EVALUATING THE POTENTIAL OF WOODY AND NONWOODY INVASIVE ALIEN PLANT SPECIES FOR BIO-OIL AND BIOGAS PRODUCTION

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SUPERVISOR'S APPROVAL

As the candidate's supervisor, I have approved this review and proposal for submission.

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This section contains work that has been published or is to be published and the contribution of this research work.

Publication

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- The paper is published in the Energies Journal - Special Issue of "Renewable Energy Integration into Agricultural and Food Engineering".

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Local Conferences

- Chapter 3 was presented at the Postgraduate Research and Innovation Symposium, University of KwaZulu-Natal (PRIS). The conference was held in Durban, South Africa (2023 and 2024).
- The research won 1st place in the School of Engineering & School of Mathematics, Statistics, and Computer Science Flash presentation category for the 2024 PRIS.

- The thesis was presented at the South Africa Institute of Agricultural Engineers (SAIAE) and Pan African Society for Agricultural Engineering (PASAE) International Symposium 2024. The conference was held in the Western Cape, South Africa (October 2024).

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ABSTRACT

Biomass energy, converted into biofuels such as biogas, bio-oil, and biochar, offers clean alternatives for energy and transport. However, in South Africa, securing sustainable feedstock without impacting food security, water, and land remains a challenge. This study seeks to bridge this gap by assessing the potential of woody invasive alien plant species (IAPs) (*Lantana Camara, Chromoleana Odorata, Solanum Mauritianum)* and nonwoody IAPs (*Acacia Mearnsii, Eucalyptus Grandis, Pinus Patula*). The study comprised four experiments, beginning with the analysis of physical and chemical characteristics of IAPs, including proximate, structural composition, and higher heating value (HHV), to assess the suitability of IAPs for bio-oil and biogas production. The results revealed that woody invasive species had significantly higher levels of cellulose, hemicellulose, and lignin, measured at 47.5%, 22.6%, and 25.5%, respectively, compared to nonwoody IAPs, which exhibited lower concentrations of 23.6%, 15.9%, and 9.8% ($p < 0.005$). This section contributes towards the strategic selection of high-performing substrates, making bio-oil and biogas production cost-effective.

Experiment two applied multi-criteria decision-making (MCDM) methods to determine the most suitable IAPs for bio-oil and biogas production based on physical and chemical properties. Results showed that woody IAPs, particularly *E. grandis*, ranked highest for bio-oil with a relative closeness of 0.774, whereas nonwoody IAPs, particularly *L. camara* ranked highest for biogas with a relative closeness of 0.874. These results offer practical guidance for selecting effective feedstocks in renewable energy applications. Experiment three confirmed the MCDM results, showing that woody IAPs produced higher bio-oil yields (22.93 to 27.55%) than nonwoody IAPs (18.77 to 20.45%). However, the high content of oxygenated compounds in bio-oil reduced fuel quality, indicating the need for upgrading methods such as hydrodeoxygenation to enhance combustion efficiency. Experiment 4, which focused on biogas production using biochemical methane potential (BMP) tests, revealed that nonwoody IAPs produced significantly higher average methane yields ($p < 0.005$) at 162.62 Nml/g VS compared to woody species (117.69 Nml/g VS). This confirmed the suitability of nonwoody IAPs for biogas production as indicated by MCDM findings. This study supports energy efficiency and environmental sustainability in South Africa by repurposing IAPs as biofuel sources. However, the need for high capital investment underscores the importance of further research into the economic viability of large-scale production.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation	Definition
IAPs	Invasive Alien Plant species
GHGs	Greenhouse Gases
MCDM	Multi-Criteria Decision-Making
A. mearnsii	*Acacia mearnsii*
E. grandis	*Eucalyptus grandis*
P. patula	*Pinus patula*
L. camara	*Lantana camara*
C. odorata	*Chromolaena odorata*
S. mauritianum	*Solanum mauritianum*
KZN	KwaZulu-Natal
SAPIA	Southern African Plant Invaders Atlas
CH_4 NL	Methane Normal Litre
VS	Volatile Solids
gCO_2e/kWh	grams of carbon dioxide equivalent per kilowatt-hour
HHV	Higher Heating Value
MC	Moisture Content
VC	Volatile Content
AC	Ash Content

FC	Fixed
C	Carbon
H	Hydrogen
N	Nitrogen
O	Oxygen
S	Sulphur
AHP	Analytical Hierarchy Process
TOPSIS	Technique for Order of Preference by Similarity to Ideal Solution
FMCDM	Fuzzy Multi-Criteria Decision-Making
ANP	Analytic Network Process
FAHP	Fuzzy Analytical Hierarchy Process
VIKOR	VlseKriterijumska Optimizacija I Kompromisno Resenje
HTL	Hydrothermal Liquefaction
VRT	Vapor residence time
GC–MS	Gas Chromatography-Mass Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
AD	Anaerobic digestion
C/N	Carbon to Nitrogen ratio
OLR	Organic Loading Rate

BMP	Biochemical Methane Potential
AMPTS	Automatic Methane Potential Test System
a	Coefficient of carbon
b	Coefficient of hydrogen
c	Coefficient of oxygen
d	Coefficient of nitrogen
CH_4^{Theo}	Theoretical methane

1. INTRODUCTION

Approximately 45% of South Africa's population still faces challenges related to inadequate access to energy resources (Mhlanga and Garidzirai, 2020). This problem is caused by the country's reliance on fossil fuels, outdated energy infrastructure, and slow transition to renewable energy sources (Pollet *et al.*, 2015). The use of fossil fuels has generated approximately 434.5 Tg of carbon dioxide annually with severe climate and health risks (Gasparotto and Martinello, 2021; Vera *et al.*, 2022). Furthermore, the mining and transportation of coal, a main source of energy, have high capital costs, which were estimated to be between R6 358 million and R12 690 million each year by Mugido *et al.* (2014). South Africa has faced ongoing load-shedding since 2007, reflecting environmental and economic challenges (Cloete *et al.*, 2023). These persistent issues emphasise the need to explore affordable and sustainable energy solutions.

Renewable energy contributes only 7.3% to South Africa's energy mix, lagging China with 17.8% (Zhang *et al.*, 2010) and India with 12.5% (Tripathi *et al.*, 2016). Within 7.3%, biomass energy is reviewed under others with only a 0.2% contribution (Akinbami *et al.*, 2021; Adebiyi and Moloi, 2024). Despite this, a study highlighted that biomass energy is accessible, affordable, reliable, and cost-effective with fewer carbon emissions (Shrivastava *et al.*, 2021). However, the minimum exploration of biomass energy in South Africa is due to competing demand for land, food security risks, pressure on water resources, and limited access to efficient conversion technologies (Rial, 2024). This underscores the importance of enhancing the use of biomass for sustainable energy generation.

As a strategy to bypass land and food security conflicts, invasive alien plant species (IAPs) have emerged as promising alternative feedstocks. Invasive alien plant species are plants introduced beyond their natural range that spread rapidly and often outcompete native vegetation. In South Africa, the Southern African Plant Invaders Atlas (SAPIA) has recorded over 500 genera of invasive plants, covering at least 10 million hectares of land (Maluleke *et al*., 2021). Prominent species include Eucalyptus, and Pinus, which were originally introduced for timber production but have since proliferated, disrupting ecosystems, undermining livelihoods, and placing a significant burden on the economy (Pyšek *et al*., 2020; Maluleke *et al*., 2021). Traditional management practices, such as mowing or burning to rid the land of

IAPs, are not enough, as they can promote vegetation regrowth and require significant financial investment (Schmiedel *et al.*, 2016). Compared to other South African energy crops such as food crops, cow manure, and municipal waste, IAPs generate fewer greenhouse gas emissions (GHGs) and require minimal inputs such as water or fertilisers, making them an affordable, accessible, and eco-friendly energy resource (Kadiyala *et al.*, 2016).

Biomass energy is generated through thermochemical or biochemical degradation (Poornima *et al.*, 2024). These conversions of biomass yield biofuels such as biogas, bio-oil, biochar, and biodiesel that can serve as sources for thermal energy, power production, transport fuel, and chemical feedstock (Hu and Gholizadeh, 2020). Regardless of the various applications of biofuels, only 0.1% of biofuels contribute to the South African energy mix, creating a niche area for research and development (Akinbami *et al.*, 2021). The limited exploration of biofuels is mainly due to insufficient capacity to characterise the diverse physical and chemical properties of biomass, which vary with growing conditions. (Akinbami *et al.*, 2021; Ayaa *et al.*, 2022). Therefore, there remains a clear research area in evaluating IAPs for energy generation.

To address the limited exploration of biofuel production in South Africa, this study bridges the gap by providing an evaluation of woody and nonwoody IAPs for bio-oil and biogas production. The primary objectives of this study is to; (1) conduct structural, elemental, thermal and proximate analysis of three woody IAPs (*Acacia mearnsii*, *Eucalyptus grandis*, and *Pinus patula*) and three nonwoody IAPs (*Lantana camara*, *Chromolaena odorata*, and *Solanum mauritianum*) to assess their viability for biofuel production, (2) Apply multi-criteria decision-making (MCDM) to identify the most suitable IAPs for optimal bio-oil and biogas, (3) perform pyrolysis experiment to investigate the bio-oil production potential of selected IAPs and (4) conduct anaerobic digestion experiments to assess biogas yield from the same species.

The uniqueness of this study lies in the dual benefits of addressing the ecological challenge of invasive species while promoting renewable energy generation. Biomass characterisation enables identification of high-performing substrates, minimising post-processing requirements and enhancing the cost-efficiency of biofuel production. The application of MCDM offers a structured and repeatable framework that enables the evaluation of multiple performance criteria, making it a valuable tool for the accurate and cost-effective selection of optimal design

parameters in engineering and energy systems. The research introduces a dual-pathway approach to determine species suited for either thermochemical or biochemical processes, a study limited to South Africa.

1.1 Problem Statement

South Africa relies heavily on coal for about 80% of its energy supply (Makgetla and Patel, 2021). This heavy reliance on fossil fuels has led to emissions of GHGs, with South Africa ranked as the 12th largest emitter in the world (Vera *et al.*, 2022). Along with climate change, GHGs adversely affect human health by increasing the risk of respiratory diseases with prolonged exposure (Naiyer and Abbas, 2022). An investment of US$ 25.6 billion in 2011 was set for electricity generation using coal in South Africa (De Groot *et al.*, 2013), illustrating a meaningful financial focus on coal while other alternatives, such as renewables, remain underdeveloped. These encompass the ecological, social, and economic challenges associated with relying on fossil fuels as the primary energy source in South Africa (Cloete *et al.*, 2023).

One of the known causes contributing to the challenges of insufficient energy in South Africa are, the lack of investment in expanding the energy capacity to meet the growing demand, reliance on old and inefficient coal power plants, and lack of diversifying energy sources such as renewables (Inglesi and Pouris, 2010; Pollet *et al.*, 2015). Agricultural, residential, and industrial energy usage accounts for approximately 3%, 25%, and 37%, respectively, with the remaining 35% attributed to the transport and commercial sectors (Donev *et al.*, 2012). Without efficient and reliable energy sources, productivity within these sectors could be compromised, eventually impacting South Africa's economy.

Recent studies on renewable energy have been explored to mitigate the adverse effects of fossil fuels and tackle load-shedding (Farghali *et al.*, 2023). Among these options, biomass has gained attention as a feasible choice because it is readily available, cost-efficient, and also produces lower carbon emissions. However, the key challenge of biomass energy is associated with utilising staple crops, raising concerns on food security (Akinbami *et al.*, 2021). To address this challenge, this study employs IAPs as an energy substrate, motivated by their negative impact on the environment, health, and biodiversity (Pyšek *et al.*, 2020). For instance, *Prosopis* species, an IAPs, has consumed 997 m^3 of water per year, equating to 89% of water

in the Northern Cape (Witt, 2010). Furthermore, management and control methods for IAPs are inadequate, ineffective, and require higher capital investment (Schmiedel *et al.*, 2016).

There is limited research available regarding the evaluation of IAPs as biofuel substrates, leaving a gap in understanding their contribution to bio-oil and biogas production. Without a clear evaluation of IAPs as potential energy substrates, renewable energy development is limited, competition with food crops is intensified, and continued environmental degradation occurs. This study aims to evaluate IAPs as biomass for bioenergy generation, contributing towards providing safe and efficient energy while protecting the environment and maintaining livelihood.

1.2 Aim and Objectives

This research aims to assess the potential of woody and nonwoody IAPs grown in KwaZulu-Natal (KZN) for bio-oil and biogas production.

The specific objectives of this research are:

(a) To assess the physical and chemical properties of woody and nonwoody IAPs for bio-oil and biogas production.
(b) To identify which woody and nonwoody IAPs are suitable for bio-oil and biogas production.
(c) To evaluate the quantity and standard of bio-oil derived from woody and nonwoody IAPs.
(d) To evaluate the quantity and standard of biogas derived from woody and nonwoody IAPs.

1.3 Research Questions

To achieve the research objectives, the following research questions will be answered:

(a) How does the proximate, elemental, and structural composition of the IAPs affect the yield and quality of biogas and bio-oil?
(b) Which woody and nonwoody IAPs are suitable for biogas and bio-oil production?
(c) What is the potential of woody and nonwoody IAPs for bio-oil production?
(d) What is the potential of woody and nonwoody IAPs for biogas production?

1.4 Research Hypothesis

The hypothesis of this study is as follows:

(a) Woody and nonwoody IAPs with higher volatile content, cellulose, and carbon content as proximate, structural, and elemental composition, respectively, will yield higher biogas and bio-oil.
(b) Multi-criteria decision-making will indicate that woody IAPs are suitable for bio-oil, while nonwoody IAPs are suitable for biogas.
(c) Woody IAPs have a higher potential for bio-oil production due to higher volatile content, cellulose, and carbon content as proximate, structural, and elemental composition, respectively.
(d) Nonwoody IAPs have higher potential for biogas production due to higher moisture content, higher carbon-to-nitrogen ratio, and lower lignin as proximate, structural, and elemental composition, respectively.

1.5 Outline of Dissertation

This document comprises seven chapters as follows:

(a) Chapter 1: Introduction.
(b) Chapter 2: A review of IAPs, MCDM, bio-oil, and biogas production.
(c) Chapter 3: Evaluating the physical and chemical properties of woody and nonwoody IAPs for bio-oil and biogas production.
(d) Chapter 4: Multi-criteria decision-making to evaluate and prioritise IAPs suitable for bio-oil and biogas production.
(e) Chapter 5: Evaluating the potential of woody and nonwoody IAPs grown in KZN for bio-oil production.
(f) Chapter 6: Evaluating the potential of woody and nonwoody IAPs in KZN for biogas production.
(g) Chapter 7: Conclusion, recommendation, and future research opportunities.

1.6 References

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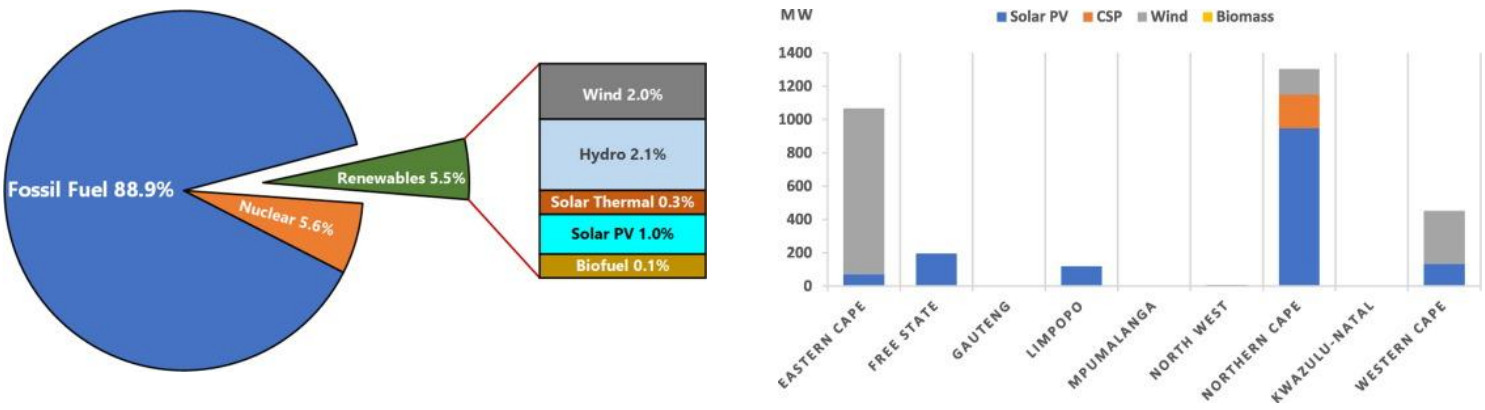
2. A REVIEW ON BIOMASS ENERGY USING IAPS FOR BIO-OIL AND BIOGAS PRODUCTION

The pursuit of sustainable energy has driven the exploration and development of alternative fuels aimed at reducing the environmental, economic, and social impacts associated with non-renewable energy sources. This research evaluation looks at four areas: biomass energy and its place in sustainable efforts; Invasive alien plant species (IAPs) and their viability as an energy substrate; Multi-Criteria Decision Making (MCDM) for biomass substrate selection; and bio-oil production and biogas production. The literature review will identify potential research gaps in biomass energy in South Africa.

2.1 Overview of Biomass Energy

Biomass is a plant material derived from energy crops, forestry plants, plant residues, and organic waste (Kalak, 2023). Biomass energy is generated through thermochemical or biochemical degradation (Poornima *et al.*, 2024). During biomass degradation, carbon dioxide is produced, which is then absorbed by plant species during regrowth, offering carbon neutrality (Ahamer, 2022). The advantages of generating electricity from biomass include energy security, reduced reliance on fossil fuels, waste reduction, and lower emissions of pollutants (Rabbi *et al.*, 2022).

Biofuel energy contributed approximately 0.1% to South Africa's energy mix, which is minimal compared to other renewable energy sources as depicted in Figure 2.1 (a). Additionally, Figure 2.1 (b) shows that certain provinces, such as KwaZulu-Natal (KZN), lack renewable energy infrastructure, underscoring the regional disparities in renewable energy deployment. Biomass energy development in South Africa faces several challenges, including limited sustainable feedstock that does not threaten food security, land and water constraints, high startup costs, and weak policy support for related technologies. (Etambakonga, 2013). This highlights the missed opportunities for biomass applications in South Africa and creates a niche area for research in this field to maximise the benefits.



(a) South African energy mix (Akinbami *et al.*, 2021)

(b) South African renewable energy comparison by province (Akinbami *et al.*, 2021)

Figure 2.1 Renewable energy comparison in South Africa

2.2 Invasive Alien Plant Species in KwaZulu-Natal

Invasive alien plants are plants that invade environments, negatively impacting biodiversity, livelihood, and economic development (Pyšek *et al.*, 2020). The species invades approximately 10 million hectares in South Africa (Maluleke *et al.*, 2021). The Southern African Plant Invaders Atlas (SAPIA) records about 500 genera of plants in South Africa, Lesotho, and Swaziland as IAPs. A study by Nel *et al.* (2004) classified 117 species as major invaders and categorised them into woody and nonwoody IAPs.

Woody IAPs are distinguished by single-stemmed trees that attain heights of up to ten meters, while nonwoody IAPs are defined by multi-stemmed shrubs reaching heights of less than two meters (Richardson and Rejmánek, 2011). While IAPs were originally introduced for beneficial purposes, such as for timber and ornamentals, Table 2.1 illustrates their widespread proliferation across the country, posing a negative impact on water resources, the environment, and biodiversity. Current control methods, such as mowing, herbicide application, contribute to soil hydrophobicity, which inhibits water infiltration and exacerbates soil erosion, ultimately depleting soil nutrients (Witt, 2010). Additionally, despite an investment of R45 million to clear 17,000 ha of IAPs, the effort was inadequate (Nkambule *et al.*, 2017). This highlights the importance of investigating more affordable and environmentally friendly approaches for managing invasive species.

