is burned; it usually contains trace amounts of silica, alumina, iron, calcium, and potassium. The qualities and application of coal in different industrial processes can be greatly impacted by the relative quantities and composition of these constituents.

Table 4.3. Petrographic composition, basic chemical and technological parameters of the examined coal.

Property	**Value**
(a) Proximate analysis (mass %) (Zhang et al. 2023)	
Moisture	9.79
Ash	11.93
Volatile	42.69
Fixed Caron	35.59
Carbon content	60.86
Hydrogen content	4.58
Sulphur content	0.77
Nitrogen content	1.67
(b) Petrographic composition (vol%) (Liu et al. 2021, Qu et al. 2018)	
Huminite in organic matter	78.6
Liptinite in organic matter	2.5
Inertinite in organic matter	18.9
Inorganic matter	1.8–3.2

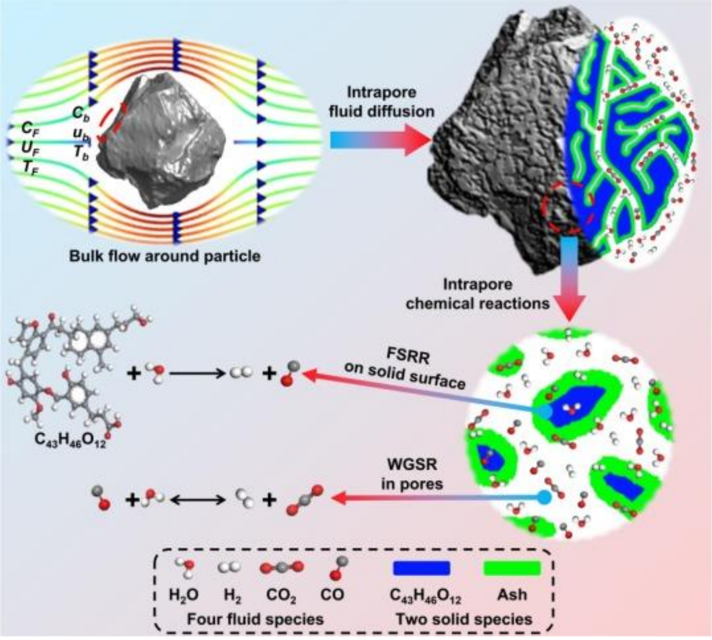


Figure 4.6. The reactive fluids transport process at the pore scale in the SCWG of single coal particle of real shape in a simple steady bulk flow composed of multi-species supercritical fluid (Zhao et al., 2024).

4.4. THERMODYMIC ANALYSIS

In our study, we used Gibbs free energy minimization to model the combined supercritical water gasification and reforming process. Many studies have found that the Gibbs free energy minimization modelling technique corresponds to experimental results (Tang & Kitagawa, 2005), (Yan et al., 2006), and (Withag et al., 2012). Given the intricacies of SCWG and reform processes, this method is favoured for calculating probable product components in the absence of reaction information. Table 4.4 displays the primary chemical processes that occur during the SCWG and reforming process.

Table 4.4. Summary of the chemical reactions in supercritical water gasification (Hantoko et al., 2018).

Reaction type	Stoichiometric reaction equation	ΔH_{298K} (MJ/kmol)	Reaction number
Simplified overall reaction of SCWG	$CH_xO_y + (2-y)H_2O \rightarrow CO_2 + (2-y+x/2)H_2$	Endothermic	R1
Water gas shift reaction	$CO+H_2O \leftrightarrow CO_2 + H_2$	−42	R2
Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$	+172	R3
Steam methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206	R4
Dry reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	+247	R5
Methane formation	$C + 2H_2 \leftrightarrow CH_4$	−74	R6
Methanation of CO_2	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	−165	R7
Methanation of CO	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	−206	R8
Hydrogenation of CO_2	$CO_2 + 2H_2 \leftrightarrow C + 2H_2O$	−90	R9
Hydrogenation of CO	$CO + H_2 \leftrightarrow C + H_2O$	−131	R10

4.4.1. Gibbs Free Energy

When a multicomponent combination achieves chemical equilibrium, the Gibbs free energy is at its lowest. The minimum in Gibbs energy occurs when the Gibbs energy of reaction ($\Delta_r G$) reaches zero. The Gibbs energy of reaction is defined as the change in Gibbs energy with respect to the extent of the reaction (Hantoko et al., 2018).

$$\Delta_r G = \frac{\partial G}{\partial \xi} \tag{4.1}$$

Where ξ represents the reaction's extent. The fact that the Gibbs energy of the reaction is not zero implies that there must be a point with lower Gibbs energy (G). In this situation, the multicomponent mixture will achieve a state with the lowest Gibbs energy. A reaction's change in Gibbs energy is the difference between the sums of the reactants' and products' chemical potentials.