Table 2.1 The main woody and nonwoody plant invaders mapped in KwaZulu-Natal

Name	Common name	Area coverage in South Africa	Infestation in KZN	Negative impact
Acacia mearnsii	Black wattle from Australia	33 species with 0.4 million ha infestation (Moyo and Fatunbi, 2010)	Northern and the Midlands areas	Reduces native crop growth by absorbing water, soil nutrients, and organic matter (Magona *et al.*, 2018).
Pinus species	Pine tree from the Northern Hemisphere	0.12 million ha (Stafford *et al.*, 2017)	Southern KZN in Sappi Pinewood Forestry	Pine has deep sinker roots that reach 2.6 meters deep and may suck 40 to 50 liters of water per day (Moran *et al.*, 2000).
Eucalyptus species	Gum tree from Australia	2.4 million ha (Poona, 2008)	KZN Forestry Midlands	Outcompetes indigenous crops for water, light, and nutrients, resulting in lower crop yields (Daba, 2016).
Lantana camara	Lantana from Central and South America	2 million ha (Bhagwat *et al.*, 2012)	KZN Around Stanger	Lantana's deep root and large leaf area index suppress the growth of native crops (Barik *et al.*, 2020).
Solanum mauritanium	Bug weed from South America	80 500 ha (Cowie *et al.*, 2018)	KZN Forestry Midlands	Invaded sites have lower soil moisture levels and vegetation diversity (Ruwanza, 2021).
Chromoleana Odorata	Siam weed	1.44 million ha (Zachariades *et al.*, 2011)	Subtropical grasslands in KZN	Suppress the growth of indigenous plant species (Zachariades and Goodall, 2002).

Researchers in regions such as the Iberian Peninsula, Poland, and Sri Lanka have investigated the potential of invasive species such as *Cortaderia selloana, Prosopis juliflora,* and *Reynoutria*, respectively, to produce renewable biofuels such as bio-oil and bioethanol (Pérez *et al.*, 2021; Bandara *et al.*, 2022; Wiatrowska *et al.*, 2022). However, existing literature in South Africa, such as studies by Mugido *et al.* (2014) and by Vera *et al.* (2022), has emphasised the environmental and economic consequences of invasive species, rather than systematically assessing their suitability for biofuel generation. This presents a critical research gap and an opportunity to explore the energy valorisation of IAPs.

The motivation for exploring IAPs as an alternative energy feedstock in South Africa is strongly supported by both their widespread availability and promising energy potential. For instance, an estimated 639,538 tonnes of harvestable invasive biomass is available in the Agulhas Plain, Western Cape Province (Stafford *et al.*, 2017). Species such as *Fallopia japonica* demonstrate impressive annual biomass yields of up to 8.6 tonnes per hectare, outperforming many native crops without requiring additional water or agricultural inputs (Van Meerbeek *et al.*, 2015). This exceptional growth performance is largely due to their adaptive traits, such as nutrient sharing, water efficiency, and resilience in harsh conditions (Keser *et al.*, 2014; You *et al.*, 2014).

Moreover, the physicochemical characteristics of certain IAPs enhance their suitability for bioenergy applications. For example, *Lantana camara*, exhibits high holocellulose content and significant sugar yields, making it particularly favourable for biogas production (Kuhad *et al.*, 2010; Vera *et al.*, 2022). These characteristics highlight the untapped energy viability of IAPs and support their valorisation through sustainable biofuel pathways, offering a dual solution for energy generation and invasive species control.

2.3 Biomass Composition Influencing the Yield and Quality of Biogas and Bio-Oil

Biomass is characterised by proximate, elemental, structural, and thermal analysis. These factors influence the type of biofuel produced, the yield, quality, and performance of biofuel plant units. Proximate composition includes moisture content, volatile content, fixed carbon, and ash content, affecting the efficiency of degradation. Elemental compositions such as carbon, nitrogen, oxygen, hydrogen, and sulphur influence the energy density of biomass. Structural composition includes cellulose, hemicellulose, and lignin, which provide energy-rich compounds. Thermal analysis includes the higher heating value (HHV). These factors are presented in Table 2.3 to illustrate their influence on bio-oil and biogas production.

Table 2.2 Substrate characterisation for biogas and bio-oil

PROXIMATE CHARACTERISTICS				
Parameters	Description	Substrate characteristics for biogas	Substrate characteristics for bio-oil	References
Moisture Content (MC)	MC is the proportion of water present in biomass. Facilitates the ease of biochemical degradation and impact energy usage in thermal processes.	The optimal MC ranges from 35 to 65%. A lower MC inhibits nutrient transfer, and a higher MC builds up oxygen, toxic to micro-organisms.	The optimal MC is below 15 % to ensure that energy is used for thermal degradation instead of biomass evaporation.	Pantini *et al.*, 2015, Melane *et al.*, 2017, Guedes *et al.*, 2018, Uzakov *et al.*, 2018.
Ash Content (AC)	AC is the number of incombustible residues after complete combustion. AC affects the efficiency of either thermal or biological degradation.	Micro-organisms are unable to convert the materials to suitable sugars, which inhibits the production of methane.	A reduction in AC from 5.36 to 1.03 % increased bio-oil from 34.71% to 61.34 %.	Vargas-Moreno *et al.*, 2012, Guedes *et al.*, 2018.

Volatile Content (VC)	VC refers to materials that are converted to gas when heated. This represents the ease of ignition, flame stability, and reactivity of the fuel.	Contributes to the organic matter that will be degraded by microorganisms. The VC of 84.24 % is a promising characteristic for biogas yield.	About 75 to 85 % of VC yielded about 40 to 42 % of bio-oil.	Cao and Pawłowski, 2012, Da Silva Ignacio *et al.*, 2019.
Fixed Carbon (FC)	FC is the solid combustible residue that remains after the sample is heated and the volatile matter is removed.	If the fixed carbon is low, that illustrates a higher VC, which is good for any biogas production.	If the fixed carbon is low, that illustrates a higher VC, which is good for any bio-oil production.	Sarkar, 2015, Da Silva Ignacio *et al.*, 2019, Reza *et al.*, 2019a.
ELEMENT CHARACTERISTICS				
Carbon (C)	Constitutes about 30 to 60% of biomass.	Suitable for the synthesis of carbohydrates that can be turned into sugars.	Higher carbon content increases the energy density of bio-oil.	Vargas-Moreno *et al.*, 2012, Melane *et al.*, 2017.
Hydrogen (H)	The increase in hydrogen increases the HHV of biofuels.	The hydrogen content increases the yield of biogas but is not as essential as the carbon content.	Remove the oxygen-containing compounds, thus HHV.	Demirbas, 2007, Vargas-Moreno *et al.*, 2012.

Oxygen (O)	Constitutes about 30 to 45% of oxygen. A high yield of oxygen results in biofuels with poor flame stability.	Oxygen acts as a toxic agent to micro-organisms, causing instability of the reaction and, thus, less methane yield.	Higher oxygen reduces the higher heating value of bio-oil, thus an inefficient combustion process.	Botheju and Bakke, 2011, Vargas-Moreno *et al.*, 2012.
Nitrogen (N)	Constitutes about 0.1 to 12% of the biomass. Nitrogen in gaseous forms is detrimental to the ecological, climate, and people's health.	The output reaction of N results in the formation of ammonia (NH_3), ammonium (NH_{4+}), nitric oxide (NO) that inhabits micro-organisms.	The output reaction of N results in the formation of nitrate ($NO_{3-}$and nitrites (NO_{2-})	Follett and Hatfield, 2001, Vargas-Moreno *et al.*, 2012.
Sulphur (S)	Constitutes about 0.01 to 2.3 % of biomass feedstock. Release gaseous forms that are detrimental to the environment.	The sulphide competes with methanogens for hydrogen and acetate, thus lowering the yield of methane.	Release gases such as sulphur dioxide (SO_2), sulphur trioxide (SO_3) during combustion.	Droux, 2004, Zhao *et al.*, 2008, Gustavsson *et al.*, 2013.
STRUCTURAL CHARACTERISTICS				
Cellulose	Polysaccharide consists of 100 to 10,000 linked units of glucose in linear chains. It can be turned into simple sugars for biofuel.	Cellulose-rich biomass results in a higher yield of methane due to xylan, which swells the cellulose, making enzymatic hydrolysis more efficient.	Cellulose rich in biomass increases the yield of bio-oil, but a high reaction time yields biochar.	Balat *et al.*, 2008, Li *et al.*, 2018, Zhong *et al.*, 2022b.

Hemicellulose	Hemicellulose is a short, highly branched polysaccharide with 20 to 40 % biomass. Contains glucose that can be hydrolysed to sugars for biofuel production.	Hemicellulose contributes to high biofuel yields; however, its degradation can lead to the buildup of volatile fatty acids, creating an acidic environment that suppresses microbial activity.	Hemicellulose results in a high yield but can influence the secondary reaction of biochar formation.	Demirbaş, 2001a, Saha, 2003, Balat, 2011, Li *et al.*, 2018, Zhong *et al.*, 2022b.
Lignin	Lignin is a polymer made of phenylpropane units, crosslinked to each other by chemical bonds. The biofuel production using lignin is low, if not impossible since the material is insoluble.	The digestion of cellulose with lignin resulted in lower yield of methane in an experiment of anaerobic digestion.	The lignin bonds are first split at 200 to 400 ℃, around 550 to 650 ℃, the production of bio-oil begins, and further at 800 ℃, the bio-oil is turned into a gas.	Weng *et al.*, 2008; Ghalia and Dahman, 2017, Li *et al.*, 2018.
Higher heating value (HHV)				
Higher heating value	The quantity of heat generated during the combustion of biomass in the presence of oxygen.	A higher heating value is required for biogas production to increase combustion efficiency.	A higher heating value is essential for bio-oil production to increase combustion efficiency.	Da Silva Ignacio *et al.*, 2019.

2.4 Multi-Criteria Decision Making to Evaluate and Prioritise IAPs Suitable for Bio-oil and Biogas Production

Biomass feedstocks have unique physical and chemical properties that impact biofuel production variations. Therefore, selecting appropriate biomass for specific biofuel production reduces economic and environmental impacts (Cobuloglu and Büyüktahtakın, 2015). Multi-Criteria Decision Making (MCDM) is a mathematical systematic approach that evaluates a set of alternatives on predefined criteria considering the goal (Madhu *et al.*, 2018). This method has been applied in selecting materials for optimal design and process parameters in engineering. Figure 2.2 illustrates different MCDMs with the number of contributions in engineering and energy. These MCDM methods are further discussed in Table 2.4. MCDM methods such as the Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) and Analytical Hierarchy Process (AHP) were employed by Abdulvahitoglu and Kilic (2022) for selecting oilseeds for biodiesel production. A study by Howari *et al.* (2023) utilised TOPSIS and Fuzzy Analytical Hierarchy Process (FAHP) to choose waste materials for pyrolysis. This highlights that while significant work has been done in biomass selection, there has been no similar research conducted in South Africa or the selection of IAPs, creating a niche area for further research.

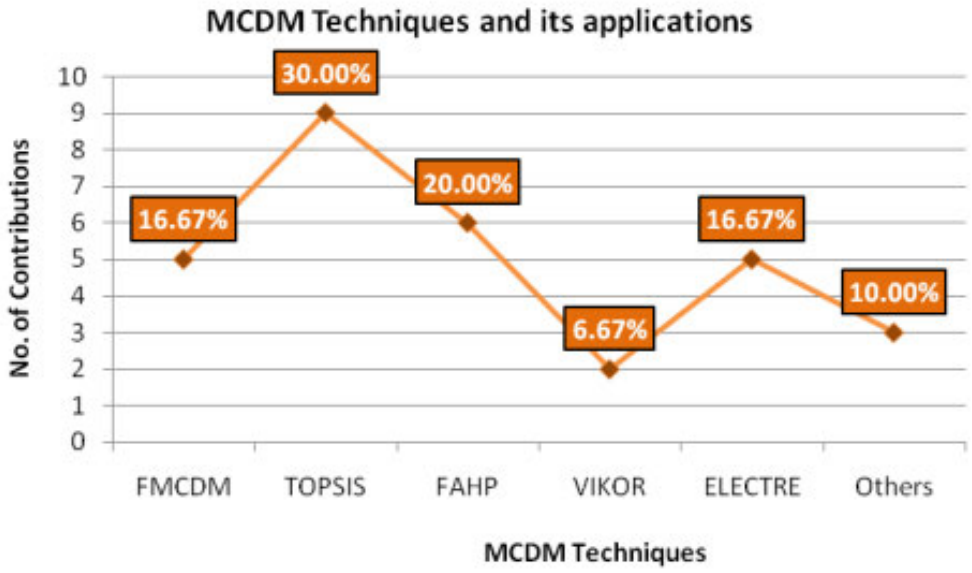


Figure 2.2 Different MCDM with number of contributions in engineering and energy (Aruldoss *et al.*, 2013)

The AHP is one of the MCDMs, proposed by Saaty (2003). This method quantifies relative priorities for a set of alternatives on a ratio scale, guided by the decision-maker's judgment (Al-Harbi, 2001). The method includes posing questions such as what is the most important criterion based on the predefined goal. To answer such questions, the decision maker must have extensive experience as well as an understanding of the criteria. The technique consists of three levels: (1) objective, (2) criteria, and (3) alternatives. At each level, a pairwise comparison matrix is used, applying the Saaty scale from 1 to 9, where 1 indicates the least importance and 9 represents the highest importance based on the goal (Vaidya and Kumar, 2006). The TOPSIS is an MCDM method used to identify the optimal solution and evaluate alternatives based on performance across several criteria (Chakraborty, 2022). This approach is based on the concept that the optimum response has the shortest distance to the positive ideal solution and the longest distance to the negative ideal solution (Madhu *et al.*, 2018). The positive ideal solution indicates the most desirable outcome, whereas the negative ideal solution represents the least desirable (Chakraborty, 2022). Researchers have found that integrating MCDM methods such as TOPSIS and AHP enhances accuracy in selecting biomass for energy purposes (Abdulvahitoglu and Kilic, 2022; Howari *et al.*, 2023).

Table 2.3 Different MDCM Techniques with application, description, advantages, and disadvantages (Aruldoss *et al*., 2013)

MCDM Techniques	Description	Applications	Advantages	Disadvantages	References
AHP	A pair-wise comparison matrix evaluates different alternatives against multiple criteria.	Engineering, food, government, health, ecology, and business.	Simple, flexible, and checks inconsistencies.	Irregularities in ranking, a greater number of pair-wise comparisons are needed.	Aruldoss *et al.*, 2013, Sipahi and Timor, 2010.
Analytic Network Process (ANP)	Develop a decision matrix incorporating various goals and all criteria.	Energy policy, product design, equipment replacement, planning	Prediction accuracy is enhanced through feedback.	Time-consuming, uncertainty not supported.	Jharkharia and Shankar, 2007.
TOPSIS	Assess the distances to both the positive ideal solution and the negative ideal solution.	Engineering, manufacturing, education, and health.	Simple, flexible, consider different multi-criteria	Depending on the weighting, difficult to handle large data sets.	Aruldoss *et al.*, 2013, Yue, 2011.
Grey analysis	This approach handles missing data and resolves limitations found in previous methods.	Forecasting Risk analysis	Ensures a unique solution under perfect information.	It does not necessarily guarantee the optimal solution."	Aruldoss *et al.*, 2013.

2.5 Bio-oil Production

Bio-oil is a dark brown liquid composed of a range of organic compounds, typically generated through the thermal or biochemical breakdown of biomass materials (Barros *et al.*, 2022). Bio-oil has various uses, including thermal energy generation, power generation, transportation fuel, and fertiliser applications (Hu and Gholizadeh, 2020). Regardless of the energy benefits of bio-oil, only 0.1% of biofuel contributes to the South African energy mix, thus providing research and development opportunities in this area (Akinbami *et al.*, 2021).

2.5.1 Factors influencing the yield and quality of bio-oil production

An overview of the variables influencing the generation of bio-oil, including reactors, biomass composition, operating parameters, pyrolysis, and conversion techniques, are outlined in this section.

2.5.1.1 Bio-oil conversion techniques

Bio-oil production can be achieved through biochemical and thermochemical routes, with thermochemical methods such as pyrolysis and hydrothermal liquefaction (HTL) being preferred due to their simplicity and lower capital costs (Xiu and Shahbazi, 2012). Pyrolysis breaks down organic matter in the absence of oxygen, yielding up to 80% bio-oil with less capital costs but higher MC content (Xiu and Shahbazi, 2012). Hydrothermal liquefaction, on the other hand, requires higher pressure conditions and higher capital costs (Ahmed *et al.*, 2018b). Pyrolysis is preferred due to its higher yield potential and opportunities for upgrading oil quality. A comparative study by Hognon *et al.* (2015) found that bio-oil produced from pyrolysis and HTL resulted in similar higher heating values. However, pyrolysis exhibited a higher yield of 60% compared to 53% in the HTL method.

2.5.1.2 Types of pyrolysis

Pyrolysis techniques include slow, fast, and flash pyrolysis. Slow pyrolysis involves low temperatures (300 to 600 ℃), resulting in increased biochar (Pahnila *et al.*, 2023). Fast pyrolysis operates at temperatures between 400 to 650 ℃, resulting in a bio-oil yield of up to

80% (Guedes *et al.*, 2018). Flash pyrolysis involves higher temperatures (800 to 1000 ℃), rapid heating rates, and longer vapor residence times, resulting in higher bio-oil yields (Fahmy *et al.*, 2020). However, flash pyrolysis requires complex equipment and higher capital expenditures and is limited to specific feedstock types (Isahak *et al.*, 2012; Pahnila *et al.*, 2023). Fast pyrolysis is preferred due to its practicality and efficiency.

2.5.1.3 Operating conditions

Temperature initiates thermal degradation. The optimal temperature range for bio-oil production is observed between 450 and 550 ℃, while higher temperatures might cause secondary cracking of syngas (Guedes *et al.*, 2018). The bio-oil yield on *Parthenium hysterophorus* was 32% at 500 ℃ and decreased to 30.93% at 600 ℃, validating the above statement (Ramesh and Somasundaram, 2022). For efficient heat transfer, the particle sizes should be less than 2 mm for optimal yield (Guedes *et al.*, 2018). In a study by Abnisa *et al.* (2011), an increase in particle size from 0.5 mm to 2 mm resulted in bio-oil yields from 27 to 45.8%, respectively.

Vapour residence time (VRT) is the duration during which vapours from the particles escape from the reactor to the condenser (Guedes *et al.*, 2018). Vapour residence time durations under 2 s are considered ideal for maximising bio-oil production (Hakeem *et al.*, 2021). The reaction time represents the duration of biomass exposure to specific pyrolysis temperatures. In experiments involving the pyrolysis of pistachio shell, the liquid product yield initially increased from 10 min (52.96 %) to 20 min (53.08 %) (Açıkalın *et al.*, 2012). However, further increases in reaction time resulted in a continuous decrease, with the liquid yield dropping to 50.13 % at 50 min. The heating rate measures the amount of heat transferred to the material (Guedes *et al.*, 2018). Slow heating rates tend to favour biochar formation, while faster rates promote the production of gases and bio-oil. This highlights that similar invasive plant species have already demonstrated favourable performance under established pyrolysis conditions.

2.5.1.4 Types of reactors

An apparatus used for the thermal breakdown of organic compounds without oxygen is called a pyrolysis reactor. Higher bio-oil yields have been demonstrated using a variety of reactor

technologies, including fluidised bed, auger, fixed bed, circulating, and rotating reactors (Isahak *et al.*, 2012). Advantages of pyrolysis reactors include reduced carrier gas requirement, less wear, and particle size variability. Rotating cone and ablative reactors offer some benefits, while circulating reactors are complex and require significant capital investment (Pahnila *et al.*, 2023). Table 2.6 provides a comparison of bio-oil yields and associated advantages and disadvantages for each reactor type.

Table 2.4 Types of pyrolysis reactors with a bio-oil yield (%) calculated on a weight basis and advantages and disadvantages (Raza *et al.*, 2021)

Type of reactor	Bio-oil yield (%)	Advantages	Disadvantages
Rotating cone	65	No inert gas requirement for mixing, less wear.	High capital cost, complex, and requires small particle size.
Circulating fluidised bed	75 to 79	Good temperature control.	Can accommodate small-scale systems with complex hydrodynamics.
Ablative	75	No inert gas requirement, large particle size.	It is expensive and has a low reaction rate.
Fixed bed	60	Offers a straightforward and dependable design.	Features a long residence time, making char removal challenging.
Vacuum	60	Capable of producing clean bio-oil without the need for a carrier gas.	The process is relatively slow due to extended solid retention time.
Blubbing fluidised bed	75	Designed for simplicity and ease of operation.	Requires small particle sizes for efficient operation.

2.5.1.5 Properties and characterisation of bio-oil

Bio-oil is a versatile oil with various chemical compounds, including alcohols, aldehydes, carboxylic acids, esters, and ketones (Machado *et al.*, 2022). Alcohols, aromatic, and aldehydes

reduce oxygen-containing compounds, thus increasing the higher heating value (Omar *et al.*, 2019). Furans, phenols, ketones, and sugar monomers are oxygen-containing organics that lead to the formation of coke due to heating in the absence of oxygen and drive off volatile compounds (Xu *et al.*, 2011). Chemical constituents can be upgraded through processes such as esterification, catalytic cracking, hydrogenation, molecular distillation, and hydrodeoxygenation (Lahijani *et al.*, 2022). These chemical compounds and functional groups are analysed by techniques such as gas chromatography-mass spectrometry (GC–MS) and fourier transform infrared spectroscopy (FTIR) (Wang *et al.*, 2020).

Physical characteristics such as water content, pH, viscosity, heating value, and density are crucial for assessing bio-oil quality (Konur, 2021). Bio-oil typically has a moisture content of 30% to 35%, which affects its heating value and storage capabilities (Pollard *et al.*, 2012). Its acidic nature poses a risk of corrosion in combustion engines and turbines. Physical properties are analysed by various equipment such as Karl-Fischer titration for MC, pH meter, viscometer test, and thermal stability is analysed by bomb calorimeter and thermogravimetric analyser (Zhang *et al.*, 2014).

Although conventional biomass sources such as algae and agricultural residues have been widely researched for bio-oil production, there is a lack of studies exploring the potential of invasive species, especially within the South African context. This presents a valuable research niche, offering the opportunity to assess whether bio-oil derived from IAPs can match the quality and energy performance of those produced from traditional biomass sources.

2.6 Biogas Production

Biogas is a flammable, colourless gas generated by the anaerobic decomposition of organic matter (Akyürek, 2023). Biogas offers environmental advantages such as carbon neutrality and minimal sulphur and nitrogen oxide emissions during production. It contributes significantly to bioheat, biopower, and biomethane for transport (Scarlat *et al.*, 2018). In South Africa, the initial biogas digester output was 0.4 MW, but only 150 are operational (Mukumba *et al.*, 2016; Nethengwe *et al.*, 2018). This highlights a limited biogas production in South Africa due to challenges in identifying optimal feedstock for enhanced biogas yield and improving digester

efficiency. Factors affecting biogas production, composition, and characteristics are reviewed in this literature to assist in the formation of biogas using IAPs.

2.6.1 Factors influencing the yield and quality of biogas production

This section provides an overview of factors such as conversion methods, digestion type, and operating conditions affecting bio-oil production.

2.6.1.1 Biogas conversion techniques

Anaerobic digestion (AD) is a biogas production technique that breaks down biodegradable organic materials without oxygen (Induchoodan *et al.*, 2022). It involves four stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as depicted in Figure 2.3. Approximately 40 billion $m^3.year^{-1}$ of biogas is generated through AD the world over, underscoring the efficiency of the AD process (Halder *et al.*, 2016). Biogas production has low operational costs and minimal nutrient and chemical requirements. However, it has a long start-up period and requires equilibrium buffers for methanogenic bacteria (Kaur *et al.*, 2024a). Researchers are currently exploring methods such as co-digestion, size reduction, and solubilisation to improve biogas quality and quantity (Heo *et al.*, 2003).

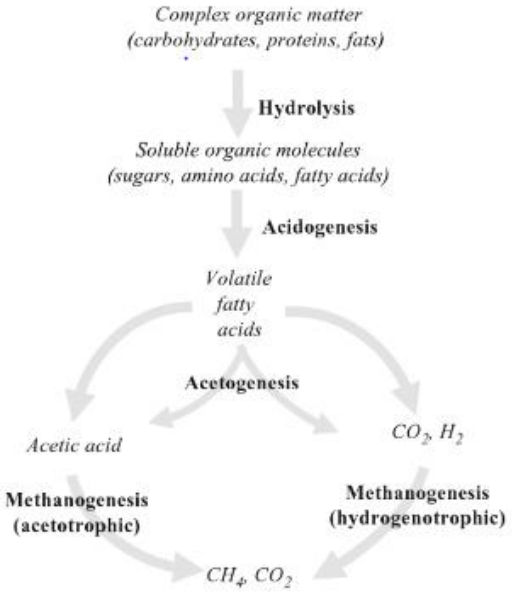


Figure 2.3 The four stages of anaerobic digestion for biogas production (Abbasi *et al.*, 2011)

2.6.1.2 Types of digestion

Anaerobic digestion (AD) is categorised into dry and wet processes. Dry AD involves solid content greater than 15%, which helps minimise energy use and handling expenses (Kothari *et al.*, 2014). However, poor internal mixing in dry systems can cause inhibitor build-up, ultimately decreasing methane production (Rocamora *et al.*, 2020). Wet digestion has a lower solid content of less than 10% and offers benefits such as higher digestion rates, dilution of toxic compounds, and improved biogas yield (García-Bernet *et al.*, 2011; Kothari *et al.*, 2014). Wet digestion is generally preferred, as evidenced by Di Maria *et al.* (2017) study, where wet digestion of municipal waste resulted in a methane yield of 0.2 $m^3.kg^{-1}$of volatile solids (VS), compared to 0.14 $m^3.kg^{-1}$of VS from solid digestion.

2.6.1.3 Operating conditions

The Carbon-to-Nitrogen (C: N) ratio plays a vital role in supporting microbial activity, with the ideal range for maximising biogas production falling between 20 and 35 (Kwietniewska and Tys, 2014; Choi *et al.*, 2020). Temperature significantly influences microbial metabolism and system efficiency, with three temperature regimes: psychrophilic, mesophilic, and thermophilic (Hao and Wang, 2015). Biogas production peaks at 35 ℃, with efficiency decreasing at higher temperatures (Nie *et al.*, 2021). pH plays a vital role in enzyme activity and microbial performance, with the ideal range for maximum biogas yield being 6.8 to 7.2 (Deepanraj *et al.*, 2014; Kwietniewska and Tys, 2014).

Total solids, varying with digestion state (wet, semi-dry, dry), affect bacterial growth and system efficiency (Abbassi-Guendouz *et al.*, 2012). Higher solids concentrations lead to decreased bacterial diversity and efficiency (Yi *et al.*, 2014). Mixing is essential in anaerobic digestion to maintain a homogeneous environment and prevent toxic by-product accumulation (Kariyama *et al.*, 2018). Organic loading rate (OLR) affects bacterial population balance and digester performance, with high OLR and low hydraulic retention time leading to substrate accumulation and digester failure performance (Van *et al.*, 2020).

2.6.1.4 Biochemical methane potential test

The biochemical methane potential test (BMP) is a technique for assessing the methane potential and biodegradability of organic materials under regulated anaerobic digestion conditions (Strömberg *et al.*, 2014). The method involves combining a substrate with an anaerobic bacteria culture, eliminating excess oxygen, and subjecting the mixture to mesophilic or thermophilic conditions for 30 to 60 days (Filer *et al.*, 2019). The BMP test is popular for its quantitative measurement of biogas production, aiding in substrate selection and cost reduction. However, challenges of the use of the BMP include a lack of standardized procedures and reporting information, data reliability concerns (Holliger *et al.*, 2016).

The BMP test uses three types of bottles: substrate, blank, and control, which are maintained in controlled environments using temperature control systems powered by solar energy or generators (Nijaguna, 2006; Pandey and Soupir, 2012; Makamure *et al.*, 2021). Mixing within the digester is achieved through mechanical pumping, hydraulic, pneumatic, or recirculation methods (Ajhar *et al.*, 2010; Arrhenius *et al.*, 2019). Gas collection systems include sampling ports, Tedlar bags, and sorbent tubes, with gas measurement techniques including liquid displacement and manometric approaches (Parajuli, 2011).

2.6.1.5 Biogas composition and characterisation

Biogas composition and characterisation involve the analysis and properties of gases produced through AD. Table 2.7 is a summary of biogas composition. These gases are analysed by gas chromatograph (Aravani *et al.*, 2022).

Table 2.5 Composition of biogas and its properties (Bharathiraja *et al.*, 2018)

Component	Concentration	Properties
CH_4	50–75% (v/v)	An energy carrier
CO_2	25–50% (v/v)	Reduces the heating value
H_2S	5000 ppm (v/v)	Corrosive, Sulphur dioxide emission during combustion
NH_3	0–500 ppm (v/v)	NOx – Emissions during combustion

N_2	0–5% (v/v)	Reduces the heating value
Water vapor	1–5% (v/v)	Encouraging corrosion in the presence of carbon dioxide (CO_2) and sulphur dioxide (SO_2)

Ppm means parts per million, v/v means volume/volume percentage.

2.7 Discussion and Conclusion

The primary objective of conducting the literature review was to evaluate the feasibility of utilising IAPs for biofuel production as renewable energy sources. The literature review highlights applications of biomass energy, including heat, electricity generation, and transport fuel with less emission of GHGs. However, the expansion in South Africa faces key challenges such as the requirement of sustainable feedstocks that do not interfere with food production, concerns over land use, and a shortage of skilled professionals to oversee and manage the technologies involved. These constraints underscore a critical research opportunity to explore alternatives that support sustainable energy development.

This review highlights the availability of IAPs in South Africa, which not only pose significant threats to the environment but also demand high capital investment for their effective management methods. While species such as *Chromolaena odorata, Pinus patula,* and *Eucalyptus grandis* have been investigated internationally as potential bioenergy feedstocks, research within the South African context has been concentrated on environmental and economic impacts, with limited attention to biofuel production. This reveals a clear research gap in evaluating their energy potential for renewable biofuels, which could offer a dual benefit of ecological restoration and sustainable energy generation.

Different characterisation techniques, such as proximate, elemental, structural, and thermal analysis, have been employed to evaluate the potential of the substrate for bioenergy generation. However, the methods do not indicate how well the materials will perform for specific biofuel production. Multi-criteria decision-making has been one of the most cost-effective and accurate methods to select materials for optimal production in engineering and energy. Despite its potential, MCDM remains underutilised in South Africa. Adopting this

approach could not only identify the most suitable IAPs for biogas and bio-oil but also promote greater awareness of its effectiveness in bioenergy research.

Bio-oil and biogas serve a wide range of energy applications, including bioheat production, electricity generation (biopower), and conversion to biomethane for use in transportation. Despite their potential, biofuels currently contribute only a minimal amount to South Africa's overall energy mix. This limited uptake is largely attributed to a shortage of skilled professionals capable of optimising conversion technologies and performing advanced fuel characterisation. To date, biogas and bio-oil production has focused on traditional substrates such as cow manure, agricultural residues, fruits, vegetables, and algae. These substrates produce various organic compounds that significantly influence the heating value and combustion efficiency of the resulting biofuels. However, invasive plants remain largely underexplored as alternative feedstocks in this context.

Overall, the literature review has revealed a gap in bioenergy production in South Africa, the need to evaluate IAPs to reduce reliance on energy food crops, characterising these species for specific biofuel production to ensure optimal good-quality yield, and lastly enhancing biogas and bio-oil conversion processes. By aiming to address these niche areas, bioenergy adoption in South Africa could potentially increase practical enterprises, optimise crop production, develop energy security, build a sustainable environment, and create substantial streams of revenue.

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3. CHARACTERISATION OF WOODY AND NONWOODY INVASIVE ALIEN PLANT SPECIES FOR BIO-OIL AND BIOGAS PRODUCTION AS RENEWABLE ENERGY SOURCES

Abstract

Bio-oil and biogas serve as crucial renewable alternatives to fossil fuels for heating, electricity generation, and transportation. However, their potential remains limited in South Africa, primarily due to the limited availability of appropriate biomass feedstocks. Therefore, this study investigated the properties of six invasive alien plant species (IAPs), three woody species (*Acacia mearnsii, Eucalyptus grandis, and Pinus patula*), and three nonwoody species (*Lantana camara, Chromolaena odorata, and Solanum mauritianum*) to assess their suitability for bio-oil and biogas production. The primary analyses conducted included structural, elemental, proximate, atomic ratio, and higher heating value (HHV) assessments. The results revealed that woody invasive species contained significantly higher levels of cellulose, hemicellulose, and lignin, measured at 47.5%, 22.6%, and 25.5%, respectively, compared to nonwoody IAPs, which exhibited lower concentrations of 23.6%, 15.9%, and 9.8% ($p < 0.005$). However, the lignin complex structure could hinder the degradation of volatile compounds in bio-oil and fermentable sugars in biogas.

The elevated carbon and hydrogen contents in both woody and nonwoody IAPs contributed to improved HHV and combustion efficiency, while the low levels of nitrogen and sulphur minimised the potential for harmful emissions. However, elevated oxygen levels in woody IAPs (45.1%) and nonwoody IAPs (43.0%) could lower biofuel energy density. The non-overlapping 95% confidence intervals for ash content between woody (2.2%) and nonwoody (8.8%) species indicate a statistically significant difference ($p < 0.05$). This may lead to inefficient biofuel conversion using nonwoody IAPs. The highest HHV was observed from elemental analysis estimation equations, with woody at 19.5 $MJ.kg^{-1}$and nonwoody IAPs at 19.1 $MJ.kg^{-1}$. Compared to South African coal, IAPs shared similarities with peat coal (17.4 to 22.4 $MJ.kg^{-1}$ which is low low-energy rank fuel but can still be utilised for heat and electricity generation. This study broadens the range of viable energy feedstocks in South Africa, supporting bio-oil and biogas production while simultaneously addressing ecological challenges posed by invasive species. However, a key limitation remains the absence of

standardised protocols for proximate analysis, which affects the consistency and comparability of results across studies. Future research should prioritise the development of methodologies to improve the reliability and reproducibility of results in this field.

3.1 Introduction

The demand for renewable energy has increased significantly in recent years due to the resource-related challenges associated with fossil fuel dependency (Álvarez-Álvarez *et al.*, 2018). Despite the growing demand, renewable sources contribute only 2.1% from hydropower, 2.0% from wind, 1.0% from solar, and 0.2% from biomass to the South African energy mix, which is insufficient to meet the demand (Bioenergy, 2021). Biomass energy derived from the degradation of organic materials serves as a source of heating and electricity generation, offering environmental and economic benefits (Hu and Gholizadeh, 2020). Biomass energy benefits are limited in South Africa due to concerns over food security and water resource constraints (Gonzalez-Salazar *et al.*, 2014; Akinbami *et al.*, 2021). This underscores the urgent need for research aimed at expanding and diversifying sustainable energy alternatives

Biomass energy produces biofuels such as biogas, bio-oil, and biochar, offering cleaner alternatives to the direct burning of biomass (Amesho *et al.*, 2024). Bio-oil is often blended with diesel and used in gas turbines, generating a capacity of 75 kW (No, 2014). Biogas is a renewable combustible gas derived from the anaerobic breakdown of organic matter (Sawyerr *et al.*, 2019b). Despite the benefits, biofuel contributes only 0.1% to the South African fuel mix, highlighting the need for further research (Akinbami *et al.*, 2021). This limitation is due to a lack of suitable biomass feedstock for specific biofuel production.

To tackle these challenges, researchers have explored IAPs as potential bioenergy substrates due to their widespread 10-million-hectare infestation, which threatens the environment and economic growth (Melane *et al.*, 2017). Methods such as herbicide use, do not only fall short but also harm soil quality and nearby crops. Although often viewed negatively, IAPs have been reported to have a moisture content of 3.78% and an ash content of 0.24%, indicating their potential for bio-oil production (Ahmed *et al.*, 2018a). Compared with food crops and municipal waste, IAPs generate fewer greenhouse gas (GHG) emissions and require minimal

inputs such as water or fertilisers, making them affordable, accessible, and eco-friendly energy resources (Kadiyala *et al.*, 2016).

Woody and nonwoody invasive species vary in characteristics due to different growth conditions, making feedstock characterisation crucial for targeted biofuel production (Ayaa *et al.*, 2022). Characterisation enables the selection of high-performing and sustainable feedstocks, ensuring optimal conversion efficiency while minimising processing cost. Characterising techniques include proximate, elemental, structural, and thermal compositions. This study aims to investigate the physical and chemical characteristics of three woody IAPs *(Acacia Mearnsii*, *Eucalyptus Grandis*, and *Pinus Patula)* and three nonwoody IAPs (*Lantana Camara*, *Chromoleana Odorata*, and *Solanum mauritianum)* for bio-oil and biogas production as renewable energy fuels. The structure of this work is as follows: (1) structural analysis via the Van Soest fibre analysis method; (2) elemental analysis via the Flash 2000 elemental analyser; (3) proximate analysis via the American Society for Testing Materials (ASTM); (4) atomic ratios, which compare IAPs with other South African energy substrates; (5) thermal analysis via HHV equations from structural, elemental, and proximate compositions. Furthermore, statistical analysis methods compare these characteristics between nonwoody and woody plants.

3.2 Materials and Methods

This section contains materials and methods used to evaluate the physical and chemical characteristics of woody and nonwoody plant species for bio-oil and biogas production.

3.2.1 Biomass collection and preparation

Three woody IAPs, namely, *Acacia mearnsii, Eucalyptus grandis, and Pinus patula,* and three nonwoody IAPs, namely, *Lantana camara, Chromoleana odorata, and Solanum mauritianum,* were evaluated for bio-oil and biogas production. The woody samples were collected from the Institute of Commercial Forestry Research, while the nonwoody species were sourced from the Athlone area. Both locations are situated in Pietermaritzburg, South Africa (coordinates: 29°37′S, 30°23′E), which experiences an average annual rainfall of 832 mm and typical temperature ranges of 11 °C (minimum) and 26 °C (maximum).

The woody part of the biomass (stem) aged 10 years was used as a working sample for woody IAPs, recommended by Cichy *et al.* (2017). These stems were chopped into 20 mm cubes to facilitate drying and grinding (Reza *et al.*, 2019a). The nonwoody biomass consisted of wood twigs and leaves that had been cut into 20 mm long pieces for drying and grinding (Borah *et al.*, 2016). All samples underwent the same preparation process: they were oven-dried at 60 °C for 24 hours using an air dryer (Eke *et al.*, 2020). After drying, the materials were ground using a stainless-steel grinder fitted with a 1 mm sieve (dimensions: 320 mm width, 450 mm height, 300 mm diameter). The ground biomass was then sealed in labelled plastic bags and stored in a desiccator to prevent moisture absorption (Shrivastava *et al.*, 2021). A schematic of the biomass preparation process is shown in Figure 3.1.



(a) Woody IAPs chips (b) Nonwoody IAP leaves and twigs (c) Grinding to 1 mm (d) Packaging and storing the prepared IAPs

Figure 3.1 Stages of preparation for woody and nonwoody IAPs for analysis

3.2.2 Experimental design

Figure 3.2 outlines the experimental design used for biomass characterisation. This section details the methodologies employed to assess structural composition, elemental makeup, proximate analysis, higher heating value (HHV), and atomic ratio

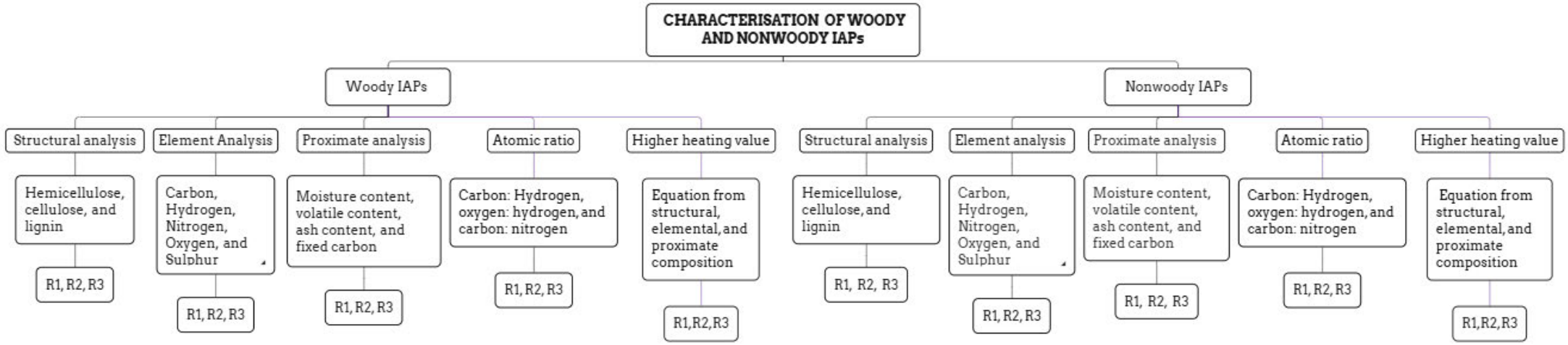


Figure 3.2 Experimental design on chracterisation of woody and nonwoody IAPs

3.2.2.1 Structural analysis

Biomass is structurally composed of cellulose, hemicellulose, and lignin. The structural analysis in this study followed the van Soest fiber method described by Singh *et al.* (2017). The experiment was conducted at Cedara College of Agriculture, Pietermaritzburg, South Africa. This method uses neutral detergent fiber (NDF) to extract non-structural components, leaving behind hemicellulose, cellulose, and lignin. Acid detergent fiber (ADF) further removes hemicellulose, isolating cellulose and lignin, while acid detergent lignin (ADL) isolates lignin alone.