$$\Delta_r G = \sum_{j=1}^{n} \mu_j n_j \tag{4.2}$$

In Eq. (2), n_j and μ_j are the molar number and the chemical potential of component j. The equation for conservation of elements can be written as:

$$\sum_{j=1}^{n} a_{ij} n_j - b_i^0 = 0, \quad \mathrm{i} = 0, \ldots, \mathrm{l} \tag{4.3}$$

Where aij is the molar number of element i in compound j, and b^0_i is the molar number of element i in the starting reactant. When a multicomponent system achieves chemical equilibrium, the Gibbs free energy is at its lowest point. Minimising the Gibbs free energy of a system with fixed T and P is a straightforward restricted optimisation problem. The constraint can be removed using the Langrange multiplier approach.

Where b^0_i is the molar number of element i in the initial reactant and a_{ij} is the molar number of element i in compound j. At chemical equilibrium, a multicomponent system has the lowest Gibbs free energy. Taking a system with fixed T and P and minimizing its Gibbs free energy is a straightforward optimization problem with constraints. The Langrange multiplier method can be used to eliminate the limitations.

$$\mu_i\,(T,p) = \mu_i^0(T) + \mathrm{RT}\ \ln f_i \tag{4.4}$$

To determine the chemical potential of component μ_i the Eq. (4) is used.

Where $\mu_i\,(T,p)$ is the chemical potential of component i in standard state, R is the ideal gas constant, and f_i is the partial fugacity of component i.

PART 5

RESULTS AND DISCUSSION

5.1. CHARACTERIZATION OF BIOMASS FEEDSTOCK

In our study, we conducted supercritical gasification experiments on two biomass types: coal and almond shell. The first experiment involved gasifying one kilogram of coal, the second experiment involved gasifying one kilogram of almond shell, and the third experiment utilized a mixed sample of 0.5 kg coal and 0.5 kg almond shell. The initial and dry sample conditions for each biomass type were analyzed to determine their moisture, ash, volatile substance, fixed carbon, sulfur content, and hydrogen yield.

Table 5.1. Experimental results of coal sample.

Properties	**Initial sample**	**Dry sample**
Moisture (Wt. %)	19.5	0
Ash (Wt. %)	14.9	18.56
Volatile substance (Wt. %)	36.51	45.36
Fixed Carbon (Wt. %)	29.05	36.09
Sulfur content (Wt. %)	1.34	1.67
Hydrogen yield (Wt. %)	2.98	3.71
Lower Calorific Value (kCal/kg)	3825	4893
Upper Calorific Value (kCal/kg)	4094	4918

The initial sample of coal contained moisture content of 19.5%, ash content of 14.9%, volatile substances of 36.51%, fixed carbon content of 29.05%, Sulphur content of 1.34%, and hydrogen yield of 2.98%. While the dry sample contained ash content, it increased to 18.56%, volatile substances to 45.36%, fixed carbon to 36.09%, Sulphur content to 1.67%, and hydrogen yield to 3.71%. Its lower calorific value (LCV) was 4893 kcal/kg, and its upper calorific value (UCV) was 4918 kcal/kg.

Table 5.2. Experimental results of almond shell.

Properties	Initial sample	Dry sample
Moisture (Wt. %)	9.56	0
Ash (Wt. %)	1.14	1.26
Volatile substance Wt. %)	75.29	83.25
Fixed Carbon (Wt. %)	14.02	15.50
Sulphur content (Wt. %)	0.23	0.25
Hydrogen yield (Wt. %)	5.32	5.88
Lower Calorific Value (kcal/kg)	4011	4497
Upper Calorific Value kcal/kg	4344	4803

The initial sample of almond shell had the following composition: moisture content was 9.56%, ash was 1.14%, volatile substances were 75.29%, fixed carbon was 14.02%, Sulphur content was 0.23%, and hydrogen yield was 5.32%. And the dry sample contained: ash content increased to 1.26%, volatile substances to 83.25%, fixed carbon to 15.50%, Sulphur content to 0.25%, and hydrogen yield to 5.8. Its LCV was 4497 kcal/kg, and its UCV was 4803 kcal/kg.

Table 5.3. Experimental results of %50 coal and %50 almond shell mixed sample.