The NDF values were measured following the NDF-ISO 16472:2006 standard, as cited by Tajfar *et al.* (2023). About 1 gram of the ground biomass sample was placed into a crucible, followed by the addition of roughly 100 ml of a neutral detergent solution (sodium borate decahydrate), 0.5 grams of sodium sulfate, and a few drops of n-octanol at room temperature. The mixture was boiled at 400 °C and then refluxed for 60 minutes from the start of boiling. The crucibles were then dried at 105 °C for 8 hours and subsequently weighed. The fiber content was calculated using Equation 3.1, as outlined by Singh *et al.* (2017).

$$\text{NDF} = \frac{(\text{Wt of crucible} + \text{NDF}) - \text{Wt of the crucible}}{\text{Wt of sample}} \times 100 \quad (3.1)$$

Where

$\text{Wt} = \text{Weight (g)}$

Acid detergent fiber (ADF) analysis was carried out based on ISO 13906:2008 guidelines (Tajfar *et al.*, 2023). This process followed a similar procedure to the NDF method, but with the use of acid detergent, specifically 1 N sulfuric acid. Cellulose and lignin concentrations were then computed using Equation 3.2.

$$\text{ADF} = \frac{(\text{Wt of crucible} + \text{ADF}) - \text{Wt of the crucible}}{\text{Wt of sample}} \times 100 \quad (3.2)$$

The acid detergent lignin (ADL) was determined according to ISO 13906:2008 methods, as referenced by Tajfar *et al.* (2023), where the content was determined by adding 72% sulfuric acid and constantly stirring for 3 h. The resulting mixture was filtered, rinsed twice with distilled water, and then dried in a hot air oven at 105 °C for eight hours. The reduction in mass was used to calculate the lignin content using Equation 3 (Singh *et al.*, 2017).

$$\text{ADL} = \frac{(\text{Wt of crucible after acid soak}) - \text{Wt of the crucible}}{\text{Wt of sample}} \times 100 \quad (3.3)$$

Equations 3.4, 3.5, and 3.6 were used to calculate the amount of hemicellulose, cellulose, and lignin in a substrate (Shrivastava *et al.*, 2021).

$$\text{Hemicellulose} = \text{NDF \%} - \text{ADF \%} \quad (3.4)$$

$$\text{Cellulose} = \text{ADF \%} - \text{ADL \%} \quad (3.5)$$

$$\text{Lignin} = \text{ADL \%} \quad (3.6)$$

- Elemental analysis

The elemental composition of biomass includes major organic elements, namely, carbon (C), sulphur (S), hydrogen (H), oxygen (O), and nitrogen (N) (Singh *et al.*, 2017). The elemental analysis was performed at the University of Kwa-Zulu Natal (UKZN) Physics and Chemistry Laboratory in Pietermaritzburg via a Thermo Scientific Flash 2000 CHNS analyser. This method, based on Singh *et al.* (2017), involved placing about 1 mg of finely powdered biomass into a tin capsule, which was then weighed and combusted at 980 °C in a helium atmosphere supplemented with oxygen. The resulting concentrations of C, H, N, and S were quantified using Eager 300 software. Oxygen content was estimated by subtracting the total CHNS content from 100%, following the method proposed by Reza *et al.* (2019b).

$$\text{Oxygen (O)} = 100 - (\text{C} + \text{H} + \text{N} + \text{S}) \quad (3.7)$$

- Proximate analysis

The proximate composition of biomass includes the percentage weight of moisture, ash, volatile matter, and fixed carbon. These properties were assessed following ASTM standard procedures.

Moisture content (MC) was measured using the ASTM D2974-8 method, as outlined by Mishra and Mohanty (2018). Around 5 grams of the solid sample was placed in a crucible and weighed at ambient temperature. It was then dried in a hot air oven at 105±3 °C for 24 hours. After drying, the sample was cooled in a desiccator, reweighed once it returned to room temperature, and the moisture content was calculated using Equation 3.8.

$$\mathrm{MC} = \frac{\mathrm{W_{si}} - \mathrm{W_{sf}}}{\mathrm{W_{si}}} \times 100 \tag{3.8}$$

Where

$\mathrm{W_{si}}$ = Initial weight of the sample before heating (g)
$\mathrm{W_{sf}}$ = Final weight of sample after heating (g)

The ash content (AC) was determined following the ASTM 3173-87 standard, as referenced by Mishra and Mohanty (2018). A 5 g dried sample was placed in a crucible and combusted in a preheated muffle furnace at 575 °C for three hours. After cooling, the residue was weighed, and ash content was derived using Equation 3.9.

$$\mathrm{AC} = \frac{\mathrm{W_{ash}}}{\mathrm{W_{sf}}} \times 100 \tag{3.9}$$

Where

W_{ash} = Weight of sample after combustion (g)

The volatile content (VC) was evaluated using the ASTM D4559-99 method. A 5 g portion of the dried, 1 mm-sized sample (from the MC determination) was placed in a furnace at 900 °C

for 7 minutes. The sample was then cooled to room temperature and weighed again, with VC calculated using Equation 3.10.

$$\mathrm{VC} = \frac{\mathrm{W_{sf}} - \mathrm{W_{remaining}}}{\mathrm{W_{sf}}} \times 100 \quad (3.10)$$

Where

$\mathrm{W_{remaining}}$ = Weight of content remaining after releasing volatile (g)

The fixed carbon (FC) content was determined via Equation 3.11 through the values of ash content and volatile content obtained via Equations 3.9 and 3.10 (Da Silva Ignacio *et al.*, 2019).

$$\mathrm{FC} = 100 - (\mathrm{AC} + \mathrm{VC}) \quad (3.11)$$

- Atomic ratio

The energy density of IAPs was evaluated using atomic ratios in comparison to various biomass substrates in South Africa, including sugar bagasse, scenedesmus obliquus microalgae, fruit and vegetable waste, and cassava tubers. Equations 3.12, 3.13, and 3.14 computed the atomic ratios of nitrogen to carbon (N: C), oxygen to carbon (O: C), and hydrogen to carbon (H: C), respectively (Fajobi *et al.*, 2022).

$$\mathrm{H{:}\,C\ Ratio} = \frac{\mathrm{H}}{\mathrm{C}} \quad (3.12)$$

$$\mathrm{O{:}\,C\ Ratio} = \frac{\mathrm{O}}{\mathrm{C}} \quad (3.13)$$

$$\mathrm{N{:}\,C\ Ratio} = \frac{\mathrm{N}}{\mathrm{C}} \quad (3.14)$$

- Higher heating value (HHV)

The HHV was calculated using established formulas from previous studies, which are based on the structural, elemental, and proximate properties of both woody and nonwoody biomass

types. This method allows for a more detailed evaluation of how these factors influence the thermal performance, energy yield, and combustion characteristics of IAPs. To enhance result accuracy, three different equations from each category were applied, as shown in Table 3.1. Additionally, the HHV values of the IAPs were benchmarked against various South African fuels such as peat, lignite, sub-bituminous, bituminous, and anthracite to evaluate their potential as viable energy sources.

Table 3.1 Higher heating value formula derived from structural, elemental, and proximate

HHV formula	References	R^2	Biomass	Accuracy (%)
HHV from structural composition				
$\mathrm{HHV} = 16.1964 + 0.0555\mathrm{L}$	(Álvarez *et al.*, 2015)	-		1.13
$\mathrm{HHV} = 0.0889 + 16.8218$	(Demirbaş, 2001b)	0.95	Wood/nonwood	0.056
$\mathrm{HHV} = 16.292 + 0.0979\mathrm{L}$	(Acar and Ayanoğlu, 2012)	0.93	Wood/nonwood	-
HHV from elemental composition				
$\mathrm{HHV} = -0.763 + 0.30\mathrm{C} + 0.525\mathrm{H} + 0.064\mathrm{O}$	(Jenkins and Ebeling, 1985)	0.792	Biomass	1.78
$\mathrm{HHV} = 0.3516\mathrm{C} + 1.16225 - 0.1109\mathrm{O} + 0.0628\mathrm{N} + 0.10465\mathrm{S}$	(Annamalai *et al.*, 1987)	0.720	Biomass	-0.59
$\mathrm{HHV} = -1.3675 + 0.3137\mathrm{C} + 0.7009\mathrm{H} + 0.0318\mathrm{O}$	(Sheng and Azevedo, 2005)	0.834	Biomass	0.07
HHV from proximate composition				
$\mathrm{HHV} = -3.0368 + 0.2218 \times \mathrm{VC} + 0.2601 \times \mathrm{FC}$	(Sheng and Azevedo, 2005)	0.617	Biomass	0.26
$\mathrm{HHV} = 23.885 - 0.430 \times \mathrm{Ash} - 0.047 \times \mathrm{VC}$	(Jenkins and Ebeling, 1985)	-	Biomass	-

$HHV = -10.81408 + 0.3133(FC + VM)$	(Jiménez and González, 1991)	1.16	Biomass	0.533

R^2 represents the coefficient of determination. C, H, O, and S denote the elemental compositions of carbon, hydrogen, oxygen, and sulphur, respectively. L refers to lignin content, while VC, MC, and FC represent the proximate composition parameters: volatile content, moisture content, and fixed carbon content, respectively.

3.2.3 Statistical analysis

Statistical analysis was conducted using SPSS software (version 11) to evaluate variations and trends in the physicochemical composition of woody and nonwoody IAPs for bio-oil production. Descriptive statistics, including mean values, were used to summarise the data. Additionally, independent t-tests (at a 5% significance level) and two-way ANOVA were employed to identify significant differences between the groups.

3.3 Results and Discussion

This section presents the key findings on the physical and chemical properties of woody and nonwoody IAPs, assessing their potential for biogas and bio-oil production as renewable energy sources. The results on structural, elemental, and proximate composition are presented in Table 3.2. Figure 3.3 represents these means with 95% confidence intervals (CI) error bars.

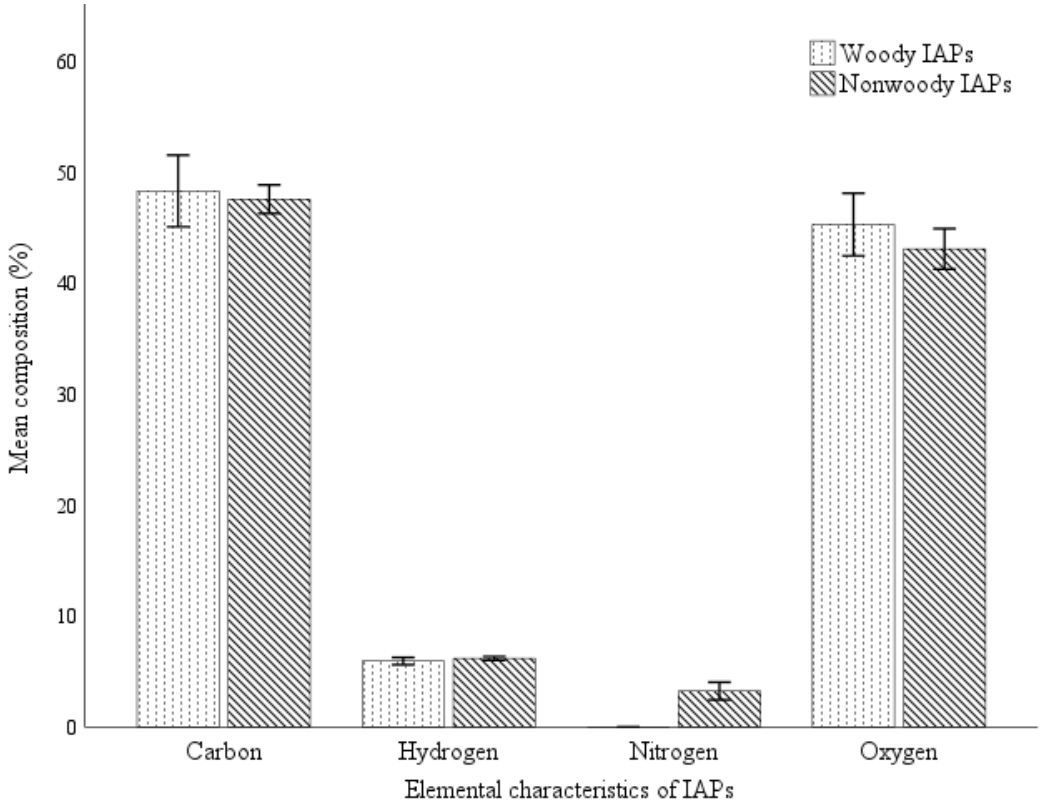
Table 3.2 The structural, elemental, and proximate composition of woody and nonwoody IAPs.

Sample name	Woody IAPs			Nonwoody IAPs		
	A. mearnsii	*E. grandis*	*P. patula*	*L. camara*	*C. odorata*	*S. mauritianum*
Structural analysis (%)						
Cellulose	43.73 ± 1.10	53.54 ± 0.11	45.27 ± 0.26	26.65 ± 0.08	24.07 ± 0.07	20.08 ± 0.17
Hemicellulose	23.67 ± 0.70	20.26 ± 0.26	23.88 ± 0.12	19.28 ± 0.02	16.18 ± 0.03	12.16 ± 0.15
Lignin	22.83 ± 0.15	23.86 ± 0.18	29.82 ± 0.12	12.23 ± 0.03	9.92 ± 0.07	7.39 ± 0.26
Elemental analysis (%)						
Carbon	44.58 ± 3.01	50.83 ± 3.06	50.52 ± 1.29	48.09 ± 1.08	46.11 ± 0.50	48.51 ± 2.20
Hydrogen	5.63 ± 0.25	6.08 ± 0.56	6.11 ± 0.37	6.08 ± 0.25	6.18 ± 0.21	6.29 ± 0.25
Nitrogen	ND	ND	ND	2.32 ± 0.10	2.86 ± 0.18	4.54 ± 0.50
Oxygen	48.79±3.53	43.09 ± 3.57	43.98 ± 0.63	43.50 ± 1.26	45.13 ± 0.50	40.65 ± 2.30
Sulphur	ND	ND	ND	ND	ND	ND
Proximate analysis (%)						
Moisture content	3.90 ± 0.09	1.89 ± 0.13	2.89 ± 0.12	4.24 ± 0.03	3.34 ± 0.59	3.61 ± 0.15
Volatile content	87.15 ± 0.21	87.90 ± 0.06	86.82 ± 0.15	84.03 ± 0.09	85.34 ± 0.45	82.89 ± 0.29
Ash content	0.94 ± 0.07	3.79 ± 0.001	1.80 ± 0001	8.14 ± 0.03	9.63 ± 0.34	9.63 ± 0.46
Fixed carbon	7.92 ± 0.08	6.42 ± 0.03	8.45 ± 0.09	3.36 ± 0.06	3.91 ± 0.38	3.87 ± 0.38

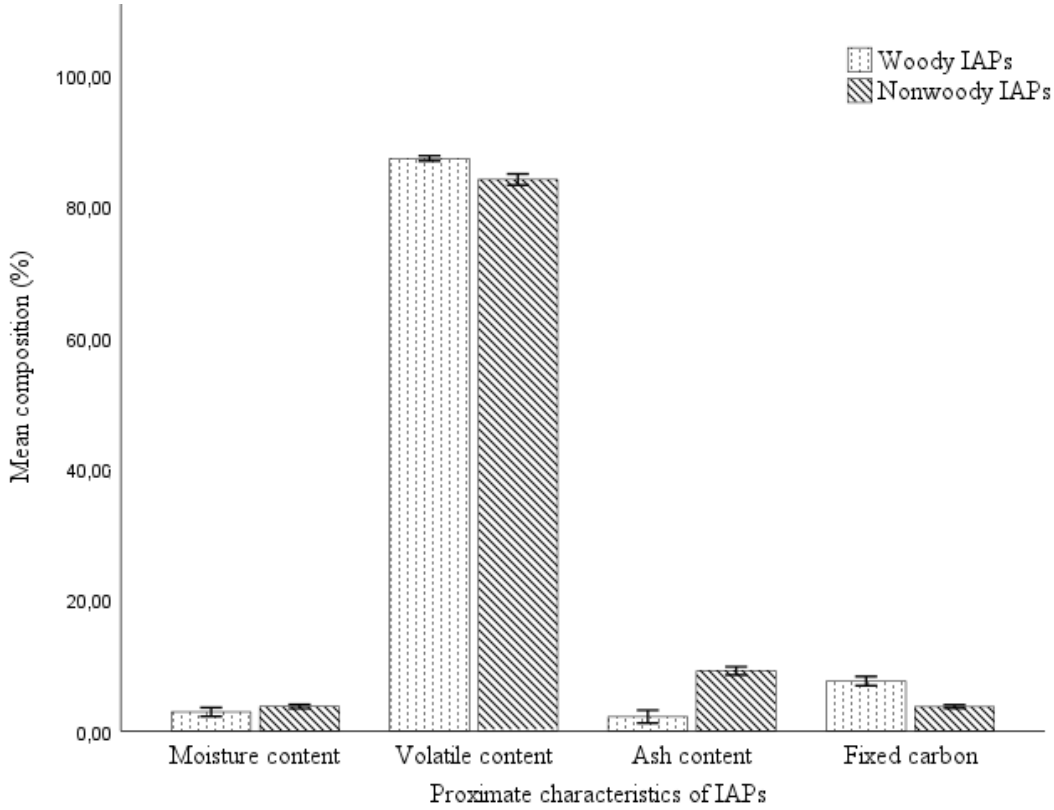
All values are means of three values ± standard deviations. ND means not detected.



(a) Structural composition



(b) Elemental composition



(c) Proximate composition

Figure 3.3 The mean structural, elemental and proximate composition of woody and nonwoody IAPs representing 95% confidence intervals (CI) errors bars

3.3.1 Structural analysis

The variations of cellulose, hemicellulose, and lignin in IAPs influence the quality and yield of biogas and bio-oil as renewable fuels, therefore, characterisation is essential to optimise production. Woody species exhibited higher cellulose (47.52%), hemicellulose (22.60%), and lignin (25.50%) contents compared to nonwoody IAPs (23.60%, 15.87%, and 9.84%, respectively; $p < 0.05$). The statistically significant differences highlighted by the non-overlapping confidence intervals in Figure 3.3(a) can be attributed to the structural maturity of woody species. Unlike perennial nonwoody species, woody plants typically have a lifespan of up to 10 years, allowing them to develop more rigid and robust tissues than do the flexible, less structured tissues of perennial nonwoody species (Shen *et al.*, 2024). This is also validated by Schädel *et al.* (2010), who reported a greater structural composition in sapwood (31%) than in herbaceous species (10%).

In terms of bio-oil production, woody IAPs, particularly *P. patula,* presented greater potential for higher yields than nonwoody IAPs did. This advantage stems from their relatively high concentrations of cellulose (ranging between 30% and 60%) and hemicellulose (20% to 40%), both of which lie within the optimal range for bio-oil production and contain volatile compounds that readily convert to condensable vapours during pyrolysis (Balat, 2011; Guedes *et al.*, 2018). Although higher bio-oil yields are expected, the stable and resistant structure of lignin favours biochar over bio-oil production, requiring higher temperatures for optimal pyrolysis (Qu *et al.*, 2011).

Cellulose and hemicellulose provide fermentable sugars that enhance biogas production facilitated by Clostridium and Methanospirillum micro-organisms (Li *et al.*, 2018). Nonwoody IAPs, particularly S. *mauritianum* presented greater potential for higher yields of biogas than woody IAPs, due to their lower levels of lignin content. Lignin hinders biodegradability by forming a complex structure that enables enzymic and bacterial degradation of cellulose and hemicellulose (Li *et al.*, 2018; Shrivastava *et al.*, 2021). This pattern is consistent with findings by Ayaa *et al.* (2022) who reported structural values of 40.2% cellulose, 21.3% hemicellulose, and 14.7% lignin in *Acacia mearnsii* and *Lantana camara*. Variability in lignin concentrations across species may be linked to environmental factors; for example, areas with high rainfall promote faster biomass accumulation and often result in reduced lignin formation.

While the abundance of cellulose and hemicellulose in woody IAPs promotes bio-oil yield and supports biogas production in nonwoody species, lignin presents processing challenges. Its decomposition necessitates more intensive energy input and pre-treatment strategies such as acid or alkaline hydrolysis, which can significantly raise operational costs. Therefore, conducting comprehensive structural analyses is essential for optimising both pyrolysis and anaerobic digestion processes. Such evaluations help guide the selection of biomass that balances economic viability with high energy output.

3.3.2 Elemental analysis

The elemental composition plays a critical role in determining both the yield and quality of bio-oil derived from IAPs, making its assessment essential. As shown in Figure 3.3 (b), the confidence intervals (CIs) for the elemental data of woody and nonwoody IAPs overlap, indicating no statistically significant difference ($p > 0.05$). This similarity is attributed to their shared biochemical components, namely cellulose, hemicellulose, and lignin, which contribute to comparable elemental profiles due to similar biosynthetic pathways. For biofuel applications, both woody and nonwoody IAPs exhibit carbon concentrations ranging from 30% to 60% and hydrogen levels between 5% and 6%, which are considered ideal for supporting high heating values (HHV) and efficient combustion in both bio-oil and biogas systems (Vargas-Moreno *et al.*, 2012; Yadav *et al.*, 2017). These fuels have the potential to enhance energy access in rural areas by providing electricity and thermal energy for cooking and lighting.

In terms of oxygen content, woody IAPs recorded approximately 45.1%, while nonwoody species had about 43.0%, as shown in Table 3.2. The study by Guedes *et al.* (2018) has obtained similar values that tend to range between 30 and 45%, and such concentrations reduce the HHV of bio-oil, resulting in poor flame stability, high viscosity, and less ignition. For biogas production, such concentrations inactive growth and activities of micro-organisms, causing instability of the reaction, long start-up, and ultimately reduction in biogas (Botheju and Bakke, 2011). Therefore, upgrading techniques such as deoxygenation are essential to improve the energy density of biofuels (Lian *et al.*, 2017). Regarding nitrogen and sulphur content, woody IAPs showed around 3.2% nitrogen and no detectable sulphur, while nonwoody IAPs had neither element detected. This absence can be explained by the limitations of CHNS elemental

analyzers, which often cannot detect elements present at concentrations below 1% (Darvell *et al.*, 2012). The negligible nitrogen and sulphur levels are beneficial from an environmental standpoint, as they minimise the potential for harmful nitrogen and sulphur oxide emissions during combustion. The elemental composition of woody and nonwoody biomass in a study by Ayaa *et al.* (2022) was comparable to that of carbon (35.2 to 47.8%), hydrogen (4.5 to 6.3%), oxygen (44.2 to 58.1%), nitrogen (0.05 to 1.5%), and sulphur not detected.

Overall, both woody and nonwoody IAPs exhibit favourable characteristics for bio-oil and biogas production. This contributes to selecting appropriate substrate for specific fuel production, optimising time, cost, and energy efficiency. Future research should focus on appropriate upgrading techniques to enhance fuel quality.

3.3.3 Proximate analysis

The proximate composition plays a critical role in determining the efficiency of pyrolysis and anaerobic digestion, as well as the resulting yield and quality of bio-oil and biogas. Therefore, its assessment is essential. The proximate analysis revealed moisture content values of 2.9% for woody IAPs and 3.75% for nonwoody IAPs, as presented in Table 3.2. According to Figure 3.3 (c), the overlapping confidence intervals (CIs) suggest no statistically significant difference in moisture content between the two biomass types ($p > 0.05$). Both IAP groups exhibit promising characteristics for enhancing bio-oil production due to their low moisture levels under 10%, which ensures that more thermal energy is directed toward the pyrolysis process rather than evaporating water (Melane *et al.*, 2017).

However, the requirements differ for biogas generation, where moisture levels in the range of 35% to 65% are necessary to support microbial activity, facilitate nutrient transport, and dilute inhibitory compounds (Avinash and Mishra, 2023). Based on the observed moisture content, both woody and nonwoody IAPs are more favorable for bio-oil production rather than biogas. When compared to other biomass types, which typically show moisture content ranging between 6.48% and 7.13%, the IAP values in this study are relatively lower (Shrivastava *et al.*, 2021). This may be attributed to the lack of standardised methods for determining proximate analysis, as shown in studies by Reza *et al.* (2019b), who conducted their analysis at 105 °C for only 3 hours, and by Bhavsar *et al.* (2018) at 105 °C for 24 hours.

The mean volatile content was 87.3% for woody IAPs and 84.1% volatile content for nonwoody IAPs with significant variation ($p < 0.05$). The difference is attributed to variation in the cellulose and hemicellulose, as discussed in section 3.3.1. These concentrations refer to material that turns into gas when heated, offering the potential for conversion into usable gases or condensed into bio-oil (Da Silva Ignacio *et al.*, 2019). The VC obtained in this study is coherent with the study conducted by Singh *et al.* (2017) on nonwoody biomass, with ranges from 80.21 to 86.84%.

The results in Table 3.2 indicated that woody IAPs exhibited lower ash content (2.2%) and higher fixed carbon (7.6%) compared to nonwoody IAPs (8.8% and 3.5%, respectively; $p < 0.05$). Ash content also plays a critical role, particularly in downstream processing challenges. A study by Bakker and Elbersen2005) noted that higher ash levels in nonwoody plants are linked to silica accumulation, which reinforces cell walls as a defence against environmental stress. In this study, the ash content of woody IAPs falls within the acceptable range of 0.1% to 5%, making them suitable for bio-oil and biogas conversion. On the other hand, nonwoody IAPs exhibit ash concentrations exceeding this threshold, which could result in problematic compounds such as silica, leading to slag formation, equipment corrosion, and potential damage to pyrolysis reactors and anaerobic digesters (Vassilev *et al.*, 2017).

The higher fixed carbon in woody IAPs is due to increased lignin and carbon content (Pasangulapati *et al.*, 2012), such concentration favours biochar over bio-oil and is less digestible for biogas production. The ash content results align with Melane *et al.* (2017), while the fixed findings are consistent with Singhal *et al.* (2017) research work. Based on proximate composition, both woody and nonwoody IAPs are better suited for bio-oil production due to lower levels of moisture content and high fixed carbon. Pre-treatment methods are recommended for higher levels of ash and fixed carbon. Further research should focus on allocating standardised testing methods for proximate analysis to ensure reliable and comparable results.

3.3.4 Atomic Ratio

Table 3.3 presents the atomic ratios of hydrogen to carbon (H: C), oxygen to carbon (O: C), and carbon to nitrogen (C: N) for both woody and nonwoody IAPs, along with other South

African biomass types such as Scenedesmus obliquus microalgae, sugarcane bagasse, fruit and vegetable residues, and cassava tubers. These comparisons illustrate the competitiveness of IAPs as potential feedstocks for bio-oil and biogas production when benchmarked against conventional substrates.

Table 3.3 Comparison of atomic ratios of woody and nonwoody species with other South African energy substrates.

Biomass	H: C	O: C	N: C	References
Woody IAPs	1.47	0.70	ND	Present study
Nonwoody IAPs	1.55	0.68	0.058	Present study
Sugar bagasse	1.62	0.73	0.0027	(Onokwai *et al.*, 2024)
Scenedesmus obliquus microalgae	2.33	0.71	0.135	(Mustapha *et al.*, 2023)
Fruit and vegetable waste	1.78	0.57	0.047	(Sawyerr *et al.*, 2019b)
Cassava tuber	1.33	0.58	0.028	(Sawyerr *et al.*, 2019b)

IAPs are presented in mean values, while other substrates are single literature-based values.

The H: C ratio, which reflects hydrogen availability, is critical for hydrodeoxygenation reactions that enhance the energy stability of bio-oil and biogas (Gollakota *et al.*, 2023). Woody and nonwoody IAPs exhibited moderate H: C ratios (1.47 and 1.55, respectively), indicating a reasonable trade-off between stability and energy output. In contrast, other biomass types, such as fruit waste, vegetable waste, sugarcane bagasse, and microalgae, showed higher H: C values, generally associated with elevated HHVs. However, feedstocks such as fruit and vegetable waste present challenges due to their high moisture content (58.4%), which increases transportation and processing costs while lowering energy conversion efficiency (Melane *et al.*, 2017). Although sugarcane bagasse is economically attractive, its lignin content (27.8%) imposes higher energy demands for conversion (Onokwai *et al.*, 2024). Microalgae, despite its high yield potential, requires controlled cultivation systems and intensive monitoring, leading to significantly higher operating costs (Sekar *et al.*, 2021). As such, while these alternatives

may offer greater calorific potential, IAPs present a more practical and economical choice for sustainable energy production.

The O: C ratio is an indicator of oxygenated compounds, which affect thermal behavior, microbial activity, and energy density (Park *et al.*, 2021). Biomass with lower O: C ratios, such as fruit, vegetable waste, and cassava, tends to produce fewer undesirable oxygenates, thereby reducing the need for expensive upgrading processes. In contrast, sugarcane bagasse and microalgae have high O: C ratios, necessitating catalytic upgrading, which increases energy demand and greenhouse gas emissions (Mustapha *et al.*, 2023). IAPs, with their moderate O: C ratios, offer a balanced option, combining acceptable energy yield, reduced processing requirements, and environmental benefits. This makes them a promising feedstock requiring less intensive upgrading compared to higher O: C alternatives.

The C: N ratio is also essential, as it provides insight into potential nitrogen oxide (NOx) emissions during combustion and microbial growth potential in anaerobic digestion systems (Silvestre *et al.*, 2020). Woody IAPs displayed undetectable N: C ratios, suggesting minimal nitrogen content, which enhances their suitability as cleaner-burning fuels. Cassava similarly showed low nitrogen levels. However, while these low values reduce NOx emissions, they may also limit microbial activity, leading to lower biogas yields. In contrast, biomass types such as microalgae exhibit elevated N: C ratios, which can increase emission risks. To address these challenges, pre-treatment methods using zeolite-based or biochar materials can be employed to adsorb excess nitrogen compounds and mitigate emission levels during combustion (Xu *et al.*, 2023).

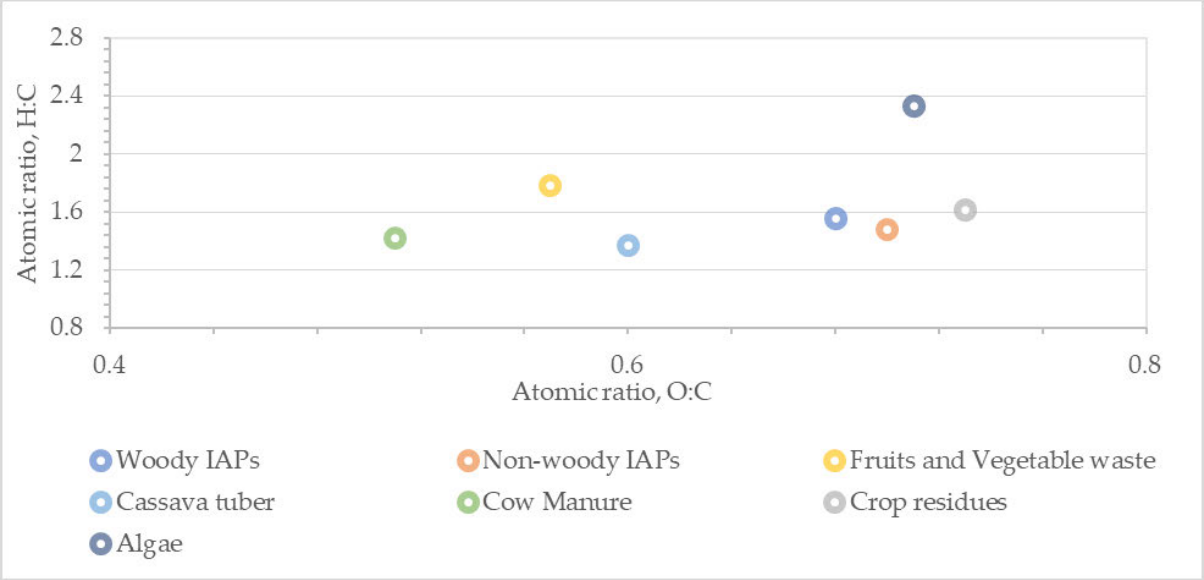


Figure 3.4 Van Krevelen diagram showing woody and nonwoody IAPs compared with other South African energy substrates

For the quality of bio-oil and biogas, the compounds in bio-oil and biogas were classified into as shown Van Krevelen diagram in Figure 3.4; lipids ($0 \leq O/C \leq 0.2$, $1.7 \leq H/C \leq 2.25$), unsaturated hydrocarbons (UHs, $0 \leq O/C \leq 0.1$, $0.7 \leq H/C < 1.7$), condensed aromatic hydrocarbons (CAHs, $0 \leq O/C \leq 1.0$, $0.3 \leq H/C \leq 0.7$), phenolic-like species ($0 \leq O/C \leq 0.6$, $0.6 \leq H/C \leq 1.3$) and saccharides (sugars, $0.5 \leq O/C \leq 0.9$, $1.2 \leq H/C \leq 2.25$) (Zhong *et al.*, 2022b). The results suggest that all the substrates generate saccharide-derived sugars such as levoglucosan and cellobiosan during cellulose and hemicellulose degradation. In bio-oil production, the sugars reduce hydrogen content, promote coke formation, which reduces energy density and increases the risk of corrosion in pyrolysis reactors (Yu *et al.*, 2016). Conversely, in biogas production, these sugars are highly digestible and serve as an energy source for micro-organisms, ultimately improving methane formation (Li *et al.*, 2018).

Although woody and nonwoody IAPs show promising characteristics, especially for bio-oil production, they may not be the most efficient substrate when compared to fruit and vegetable waste. However, fruits and vegetables also present challenges such as seasonal availability, perishability, requiring proper storage, thus contributing to higher process costs. This section contributes to a comparative assessment of IAPs, evaluating their viability as an energy substrate to optimise biofuel production.

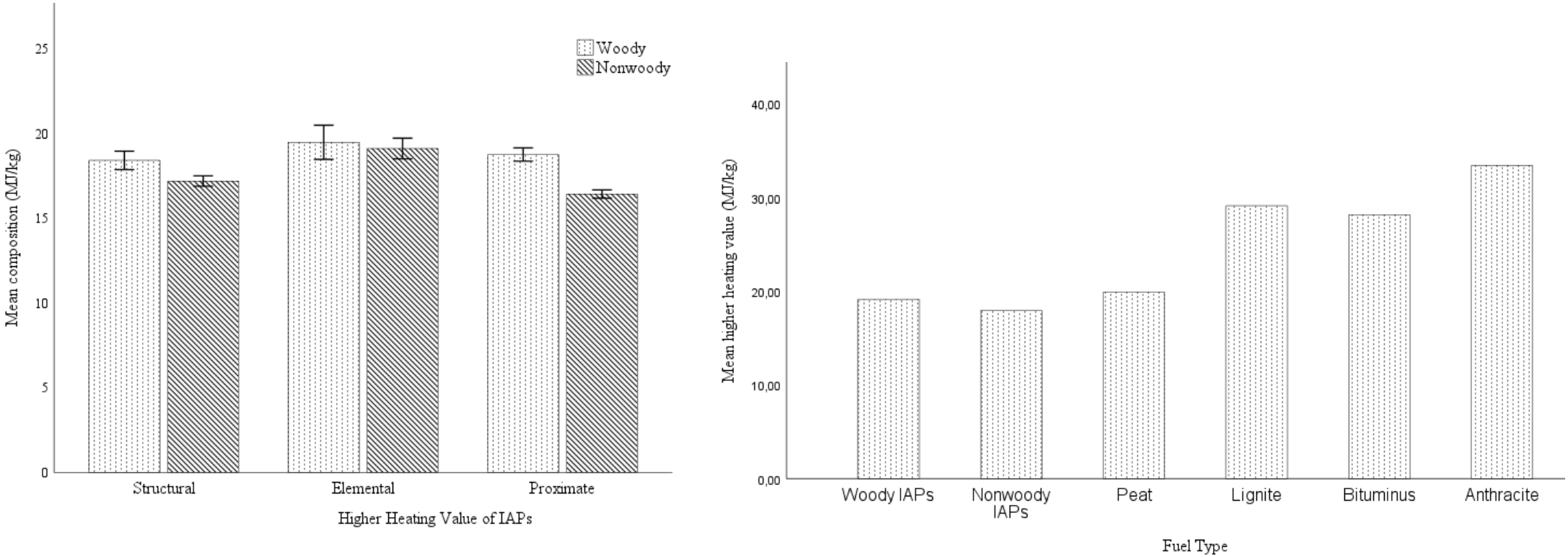
3.3.5 Higher heating values

The HHV of biomass influences the HHV of bio-oil and biogas production; hence, a comprehensive investigation is essential. Table 3.4 presents the HHV of woody and nonwoody IAPs based on structural, elemental, and proximate composition. Figure 3.4 (a) compares the HHV from the structural, elemental, and proximate compositions, while Figure 3.5 (b) compares the HHV of IAPs to South African coal.

Table 3.4 The HHV of woody and nonwoody IAPs derived from structural, elemental, and proximate compositions

Species	HHV from structural composition ($MJ.kg^{-1}$)	HHV from elemental composition ($MJ.kg^{-1}$)	HHV from proximate composition ($MJ.kg^{-1}$)
Woody IAPs			
A. mearnsii	18.28 ± 0.73	17.87 ± 0.96	18.94 ± 0.52
E. grandis	18.13 ± 0.56	20.39 ± 0.10	18.54 ± 0.72
P. patula	18.83 ± 0.87	20.20 ± 0.13	18.81 ± 0.35
Nonwoody IAPs			
L. camara	17.32 ± 0.39	19.45 ± 0.18	16.40 ± 0.12
C. odorata	17.24 ± 0.48	18.88 ± 0.29	16.71 ± 0.29
S. mauritianum	17.04 ± 0.44	19.03 ± 1.45	16.19 ± 0.31
South African Coal			
Coal	Higher heating value ($MJ.kg^{-1}$) (Gouws *et al.*, 2021)		
Peat	17.4 to 22.4		
Lignite	26.5 to 31.7		
Bituminous	19.9 to 36.4		
Anthracite	30.6 to 36.2		

All values are means of three values ± standard deviations.



(a) Comparison of HHV of IAPs from structural, elemental, and proximate analysis

(b) Comparing IAPs with South African coal

Figure 3.5 HHV of IAPs from structural, elemental, and proximate composition compared to South African coal

Table 3.5 shows that the HHV of woody IAPs based on structural composition was 18.4 $MJ.kg^{-1}$, whereas that of nonwoody IAPs was 17.2 $MJ.kg^{-1}$. The non-overlapping confidence intervals (CIs) in Figure 3.5 (a) suggest a statistically significant difference (p-value), which can be attributed to variation in cellulose, hemicellulose, and lignin as discussed in Section 3.3.1. The HHV of woody IAPs based on elemental composition was 19.5 $MJ.kg^{-1}$, whereas that of nonwoody IAPs was 19.1 $MJ.kg^{-1}$. The overlapping CIs indicate no significant differences, and this is attributed to their similarity in their elemental compositions, as discussed in section 3.3.2.

As shown in Table 3.5, the higher heating value (HHV) derived from the structural composition of IAPs averaged 18.4 $MJ \cdot kg^{-1}$, compared to 17.2 $MJ \cdot kg^{-1}$ for nonwoody IAPs. The distinct, non-overlapping confidence intervals (CIs) presented in Figure 3.5(a) indicate a statistically significant difference, which is likely due to differences in their cellulose, hemicellulose, and lignin contents, as outlined in Section 3.3.1. In contrast, HHV values based on elemental composition were 19.5 $MJ \cdot kg^{-1}$ for woody IAPs and 19.1 $MJ \cdot kg^{-1}$ for nonwoody IAPs. The overlapping CIs in this case suggest that the differences are not statistically significant, likely due to the similar elemental profiles of both biomass types, as discussed in Section 3.3.2. Overall, woody IAPs had higher HHV compared to nonwoody IAPs due to their high lignin content, which provides energy-rich carbon. This aligns with a study by Maksimuk *et al.* (2021) showing values between 17.22 to 17.56 $MJ.kg^{-1}$ for cellulose and between 23 to 27 $MJ.kg^{-1}$ for lignin. Furthermore, the higher ash content translates to incombustible residues and contributes to an inefficient conversion process (Fajobi *et al.*, 2022). The results of this study mean, bio-oil and biogas derived from woody IAPs may have more energy per unit fuel compared to those derived from nonwoody.

Among the three methods used, the elemental composition yielded the HHVs, as illustrated in Figure 3.4(a). This outcome is primarily linked to the presence of combustible elements such as carbon and hydrogen (Krička *et al.*, 2017; Wang *et al.*, 2021). According to Sheng and Azevedo (2005), HHV estimations based on proximate composition are less direct, as they also reflect the influence of non-combustible components such as moisture and ash. The findings of this research are consistent with Kutlu and Kocar (2018), who reported HHV ranges of 17–20 $MJ \cdot kg^{-1}$ for woody biomass and 15–19 $MJ \cdot kg^{-1}$ for nonwoody biomass.