Properties	Initial sample	Dry sample
Moisture (Wt. %)	16.10	0
Ash (Wt. %)	8.50	10.19
Volatile substance (Wt. %)	52.81	63.32
Fixed Carbon (Wt.%	22.10	26.50
Sulphur content (Wt. %)	0.66	0.79
Hydrogen yield (Wt. %)	3.97	4.76
Lower Calorific Value (kcal/kg)	3798	4670
Upper Calorific Value kcal/kg	4102	4918

The initial sample had the following composition: 16.10% moisture, 8.50% ash, 52.81% volatile chemicals, 22.10% fixed carbon, 0.66% Sulphur, and 3.97% hydrogen yield.

Dry sample: increases in fixed carbon to 26.50%, Sulphur content to 0.79%, hydrogen yield to 4.76%, volatile compounds to 63.32%, and ash content to 10.19%. Its LCV was 4670 kcal/kg, and its UCV was 4918 kcal/kg.

5.2. GASIFICATION PERFORMANCE

The gasification performance was evaluated based on the yield and composition of hydrogen produced from each biomass type. The results indicate that almond shell produced the highest hydrogen yield, followed by the mixed sample and then the coal sample. The efficiency of gasification was influenced by the inherent properties of each biomass type, including moisture content, volatile substances, and fixed carbon content.

5.3. HYDROGEN YIELD AND COMPOSITION

The hydrogen yield was measured in both initial and dry sample conditions. Almond shell demonstrated the highest hydrogen yield of 5.88% in dry conditions, which is significantly higher than coal (3.71%) and the mixed sample (4.76%). The higher volatile substance content in almond shell contributed to its superior hydrogen yield compared to coal. The mixed sample's hydrogen yield was intermediate, reflecting the combined characteristics of both biomass types.

5.4. EFFECT OF OPERATIONAL PARAMETERS

The operational parameters, such as temperature, pressure, and residence time, played a critical role in the gasification process. Higher temperatures and pressures generally enhanced the gasification efficiency and hydrogen yield. However, the specific influence of these parameters varied with the type of biomass. The type of biomass and the ratio of different biomass types affects the overall gasification performance, as seen with the mixed sample producing intermediate results between coal and almond shell.

5.5. COMPARISON WITH CONVENTIONAL METHODS

Compared to conventional gasification methods, supercritical gasification demonstrated several advantages:

- Higher hydrogen yield: The use of supercritical water facilitated more efficient breakdown of biomass, particularly for almond shell.
- Lower tar formation: The process resulted in lower tar formation, which is a common issue in traditional gasification methods.
- Processing Time: Faster reaction times under supercritical conditions reduce the overall processing time compared to conventional methods.
- Environmental Impact: Lower emissions and cleaner by-products make supercritical gasification.
- Operational efficiency: Supercritical gasification allowed for continuous operation with higher throughput.

However, there were also challenges, including the need for high-pressure equipment and the associated safety and maintenance concerns.

5.6. ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

The environmental impact of supercritical gasification was assessed in terms of emissions and by-products. The process produced lower emissions of Sulphur and other pollutants compared to conventional methods, due to the efficient breakdown of Sulphur compounds in supercritical water. Economically, the higher hydrogen yield and lower tar production could offset the initial investment in high-pressure equipment, making supercritical gasification a viable option for sustainable hydrogen production

PART 6

RECOMMENDATIONS AND CONCLUSION

6.1. SUMMARY OF FINDINGS

The study demonstrated that supercritical gasification is an effective method for hydrogen production from biomass. Almond shell, with its high volatile substance content, produced the highest hydrogen yield. The mixed sample also showed promising results, benefiting from the characteristics of both coal and almond shell. Operational parameters significantly influenced gasification performance, with higher temperatures and pressures enhancing efficiency.

6.2. CONTRIBUTIONS TO KNOWLEDGE

This study adds to the understanding of biomass gasification in supercritical circumstances. It emphasises almond shell's potential as a superior feedstock for hydrogen production, as well as the significance of optimising operating parameters to maximise yield. The comparison with conventional procedures provides useful insights into the benefits and drawbacks of supercritical gasification.

6.3. LIMITATIONS OF THE STUDY

The limitations of the study include the size of the studies, which were conducted on a laboratory scale. The results may vary in industrial applications due to differences in biomass characteristics and operational conditions. Additionally, the economic analysis was preliminary and requires further detailed assessment to fully understand the cost implications of scaling up the process.

6.4. CONCLUSION

Supercritical gasification represents a promising advancement in the field of biomass-to-hydrogen conversion. The findings of this study indicate that supercritical water can significantly enhance hydrogen production from biomass, especially from high-volatile feedstocks like almond shell. While challenges remain, particularly in scaling up and economic feasibility, the potential benefits in terms of efficiency, environmental impact, and hydrogen yield make supercritical gasification a compelling area for further research and development. This thesis provides a foundation for future studies and highlights the critical factors that will drive the successful implementation of supercritical gasification technologies.

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RESUME

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