Table 3.4 further compares different South African coal with IAPs, revealing that IAPs resemble peat fossil fuel as shown in Figure 4.3 (b). This is a low rank fossil fuel characterised by high micro-porosity and lower carbon levels, but can still be utilised as fuel for heat and electricity generation (Falcon and Ham, 1988; Karvonen *et al.*, 2018). Compared to high-grade coals such as anthracite and bituminous coal, IAPs generally exhibit lower carbon content, higher moisture levels, and reduced energy density (Engelbrecht *et al.*, 2007; Makgato and Chirwa, 2017). This section contributed toward assessing the viability of each composition on the energy density of biofuels, further assessing the energy potential of IAPs compared to coal.

3.4 Conclusion

This research investigated the physicochemical properties of woody and nonwoody IAPs to assess their potential as renewable feedstocks for bio-oil and biogas generation. By analysing proximate, elemental, and structural characteristics, the study identified key biomass traits that enhanced both the yield and quality of biofuels. For example, elevated levels of carbon and hydrogen were positively associated with higher heating values (HHV), thus improving combustion efficiency. Conversely, high oxygen content introduced challenges such as chemical instability and corrosion. These insights enabled the strategic selection of high-performing biomass substrates, reducing the need for post-processing and making bio-oil production more cost-effective. Additionally, understanding these characteristics facilitated the optimisation of pyrolysis and anaerobic digestion processes. Due to the complex and energy-dense nature of lignin in certain IAPs, greater energy input was required for breakdown. Recognising this allowed for better adjustment of process parameters and the design of advanced systems to enhance fuel production efficiency.

Using proximate, elemental, and structural analysis to estimate the HHV of IAPs provided a comprehensive and more accurate methodology for predicting energy output. The comparative analysis of IAP-derived energy content to various coal types offered a benchmark for evaluating the practical feasibility of bio-oil and biogas as fossil fuel alternatives. This study underscored the value of converting IAPs into bio-based fuels, presenting a dual benefit of mitigating invasive species while offering a sustainable energy solution. Additionally, removing IAPs contributed to the restoration of arable land, thereby improving local agricultural productivity. Future work could explore improved IAP harvesting strategies and the feasibility of establishing biomass conversion facilities within the South African context.

Chapter 4 focused on identifying which IAPs were most suitable for bio-oil and biogas production based on the evaluated parameters.

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4. MULTI-CRITERIA DECISION MAKING TO EVALUATE AND PRIORITISE IAPs SUITABLE FOR BIO-OIL AND BIOGAS PRODUCTION

Abstract

Invasive Alien Plant species (IAPs) present a beneficial opportunity as a potential substrate to produce biofuels that can be utilised as sources of renewable energy. However, the variation in their energy characteristics restricts the optimal production of biofuels and maximises operational costs. Therefore, this study aims to address this challenge by applying a multi-criteria decision-making (MCDM) approach, specifically the Analytic Hierarchy Process (AHP), to evaluate the relative importance of biomass characteristics, including proximate, elemental, and structural composition, concerning bio-oil and biogas production. The technique for order preference by similarity to ideal solution (TOPSIS) method further evaluates the set of alternatives, which are woody IAPs *(Acacia Mearnsii*, *Eucalyptus Grandis*, and *Pinus Patula)* and nonwoody IAPs (*Lantana Camara*, *Chromoleana Odorata*, and *Solanum mauritianum)* on predefined criteria and selects or ranks the most ideal IAPs for bio-oil and biogas production.

The findings of this study illustrated that the ideal biomass characteristics for optimal bio-oil were hydrogen, carbon, and volatile matter, with a consistency ratio of 0.079 within an acceptable threshold of 0.1, illustrating the accuracy and uniformity of the pairwise comparison matrix. The most suitable IAPs for bio-oil were *E. grandis* with a relative closeness of 0.774, and the least ideal was *S. mauritianum* with a relative closeness of 0.416. Characteristics such as Carbon/Nitrogen ratio, volatile content, and moisture content were suitable for biogas production with a consistency ratio of 0.081 within an acceptable threshold of 0.1, suggesting the accuracy of the comparison matrix. The most ideal IAPs for maximum biogas production were *L. camara* with a relative closeness of 0.874 and unideal *P. patula* with a relative closeness of 0.156. Comparatively, woody IAPs were suited for bio-oil, while nonwoody IAPs were suited for biogas yield. One of the limitations is that the accuracy of results depends on the decision-maker's judgment, which can introduce bias, recommending validation methods. This study highlights the importance of selecting biomass for specific biofuel, aiding energy efficiency, economic risks, and environmental management.

4.1 Introduction

Biofuels such as biogas and bio-oil have emerged as viable alternatives to fossil fuels due to their numerous applications, such as heat, electricity generation, transport fuel, and manufacturing of useful chemicals (Howari *et al.*, 2023). Additionally, environmental benefits such as carbon neutrality and low emissions of sulphur and nitrogen oxides are considered when derived from biomass (Xiu and Shahbazi, 2012). However, these benefits are limited in South Africa due to the unavailability of feedstocks for specific biofuel production. This study seeks to overcome this challenge by evaluating the potential of IAPs for biogas and bio-oil production. Their extensive infestation in South Africa not only poses environmental threats but also demands significant financial resources for control, justifying their utilisation for biofuel production (Nkambule *et al.*, 2017).

Converting IAPs into bioenergy helps mitigate their ecological impact while providing a renewable energy source, thereby promoting sustainable resource management. However, biomass characteristics vary, which influences the yield, quality, and effectiveness of bio-oil and biogas production (Madhu *et al.*, 2018). Therefore, selecting appropriate species for specific biofuels is crucial to optimise biofuel energy efficiency while minimising operational costs. To address this complexity, a Multi-Criteria Decision Making (MCDM) can be used, which evaluates a set of alternatives based on pre-defined criteria and ranks the best one amongst the set of alternatives (Madhu *et al.*, 2018). Among available MCDM, an Analytic Hierarchical Process (AHP) proposed by Saaty (2003) quantifies relative priorities for a set of criteria on a ratio scale, guided by the decision-maker's judgment. The Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) evaluates alternatives based on performance across several criteria and identifies the optimal solution (Chakraborty, 2022).

AHP and TOPSIS allow multiple criteria evaluation with simultaneous comparison of different species, checks for consistency to ensure results reliability, and are increasing in various engineering fields (Madhu *et al.*, 2018). These methods have been adopted by Howari *et al.* (2023) to rank waste biomass material for pyrolysis and by Rao and Baral (2011) for anaerobic digestion feedstock selection. These studies have not specifically focused on IAPs and have been applied in South Africa, highlighting a niche area of research. Therefore, this study aims to select and rank woody and nonwoody IAPs for bio-oil and biogas production. This is done

by adopting AHP to prioritise the set of criteria, namely, proximate, elemental, and structural, as discussed in Chapter 3. Furthermore, the TOPSIS method evaluates these alternatives, woody *(Acacia Mearnsii*, *Eucalyptus Grandis*, and *Pinus Patula)* and nonwoody IAPs (*Lantana Camara*, *Chromoleana Odorata*, and *Solanum mauritianum)* and ranks them according to their viability for bio-oil and biogas production. This section contributes toward addressing a significant gap in the region's bioenergy research and providing a structured framework for optimising biomass selection.

4.2 Materials and Methods

The following methods were used to select IAPs suitable for biogas and bio-oil production.

4.2.1 Physical and chemical characteristics of woody and nonwoody IAPs

The proximate, elemental, and structural compositions as presented in Chapter 3 were used as sets of criteria in this section. The summary of the results to be utilised to assess IAPs for bio-oil production as proposed by Madhu *et al.* (2018) is presented in Appendix A, Table 8.1. For biogas production, the addition of total solids and the carbon to nitrogen ratio (C: N) as proposed by Rao and Baral (2011) is presented in Appendix A, Table 8.2. Equation 4.1 was used to calculate the total solids.

- Total solids (TS)

A 5 g sample of woody and nonwoody IAPs was oven-dried at 105 ± 3 °C for 24 hours. After drying, the sample was cooled to room temperature (25 °C) in a desiccator, and the final mass was recorded (Da Silva Ignacio *et al.*, 2019). The total solids (TS) content was then calculated using Equation 4.1.

$$TS = \frac{M_{DRY}}{M_{TOT}} \times 100 \quad (4.1)$$

Where

M_{TOT} = Mass of total sample (%)

M_{DRY} = Mass of dry sample (%)

4.2.2 Integrated AHP and TOPSIS experimental design

The experimental design used to select and rank woody and nonwoody IAPs integrating the AHP and TOPSIS methods is presented in Figure 4.1.

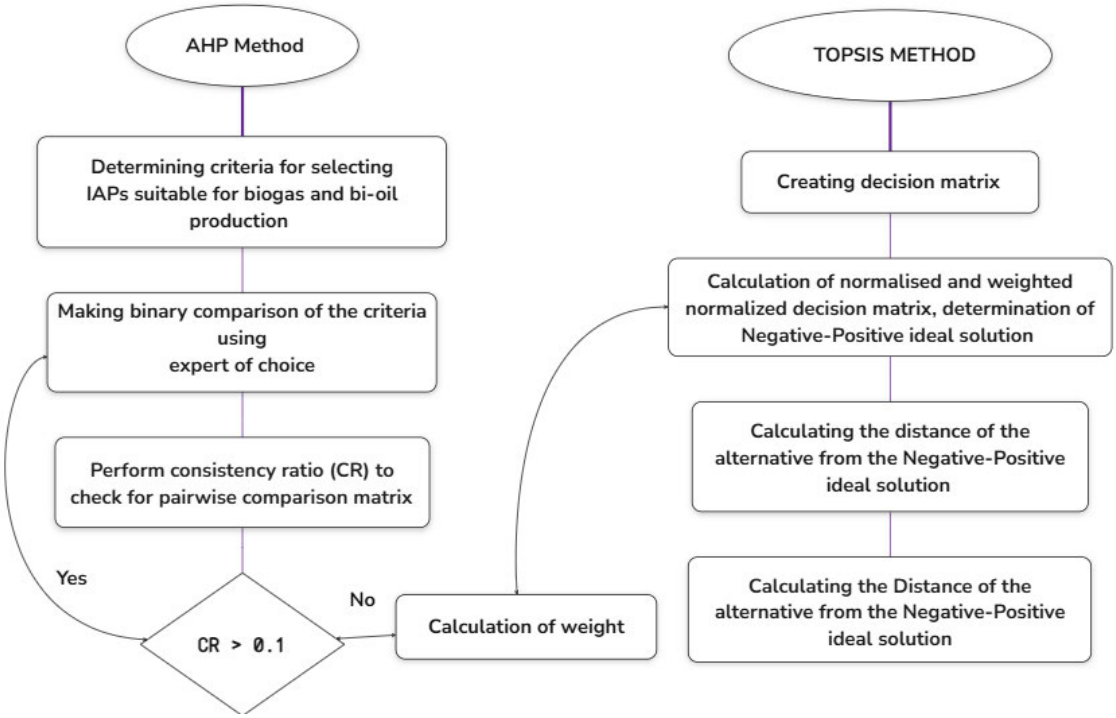


Figure 4.1 Experimental design to select and rank woody and nonwoody invasive alien plant species (Dagistanli and Üstün, 2023)

4.2.2.1 The analytical hierarchy process (AHP)

The procedure used to implement the AHP method for this research work is as follows:

- Step 1: Defining the goal, criteria, and alternatives.

The goal of this research was to establish which woody and nonwoody IAPs are suitable for biogas and bio-oil production. Woody and nonwoody IAPs were assessed as a set of alternatives based on criteria such as structural, elemental, and proximate composition. Tables

8.1 and 8.2 in Appendix A present the criteria and alternatives for bio-oil and biogas, respectively.

- Step 2: Create a pairwise comparison matrix using the semantic table.

Once the goal, criteria, and alternatives were defined, a pairwise comparison matrix was computed. This was done by assigning the relative importance score between the two compared criteria using the 1 to 9 Saaty scale of relative significance presented in Table 4.1. The scores for bio-oil yield were based on Madhu *et al.* (2018), while those for biogas followed Rao and Baral (2011).

Table 4.1 The Saaty scale for computation of pairwise matrix (Afshari *et al.*, 2010)

Intensity of importance	Definition	Explanation
1	Equal importance	Two activities contribute equally to the objective
2	Weak or Slight	
3	Moderate Importance	Experience and judgment slightly favour one activity over another
4	Moderate Plus	Experience and judgment strongly favour one activity over another
5	Strong Importance	
6	Strong Plus	
7	Very Strong	An activity is favoured very strongly over another
8	Very, very Strong	
9	Extreme Importance	The evidence favouring one activity over another is of the highest possible order of affirmation.

Equation 4.2 presents a triangular pairwise matrix (A) which is n × n, with n representing the number of criteria, a numerical integer (a_{ij}) representing the relative importance of criteria i over criteria j. The upper triangle is donated by (a_{ij}), lower triangle by ($\frac{1}{a_{ij}}$) and the diagonal element is always 1 since the criterion is equally important to itself (Madhu *et al.*, 2018).

$$A = \begin{bmatrix} a_{ij} & \cdots & a_{in} \\ \vdots & \ddots & \vdots \\ \frac{1}{a_{ij}} & \cdots & \frac{1}{a_{in}} \end{bmatrix}, \qquad a_{ij} = 1, \quad \frac{1}{a_{in}} = 1 \tag{4.2}$$

- Step 3: Synthesis of the pairwise comparison matrix

Normalise each element by dividing it by the sum of its column, as presented in Equation 4.3. The priority vector was obtained by averaging each row in the pairwise comparison matrix, and the weight was obtained by dividing the number of criteria by the priority vector in Equation 4.4.

$$N_{ij} = \frac{a_{ij}}{\sqrt{\sum_{i=1}^{n} a_{ij}}} \tag{4.3}$$

Where

N_{ij} = Normalised matrix

a_{ij} = Numerical integer

$$W_i = \frac{1}{n} \times \sum_{i=1}^{n} N_{ij} \tag{4.4}$$

Where

W_i = Weight of criterion i

N_i = Normalised matrix

- Step 4: Calculating the Consistency Ratio (CR) of the matrix

Compute the Eigenvalue (τ_{max}) by dividing the weight by the priority vector and finding the average in Equation 4.5 (Al-Harbi, 2001). The Consistency Index (CI) is calculated in Equation

4.6. Then the CR is determined by the CI and Random Index (RI), with RI obtained from Table 4.2 and Equation 4.7.

Table 4.2 Average random consistency (RI) (Afshari *et al.*, 2010)

Size of matrix	1	2	3	4	5	6	7	8	9	10
Random consistency	0	0	0.58	0.9	1.12	1.24	1.32	1.41	1.451	1.49

$$\tau_{max} = \frac{1}{n} \times \sum_{i=1}^{n} \frac{(A \times W)_i}{W_i} \quad (4.5)$$

Where

τ_{max} = Eigenvalue

W = Priority vector

$$CI = \frac{\tau_{max} - n}{n - 1} \quad (4.6)$$

Where

CI = Consistency Index

$$CR = \frac{CI}{RI} \quad (4.7)$$

Where

CR = Consistency Ratio

RI = Random Index

If CR < 0.1, the judgments are considered consistent.

If CR $\geq$ 0.1, the judgments are inconsistent, and you may need to revise the pairwise comparisons.

4.2.2.2 Technique for order of preference by similarity to ideal solution (TOPSIS)

The procedure to implement the TOPSIS methods for this research was as follows, and was proposed by Madhu *et al.* (2018) and Howari *et al.* (2023) for bio-oil yield and by Rao and Baral (2011) for biogas yield.

- Step 1: Normalisation of the evaluation decision matrix.

This step was conducted to convert the raw decision matrix into a normalized decision matrix to ensure that all criteria are on the same scale using Equation 4.8.

$$r_{ij} = \frac{a_{ij}}{\sqrt{\sum_{i=1}^{n} a_{ij}^{2}}} \qquad i = 1, 2, 3 \ldots\ldots n \qquad j = 1, 2, 3 \ldots \ldots n \tag{4.8}$$

Where

r_{ij} = Normalised value of an alternative i with criterion j

a_{ij} = Numerical integer of an alternative i with criterion j

- Step 2: Construction of a normalised matrix

The weighted normalised matrix was calculated by multiplying the normalised values, r_{ij} With the associated weight from the AHP method as shown in Equation 4.9.

$$v_{ij} = r_{ij} \times W_i \qquad i = 1, 2, 3 \ldots\ldots n \qquad j = 1, 2, 3 \ldots \ldots n \tag{4.9}$$

Where

v_{ij} = Weight normalised matrix

- Step 3: Positive and Negative ideal solution

The positive ideal solution (A^*) indicate the most preferred solution and the negative ideal solution (A^-) indicate the least preferred solution. Equations 4.10 and 4.11 illustrate the denotation of positive and negative ideal solutions.

$$A^* = v_1{}^*, \ldots\ldots\ldots, v_i{}^* \quad (4.10)$$

$$A^- = v_1{}^-, \ldots\ldots\ldots, v_i{}^- \quad (4.11)$$

Where

A^* = Positive ideal solution

A^- = Negative ideal solution

- Step 4: Distance calculation

This is the distance of each alternative from the positive and negative ideal solution. Positive distance is denoted as $D_j{}^*$ and negative distance as $D_j{}^-$, which are calculated using Equations 4.12 and 4.13, respectively.

$$D_j{}^* = \sqrt{\sum_{i=1}^{n}(v_{ij} - v_i{}^*)^2} \qquad j = 1, 2, 3 \ldots\ldots n \quad (4.12)$$

$$D_j{}^- = \sqrt{\sum_{i=1}^{n}(v_{ij} - v_i{}^-)^2} \qquad j = 1, 2, 3 \ldots\ldots n \quad (4.13)$$

Where

$D_j{}^*$ = Positive distance

$D_j{}^-$ = Negative distance

- Step 5: Calculate the relative closeness to the ideal solution.

Determine the relative closeness of each alternative to the ideal solution by considering both the distance to the ideal solution and the distance to the anti-ideal solution. The relative closeness was denoted by $CC_j{}^*$ and calculated in Equation 4.14.

$$CC_j{}^* = \frac{D_j{}^-}{D_j{}^- + D_j{}^*} \qquad j = 1, 2, 3 \ldots\ldots n \quad (4.14)$$

Where

CC_j^* = Relative closeness

Step 6: Ranking of alternatives.

Rank the alternatives based on their relative closeness. The alternative with the highest closeness value will be considered the best.

4.3 Results and Discussion

This section presents the key findings on the suitability of woody and nonwoody IAPs for bio-oil and biogas using AHP and TOPSIS methods.

4.3.1 Integrated AHP and TOPSIS methods for bio-oil production

A quantitative analysis of results and a discussion of AHP and TOPSIS to assess IAPs for bio-oil production is presented in this section.

- AHP method for bio-oil production

A pairwise comparison matrix presented in Table 4.3 was used to quantify how important each criterion is over another for bio-oil production. A Saaty scale of relative importance that ranges from 1 to 9 in Table 4.1 was used to rate the relative importance between the two criteria. In Table 4.3, all diagonal elements were equal to 1, representing equal importance to the objective. Cellulose was assigned Saaty values of 2 and 3 when compared to hemicellulose and lignin, respectively, indicating that it is slightly more important than hemicellulose and moderately more important than lignin. This is due to cellulose's thermal stability and degradability when compared to hemicellulose and lignin, respectively (Shi *et al.*, 2023). These results align with a bio-oil yield of 0.2, 0.45, and 0.5 % in lignin, hemicellulose, and cellulose, respectively (Zhong *et al.*, 2022a). Cellulose was assigned a Saaty value of 9, 9, and 8 when compared to moisture content, ash content, and oxygen, respectively. This indicates that cellulose is more important than moisture content, ash content, and very strongly important than oxygen. This is because moisture and ash levels lower combustion efficiency, and oxygen content lowers the

energy density of bio-oil (Tanneru *et al.*, 2014). However, volatile content, carbon, and hydrogen were rated more important than cellulose (Saaty = 0.5, 0.5, and 0.3, respectively) due to their direct influence on bio-oil yield and heating value. This section addresses the research question regarding the contribution of each criterion to bio-oil production.

Table 4.3 Pairwise comparison matrix and AHP result for optimal bio-oil production

	Cellulose	Hemicellulose	Lignin	Moisture content	Volatile content	Ash content	Fixed carbon	Carbon	Hydrogen	Oxygen	Weight	Rank
	Benefit	Benefit	Cost	Cost	Benefit	Cost	Cost	Benefit	Benefit	Cost		
Cellulose	1.00	2.00	3.00	9.00	0.50	9.00	5.00	0.50	0.33	8.00	0.124	4
Hemicellulose	0.50	1.00	3.00	8.00	0.33	9.00	4.00	0.33	0.25	7.00	0.097	5
Lignin	0.33	0.33	1.00	5.00	0.20	6.00	5.00	0.20	0.20	6.00	0.066	6
Moisture content	0.11	0.13	0.20	1.00	0.13	1.00	0.25	0.11	0.11	2.00	0.018	8
Volatile content	2.00	3.00	5.00	8.00	1.00	9.00	8.00	1.00	0.25	8.00	0.174	3
Ash content	0.11	0.11	0.17	1.00	0.11	1.00	0.25	0.11	0.11	3.00	0.019	9
Fixed carbon	0.20	0.25	0.20	4.00	0.13	4.00	1.00	0.13	0.14	3.00	0.035	7
Carbon	2.00	3.00	5.00	9.00	1.00	9.00	8.00	1.00	2.00	9.00	0.216	2
Hydrogen	3.00	4.00	5.00	9.00	4.00	9.00	7.00	0.50	1.00	9.00	0.237	1
Oxygen	0.13	0.14	0.17	0.50	0.13	0.33	0.33	0.11	0.11	1.00	0.014	10
$\tau_{max} = 11.07$ CI $= 0.119$ RI $= 1.49$ CR $= 0.079$												

Benefit = higher values indicate better performance, Cost = lower values are more desirable

After constructing a pairwise comparison matrix in Table 4.3, a normalised pairwise comparison matrix in Table 8.3 (Appendix A) was generated to determine the weight of each criterion concerning optimal bio-oil production. The results in Table 4.4 indicated hydrogen had the highest weight 0.237 (23.9 %) ranking number 1 due to its role in enhancing HHV and reducing oxygen-containing compounds (Wang *et al.*, 2021). In contrast, the oxygen content had the lowest weight at 0.014 (1.4 %), ranking number 10 because it lowers energy density and causes potential corrosion in the reactor (Guedes *et al.*, 2018). The rankings of the remaining criteria with interpretation are detailed in Table 4.4. The findings of this study align with those obtained by Howari *et al.* (2023). The consistency ratio (CR) of 0.079, which is within the threshold of 0.1, indicates the accuracy and reliability of the decision matrix and weighted criteria. The results of this study are similar to those obtained by Madhu *et al.* (2018) with a CR of 0.078.

Table 4.4 The weights of each criterion for bio-oil production generated by the AHP method

Criterion	Weights	Ranks	Contribution to bio-oil production	References
Cellulose	0.124	4	Have volatile compounds that condense into bio-oil but may generate oxygenated compounds, lowering energy density.	Antar *et al.*, 2021
Hemicellulose	0.097	5	Have volatile compounds that turn into bio-oil but contribute to thermal instability.	Shi *et al.*, 2023
Lignin	0.066	6	Forms a complex structure that enables enzymic and bacterial decomposition of cellulose and hemicellulose.	Li *et al.*, 2018; Shrivastava *et al.*, 2021
Moisture content	0.018	8	Reduces energy for pyrolysis and results in bio-oil with higher water levels, thus combustion inefficiency.	Melane *et al.*, 2017
Volatile content	0.174	3	Contains vapours that condense into bio-oil.	Da Silva Ignacio *et al.*, 2019

Ash content	0.019	9	Induce sintering that reduces heat transfer, favouring biochar instead of bio-oil production.	Vassilev *et al.*, 2017.
Fixed carbon	0.035	7	Less degradable, resulting in biochar production.	Da Silva Ignacio *et al.*, 2019.
Carbon	0.216	2	Increases higher heating value but also results in the formation of coke and char that reduces conversion efficiency.	Hu *et al.*, 2020.
Hydrogen	0.237	1	Contribute to the higher heating value of bio-oil while reducing oxygen-containing compounds.	Wang *et al.*, 2021.
Oxygen	0.014	10	Lowers the heating value of bio-oil, resulting in high viscosity and less ignition.	Guedes *et al.*, 2018.
$\tau_{max} = 11.07$ CI = 0.119 RI = 1.49 CR = 0.079				

- TOPSIS method for bio-oil production

The TOPSIS method was utilised to select and rank woody and nonwoody IAPs based on their suitability for bio-oil production. The weights of each criterion derived from AHP in Table 4.4 were used to construct a weight-normalised matrix, leading to a positive ideal (A^*) and a negative ideal (A^-) solution in Table 4.5. Positive ideal solutions represent optimal biomass composition for optimal bio-oil production, characterised by the highest benefits (hydrogen = 0.1, carbon = 0.09, volatile content = 0.073) and lowest cost (ash = 0.001, moisture = 0.004, fixed carbon = 0.02). This suggests that biomass with higher levels of hydrogen, carbon, and volatile matter, and lower levels of oxygen, moisture, and ash content, is ideal for bio-oil production. Conversely, the negative ideal solution represents the least favourable biomass composition, characterised by low benefit (hydrogen = 0.089, carbon = 0.082, volatile content = 0.069) and highest cost (ash = 0.012, moisture = 0.009, fixed carbon = 0.008). These characteristics suggest a lower yield of hydrogen, carbon, and higher levels of ash, moisture, reduced energy density of bio-oil as discussed in Table 4.4.

The separation measure quantifies how far each alternative is from positive and negative ideal solutions, with relative closeness measuring how well an alternative performs in comparison to both. The results in Table 4.6 illustrate that *E. grandis* had the smallest distance to the positive ideal solution (0.016) and the largest to the negative ideal solution (0.055), ranking the highest among IAPs suitable for bio-oil production. This is attributed to its high carbon, hydrogen, and cellulose, which are key factors contributing to optimal bio-oil production as described in Table 4.4. Following *E. grandis*, *A. mearnsii* ranked second, while *P. patula* ranked third as shown in Figure 4.2. Despite *P. patula* having higher carbon and hydrogen content, its higher lignin and ash content reduced its degradability, making it less suitable than *A. mearnsii.* Nonwoody IAPs such as *L. camara, C. odorata,* and *S. mauritianum* were lower-ranked species for bio-oil production as shown in Figure 4.2 because these had a larger distance relative to the positive ideal solution and smaller value relative to the negative ideal solution, making them less suitable for bio-oil production. This is observed in *S. mauritianum* being the least suitable species because of lower cellulose, hemicellulose, volatile content and higher ash content, fixed carbon, and moisture content. This section addresses the research question regarding the suitability of woody and nonwoody IAPs for bio-oil production.

Table 4.5 Weight normalised matrix with negative and positive ideal solution for bio-oil production

IAPs	Cellulose	Hemicellulose	Lignin	Carbon	Hydrogen	Oxygen	Moisture Content	Volatile Content	Ash Content	Fixed Carbon
	Benefit	Benefit	Cost	Benefit	Benefit	Cost	Cost	Benefit	Cost	Benefit
L. camara	0.036	0.039	0.013	0.088	0.097	0.006	0.009	0.070	0.010	0.008
C. odorata	0.032	0.033	0.015	0.085	0.098	0.006	0.007	0.071	0.010	0.008
S. mauritianum	0.027	0.025	0.011	0.089	0.100	0.005	0.008	0.069	0.012	0.009
A. mearnsii	0.059	0.048	0.035	0.082	0.089	0.006	0.008	0.072	0.001	0.019
E. grandis	0.072	0.041	0.024	0.093	0.099	0.006	0.004	0.073	0.005	0.015
P. patula	0.061	0.048	0.045	0.093	0.097	0.006	0.006	0.072	0.002	0.020
A^-	0.027	0.025	0.045	0,082	0.089	0.006	0.009	0.069	0.012	0.008
A^*	0.072	0.048	0.011	0.093	0.100	0.005	0.004	0.073	0.001	0.020

Table 4.6 Results of TOPSIS with ranks on the ideal IAPs for bio-oil

IAPs	Distance to negative ideal solution (D_j^-)	Distance to positive ideal solution (D_j^*)	Relative closeness (CC_j)	Rank
L. camara	0.037	0.041	0.474	4
C. odorata	0.034	0.046	0.423	5
S. mauritianum	0.038	0.053	0.416	6

A. mearnsii	0.042	0.031	0.573	2
E. grandis	0.055	0.016	0.774	1
P. patula	0.045	0.036	0.559	3

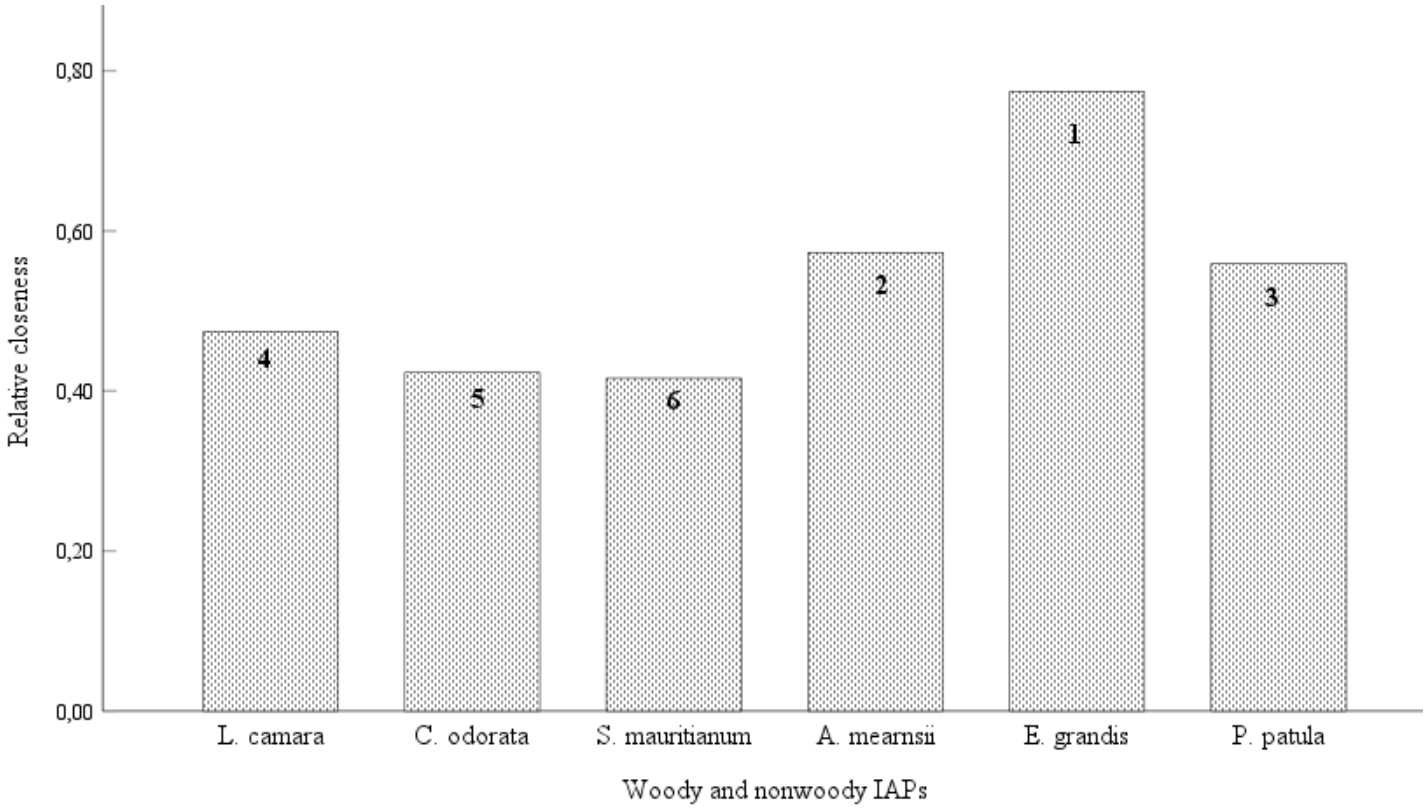


Figure 4.2 TOPSIS result ranking IAPs suitable for optimal bio-oil production

4.3.2 Integrated AHP and TOPSIS methods for optimisation of biogas

A quantitative analysis of results and discussion of AHP and TOPSIS for optimal biogas production is outlined in this section.

- AHP method for biogas production

A pairwise comparison matrix presented in Table 4.7 was used to quantify how important each criterion is over another for biogas production. Cellulose was assigned a Saaty value of 2, 3, 8, and 9 when compared to hemicellulose, lignin, oxygen, and ash content, respectively. This indicates that cellulose is slightly more important than hemicellulose, moderately more than lignin, and extremely more important compared to ash and oxygen. This is because cellulose is degradable into fermentable sugars that can be turned into biogas. Hemicellulose is easily degradable but contains fewer fermentable sugars than cellulose. Lignin is highly insoluble, creating a barrier for cellulose degradation and oxygen reduces microbial growth, thus less biogas production (Li *et al.*, 2018). However, C: N, total solids, and moisture content were rated moderately and slightly more important than cellulose (Saaty = 0.33, 0.5, and 0.33, respectively) due to their direct influence on the growth and activities of micro-organisms that induce biogas production (Matheri *et al.*, 2018).

A normalised pairwise comparison matrix was constructed to generate the weight of each criterion concerning optimal biogas production in Table 4.8. The results indicated that the C: N ratio had the highest weight, 0.259, ranking number 1 due to its role in regulating the growth and activities of micro-organisms essential for the degradation of organic compounds (Yan *et al.*, 2015). In contrast, ash content had the lowest weighting (0.013), ranking 10^{th}, as it hinders mass transfer, disrupts the system pH, and inhibits microbial activity, all of which negatively impact biogas production. The rankings of the remaining criteria with interpretation are detailed in Table 4.8. The consistency ratio of 0.081, which is within the threshold of 0.1, indicates the accuracy and reliability of the decision matrix and weighted criteria. Most literature studies focused on biogas production and investigating supply chains such as transportation, pre-treatment, and storage. However, less work has been conducted on assessing the physicochemical characteristics of IAPs (Ossei-Bremang and Kemausuor, 2021).

Table 4.7 Pairwise comparison matrix and AHP result for optimal biogas production

	Cellulose	Hemicellulose	Lignin	C/N	Oxygen	Total solids	Moisture Content	Volatile Content	Ash Content	Fixed carbon
	Benefit	Benefit	Cost	Benefit	Cost	Benefit	Benefit	Benefit	Cost	Cost
Cellulose	1.00	2.00	3.00	0.33	8.00	0.50	0.33	0.25	9.00	5.00
Hemicellulose	0.50	1.00	3.00	0.25	7.00	0.33	0.25	0.20	9.00	4.00
Lignin	0.33	0.33	1.00	0.13	6.00	0.20	0.17	0.14	7.00	3.00
C/N	3.00	4.00	8.00	1.00	9.00	4.00	3.00	2.00	9.00	8.00
Oxygen	0.13	0.14	0.17	0.11	1.00	0.14	0.13	0.11	2.00	0.33
Total solids	2.00	3.00	5.00	0.25	7.00	1.00	0.50	0.33	8.00	6.00
Moisture Content	3.00	4.00	6.00	0.33	8.00	2.00	1.00	0.33	9.00	5.00
Volatile Content	4.00	5.00	7.00	0.50	9.00	3.00	3.00	1.00	9.00	7.00
Ash Content	0.11	0.11	0.14	0.11	0.50	0.13	0.11	0.11	1.00	0.33
Fixed Carbon	0.20	0.25	0.33	0.13	3.00	0.17	0.20	0.14	3.00	1.00
$\tau_{max} = 11.086$ CI $= 0.121$ RI $= 1.49$ CR $= 0.081$										

Benefit = higher values are desirable, Cost = lower values are desirable

Table 4.8 The weights of each criterion to illustrate their contribution to biogas production

Criterion	Weights	Rank	Contribution to biogas	References
Cellulose	0.090	5	Provide fermentable sugars as the key energy source for micro-organisms.	Li *et al.*, 2018.
Hemicellulose	0.071	6	Supply fermentable sugars, but the accumulation of volatile fatty acids creates an acidic environment that inhibits microbial growth.	Li *et al.*, 2018.
Lignin	0.046	7	Embeds the microfibrils of cellulose, decreasing the ability of the polymer to be degraded.	Weng *et al.*, 2008.
C: N	0.259	1	Regulating the growth and activities of micro-organisms essential for the decomposition of organic compounds.	Yan *et al.*, 2015.
Oxygen	0.016	9	Act as a toxic agent to micro-organisms, causing instability of the reaction, reducing biogas production.	Botheju and Bakke, 2011.
Total solids	0.113	4	Influence the growth and activities of micro-organisms, efficiency of digestion, and thus yield of biogas.	Abbassi-Guendouz *et al.*, 2012.
Moisture Content	0.146	3	Essential for microbial growth, nutrient transfer, and dilute inhibitors.	Avinash and Mishra, 2023.
Volatile Content	0.219	2	Fraction that provides biodegradable material for microbial conversion.	Fajobi *et al.*, 2022.
Ash Content	0.013	10	Toxic components that influence sintering, slag the reaction, and enhance corrosion and abrasion.	Vassilev *et al.*, 2017.
Fixed Carbon	0.027	8	This is carbon that is not readily degradable and may lead to char formation, reducing gaseous output.	Da Silva Ignacio *et al.*, 2019.
$\tau_{max} = 11.086$ CI $= 0.121$ RI $= 1.49$ CR $= 0.081$				

- TOPSIS method for biogas production

The TOPSIS method was utilised to select and rank woody and nonwoody IAPs based on their suitability for optimal biogas production. The weights of each criterion derived from AHP in Table 4.8 were used to construct a weight-normalised matrix, leading to a positive ideal (A^*) and negative ideal solution (A^*) in Table 4.9. The results indicated that the positive ideal solutions were the maximum value of benefit criteria, such as cellulose, hemicellulose, C/N, total solids, moisture content, and volatile content, that influence nutrient transfer and microbial activities. The negative ideal solutions were the minimum values of cost criteria such as lignin, oxygen, ash content, and fixed carbon.

The separation measure quantifies how far each alternative is from positive and negative ideal solutions, with relative closeness measuring how well an alternative performs in comparison to both. Table 4.10 showed that *L. camara* had smallest distance to the positive ideal solution (0.028) and the largest to the negative ideal solution (0.196) ranking the highest among IAPs suitable for biogas production This is due to its balanced C/N, optimal volatile solids and lower lignin content, which promote microbial activities, allowing degradation of cellulose and hemicellulose (Matheri *et al.*, 2018). Following *L. camara*, *C. odorata* ranked second, while *S. mauritiunum* ranked third, as shown in Figure 4.2, due to the C/N ratio of 16.13 and 10.65, respectively. Woody IAPs were lower ranked species for biogas production as shown in Figure 4.2, due to no detectable nitrogen, ultimately influencing the C/N ratio. This section addresses the research question regarding the suitability of woody and nonwoody IAPs for biogas production.

Table 4.9 Weight normalised matrix with negative and positive ideal solution for biogas production

IAPs	Cellulose	Hemicellulose	Lignin	C/N	Oxygen	Moisture content	Total solids	Volatile content	Ash content	Fixed carbon
	Benefit	Benefit	Cost	Benefit	Cost	Benefit	Benefit	Benefit	Cost	cost
L. camara	0.026	0.028	0.009	0.189	0.007	0.075	0.046	0.088	0.007	0.006
C. odorata	0.023	0.024	0.011	0.147	0.007	0.058	0.046	0.089	0.007	0.006
S. mauritianum	0.020	0.018	0.008	0.097	0.006	0.063	0.046	0.086	0.008	0.007
A. mearnsii	0.043	0.035	0.024	0.000	0.007	0.069	0.046	0.091	0.001	0.015
E. grandis	0.052	0.030	0.017	0.000	0.006	0.033	0.047	0.092	0.003	0.012
P. patula	0.044	0.035	0.032	0.000	0.007	0.050	0.046	0.091	0.002	0.015
A^-	0.020	0.018	0.032	0.000	0.007	0.033	0.046	0.086	0.008	0.015
A^*	0.052	0.035	0.008	0.189	0.006	0.075	0.047	0.092	0.001	0.006

Table 4.10 Results of TOPSIS with ranks on the ideal IAPs for bio-oil

IAPs	Distance to negative ideal solution (D_j^-)	Distance to positive ideal solution (D_j^*)	Relative closeness (CC_j)	Rank
L. camara	0.196	0.028	0.874	1
C. odorata	0.151	0.055	0.733	2
S. mauritianum	0.105	0.100	0.512	3

A. mearnsii	0.047	0.190	0.199	4
E. grandis	0.038	0.194	0.165	5
P. patula	0.036	0.193	0.156	6

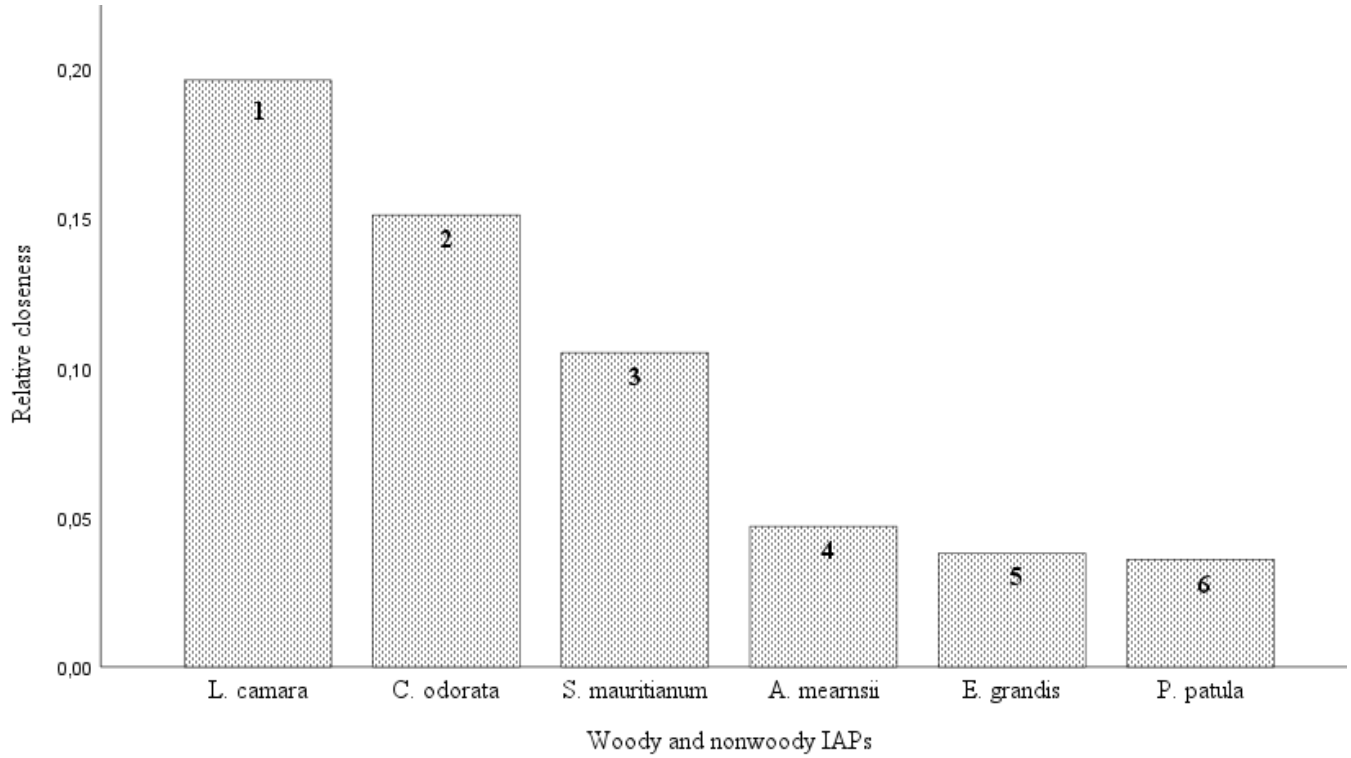


Figure 4.3 The TOPSIS results ranking IAPs suitable for optimal bio-oil production

4.4 Conclusion

The aim of this study was to identify the most suitable woody and nonwoody IAPs for optimal bio-oil and biogas production through the integration of the AHP and TOPSIS methods. The AHP analysis revealed that hydrogen (23.7%) and carbon (21.6%) were the most critical factors for bio-oil production, given their strong positive correlation with biomass energy content and combustion efficiency. For biogas production, the carbon-to-nitrogen ratio (25.9%) and volatile matter content (21.9%) emerged as the most influential criteria. In contrast, oxygen and moisture content received the lowest weights, reflecting their negative impact the thermal degradation performance for bio-oil production, and activity of microorganisms in biogas generation.

The TOPSIS analysis produced a clear and systematic ranking of the evaluated species, highlighting *Eucalyptus grandis* (0.774) and *Acacia mearnsii* (0.573) as the most suitable for bio-oil production. Their high rankings are linked to elevated cellulose, carbon, and volatile matter contents, along with lower ash and moisture levels. In contrast, the nonwoody species *Lantana camara* (0.874) and *Chromolaena odorata* (0.733) ranked first and second, respectively, for biogas production. Overall, the results indicate that woody IAPs are better suited for bio-oil production, whereas nonwoody IAPs are more favourable for biogas production.

This integrated approach enables quantitative scoring based on multiple critical factors, rather than relying on a single property, allowing for a more comprehensive and balanced assessment of each species potential. This study is among the first to apply the AHP and TOPSIS models to invasive plant species in a South African context, addressing a key gap in the literature where most existing studies have concentrated on conventional biomass (e.g., rice straw, bagasse, or forestry residues). The practical significance of the AHP and TOPSIS framework lies in its ability to guide biomass selection and pre-treatment strategies. It supports the development of localised, sustainable energy solutions by informing which IAPs should be harvested and processed for maximum energy return. It provided a robust and reproducible pathway for translating scientific characterisation into actionable biomass selection strategies, supporting both renewable energy generation and environmental management objectives. A recommendation would be conducting the pyrolysis and anaerobic digestion process to validate the two proposed methods, which are conducted in Chapters 5 and 6, respectively.

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5. ASSESSMENT AND VALIDATION of BIO-OIL PRODUCTION FROM SELECTED WOODY AND NON-WOODY INVASIVE ALIEN PLANTS

This chapter evaluates the yield and quality of bio-oil derived from woody and nonwoody IAPs as a source of renewable energy. It also reviews and validates the findings presented in Chapter 4 regarding the selection of IAPs most suitable for optimal bio-oil production.

Abstract

The growing environmental concerns and depletion of fossil fuels have intensified the global shift toward renewable energy sources such as bio-oil. However, conventional feedstocks such as algae and crop residues often yield highly oxygenated bio-oil, resulting in lower energy content and increased pollutant emissions, challenging their sustainability. In response, this study aims to investigate the potential of woody and nonwoody (IAPs) as alternative biomass feedstocks. The IAPs were pyrolysed in a fixed bed reactor at a temperature of 450 ℃, with a heating rate of 5 ℃. min^{-1}, particle size of 1 mm, reaction period of 90 min, gas flow rate of 50 ml. $\mathrm{m}^{-1}$and vapor residence time of 88 s. The bio-oil from IAPs was chemically analysed using the Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS) methods. The HHV was estimated from similar IAPs studies available in the literature. The results indicated that woody IAPs produced higher bio-oil yield (24.66%) compared to nonwoody IAPs (19.44%), with a significant difference ($p < 0.05$). These yields were lower than those reported in other studies, emphasising that bio-oil output is highly dependent on many factors such as reactor design, operational parameters, and feedstock characteristics.

Functional groups such as 1˚, 2˚ amines, amides, alkanes, and aldehydes suggest high energy density and stability characteristics of fuel to increase the efficiency and performance of fuel. However, a quantitative analysis using the GC-MS indicated that these compounds from FTIR are at a lower concentration. The most abundant chemical compounds are phenols, ketones, and acids. The compounds contribute to oxidation reactions leading to residue formation, increased viscosity, poor atomisation, and potential corrosion of fuel systems, all lower combustion efficiency. The estimated HHV of bio-oil from woody and nonwoody IAPs based

on literature sources was 24.28 $MJ.kg^{-1}$ and 22.16 $MJ.kg^{-1}$, respectively, which was considerably lower than fossil fuels, between 42.9 to 47 $MJ.kg^{-1}$Given these differences, bio-oil from woody and nonwoody IAPs may require upgrading techniques to remove excess oxygen and blend with fossil fuels to enhance its combustion properties. Bio-oil production demands significant capital investment for IAPs eradication, pre-processing, pyrolysis, and upgrading. These findings highlight the necessity for further investigation into the techno-economic viability of scaling up bio-oil production within the South African context

5.1 Introduction

Bio-oil consists of various hydrocarbon compounds formed through the pyrolysis of organic biomass (Caputo *et al.*, 2005). It has been considered a viable substitute for petroleum fuel with several benefits, such as carbon neutrality and minimal sulphur and nitrogen oxide emissions (Isahak *et al.*, 2012; Xiu and Shahbazi, 2012). Among the pyrolysis methods, fast pyrolysis is preferred due to its efficiency, yielding up to 80% of bio-oil (Fahmy *et al.*, 2020). For instance, Arrow Products in the USA has demonstrated a 5MW capacity using bio-oil combustion (Caputo *et al.*, 2005). Despite its potential, biofuels contribute less than 0.1% to South Africa's energy supply, emphasising the need for further research in this area (Akinbami *et al.*, 2021).

A key challenge in bio-oil production is finding a suitable substrate that does not compromise food security, water resources, or land use while requiring minimal investment (Akinbami *et al.*, 2021). Traditional biomass feedstocks such as algae and agricultural residues often result in bio-oil with elevated oxygen content and nitrogen oxide emissions during combustion (Sekar *et al.*, 2021; Pagano *et al.*, 2023). To overcome these limitations, this study investigates the potential of IAPs as an alternative feedstock, considering both their ecological threat and their underutilised biomass (Pejchar and Mooney, 2009). The abundance of woody IAPs, including Acacia (0.4 million ha), Eucalyptus (0.05 million ha), and Pinus (0.12 million ha), ensures a reliable biomass supply for bio-oil production (Stafford *et al.*, 2017).

This chapter aims to evaluate the yield and quality of bio-oil from three woody IAPs (*Acacia mearnsii, Eucalyptus grandis, Pinus patula*) and three nonwoody species (*Lantana camara, Chromolaena odorata, Solanum mauritianum).* This section encompasses the following: (1) thermogravimetric analysis to evaluate the pyrolysis behaviour of invasive species, (2) execution of the pyrolysis process using a fixed-bed reactor, (3) characterization of the

resulting bio-oil through Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography-Mass Spectrometry (GC-MS), and (4) estimation of the higher heating value (HHV) based on data from similar biomass types. The outcomes of the pyrolysis experiments will serve to validate the results of the multi-criteria decision-making (MCDM) methods, confirming the suitability of specific species for bio-oil production.

5.2 Materials and Methods

The following methods were used to assess the viability of woody and nonwoody IAPs for bio-oil production.

5.2.1 Biomass collection and preparation

Three woody IAPs, namely, *Acacia mearnsii*, *Eucalyptus grandis,* and *Pinus patula,* and three nonwoody IAPs, namely, *Lantana camara*, *Chromoleana odorata*, and *Solanum mauritianum,* were evaluated for bio-oil production. The preparation of woody and nonwoody IAPs, using freshly harvested and processed plant material, is explained in Section 3.2.2, Chapter 3.

5.2.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was utilised to analyse the thermal degradation of the sample to better understand the pyrolysis process and temperature ranges for pyrolysis feeding into bio-oil production. In this analysis, the DTG–60H simultaneous analyser was utilised with approximately 10 mg of the sample carefully placed in an aluminium pan within a well-balanced holder (Havilah *et al.*, 2019). The TGA method was used by Mishra and Mohanty (2018), where the sample underwent analysis at various temperatures, initially, at 30 °C, ramped up at 10 °C.min^{-1} and held for 2 min under $20\ \mathrm{ml.\,min}^{-1}$ nitrogen atmosphere. Subsequently, the sample was subjected to 600 °C and ramped up at 10 °C. min^{-1} and held for 2 min under $20\ \mathrm{ml.\,min}^{-1}$ nitrogen atmosphere for further degradation. The sample mass loss was continually recorded and displayed in TGA and Differential Thermogravimetry (DTG) curves throughout the experiment. TGA measures the change in mass of the sample, but DTG offers information on the rate of mass loss, which aids in understanding the material's heat breakdown behaviour (Bevis *et al.*, 2008).

5.2.3 Experimental procedure

The experimental procedure included reactor setup, pyrolysis process execution, and bio-oil collection and storage.

5.2.3.1 Reactor setup

The pyrolysis experiments were conducted at the University of KwaZulu-Natal Chemical Engineering Laboratory using a vertical fixed-bed reactor in Figure 5.1. The reactor setup included a stainless-steel reactor vessel (diameter: 41.5 cm, length: 3cm) mounted vertically. A ceramic sample holder with a capacity of 27 g was placed inside the reactor, which was enclosed with a heating jacket to control the temperature. A thermocouple was inserted at the reactor zone to monitor the temperature, with the temperature controller maintaining 450 ℃. The inert nitrogen gas was introduced at a flow rate of 200 $\mathrm{ml.\,m^{-1}}$ to prevent oxidation. The pyrolysis vapours were directed through a condenser, which was controlled by a water bath (5 ℃) to ensure cooling and condensation of vapours to bio-oil. The non-condensable gases were passed through a bubbler to prevent backflow into the system.

Previous studies have proposed optimal operation conditions for woody and nonwoody IAPs, including a temperature of 450 ℃ and a heating rate of $50\ ℃.\mathrm{min^{-1}}$, particle size of 1 mm, reaction period of 30 min, gas flow rate of 200 $\mathrm{ml.\,m^{-1}}$ and vapour residence time of 2 s (Garg *et al.*, 2016; Guedes *et al.*, 2018; Reza *et al.*, 2019a). Due to limited control panels in the reactor, the reaction time was measured with a stopwatch and extended to 90 minutes. The heating rate was calculated using Equation 5.3 proposed by Amr *et al.* (2023), and vapour residence time using Equations 5.1 and 5.2 by Mastral *et al.* (2002). Table 5.1 represents the revised operating conditions.

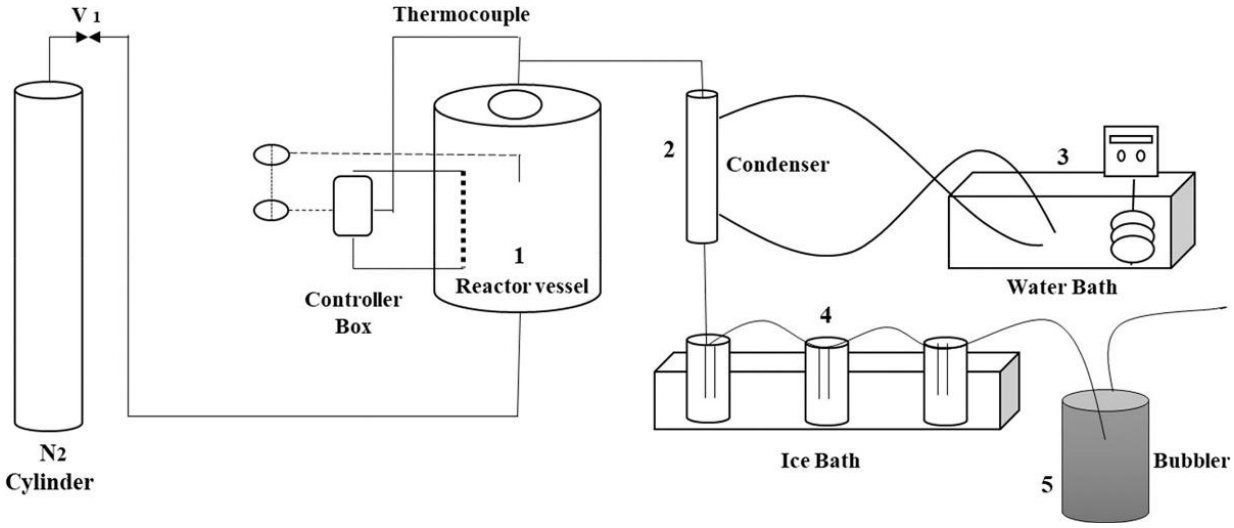


Figure 5.1 Experimental setup of the pyrolysis system used for bio-oil production (Tsipa *et al.*, 2023)

$$V = \pi r^2 h \tag{5.1}$$

Where

$V =$ The volume of the reactor (cm^3)

$r =$ Radius reactor (cm)

$h =$ Height of reactor (cm)

$$VT = \frac{V}{Q} \tag{5.2}$$

Where

$VT =$ Vapor residence time (s)

$V =$ Volume (cm^3)

$Q =$ Gas flow rate ($ml.\,min^{-1}$)

$$\beta = \frac{dT}{dt} \tag{5.3}$$

Where

$\beta =$ Heating rate ($℃.\,min^{-1}$)

$dT =$ Change in temperature (℃)

$dt =$ Change in time (min^{-1})

Table 5.1 The revised operating conditions

Pyrolysis reactor	Temperature	Reaction rate	Gas flow rate	Heating time	Vapor residence time	Particle size
Fixed bed reactor	450 ℃	5 ℃. min^{-1}	200 ml. m^{-1}	90 min	88 s	1 mm

5.2.3.2 Experimental procedure

The experiment commenced with pre-weighing the reactor, condenser, collection pipes, and bottles to account for any residues in the system. Table 5.2 presents the component weights used in the mass balance calculations (Equation 5.4). Pre-dried and ground biomass (particle size: 1mm) of approximately 26 g was weighed and loaded in a ceramic sample holder inside the fixed bed reactor. The thermocouple was installed in a reactor with a heating jacket activated, gradually increasing the temperature to the target 450 °C. The condenser connected via the pipeline system was submerged in a water bath, gradually increasing the temperature to the target 5 °C. To establish anaerobic conditions, nitrogen gas at a flow rate of 200 ml. m^{-1} was introduced, displacing any air residues in the reactor. During the pyrolysis process, nitrogen gas was used to transport the generated vapours from the reactor to a condenser, where they were cooled and subsequently collected in storage bottles. Gaseous products that did not condense were directed through a bubbler system, while the remaining solid biochar was retrieved directly from the reactor chamber. Once the reaction was complete, the entire setup was allowed to cool naturally to room temperature before the individual components were weighed. The yields of bio-oil, non-condensable gases, and biochar were then determined using the mass balance approach outlined in Equations 5.4 to 5.7.

Table 5.2 The weights of the pyrolysis system that were used to perform the mass balance equation before the experiment and after the experiment

Components of the pyrolysis reaction	Symbol	Weight
Mass of the reactor	M_r	997,4g
Mass of sample	M_s	Aiming for 26 g
Mass of condenser with a pipe	M_c	1024,1g
Mass of collection bottle	M_b	181,8g

Mass of pipe from the condenser to the collection bottle	M_p	58g

$$\sum w_{input} = \sum w_{output} + \sum w_{accumulated} \quad (5.4)$$

Where

$\sum w_{input}$ = Weight of equipment before pyrolysis (kg)

$\sum w_{output}$ = Weight of equipment after pyrolysis with bio-oil (kg)

$\sum w_{accumulated}$ = Yield of bio-oil (kg)

The yield of bio-oil, biochar, and gases is calculated with equations 5.5, 5.6, and 5.7, respectively (Garg *et al.*, 2016)

$$\text{Liquid yield (\%)} = \frac{\text{liquid (g)}}{\text{biomass fed into the reactor (g)}} \times 100 \quad (5.5)$$

$$\text{Solid yield (\%)} = \frac{\text{solid (g)}}{\text{biomass fed into the reactor (g)}} \times 100 \quad (5.6)$$

$$\text{Gases yield (\%)} = 100 - (\text{Liquid yeild} + \text{solid yield}) \quad (5.7)$$

5.2.3.3 Bio-oil characterisation

Bio-oil was characterised through chemical analysis such as Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography-Mass Spectrometry (GC-MS), and thermal analysis such as higher heating value.

- Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is the method that measures the absorption of infrared light by a sample to detect the chemical composition and molecular structure of that sample (Selvan *et al.*, 2021). The resulting peak absorption spectrum illustrates the vibration mode of chemical bonds in the sample. The functional groups of bio-oil were analysed using an FTIR spectrometer to understand the chemical nature and deduce applicability as a source of renewable energy

(Wang *et al.*, 2020). The room temperature at the Chemical Engineering Laboratory was recorded as 25 °C, and the bio-oil absorption spectra were analysed using an FTIR Bruker Tensor 27. Tsipa *et al.* (2023) employed this technique, scanning in the 400–4000 cm^{-1} range three times using 0.002 ml of bio-oil deposited in a Bruker attenuated reflected (ATR) single reflection diamond crystal. Figure 8.1 shows the table of characteristic IR absorptions, contained in Appendix B. This table was used to detect function groups in bio-oil from the generated spectra.

- Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS is an analytical technique used to identify and quantify the chemical composition of a sample to provide a comprehensive understanding of its chemical nature and application (Vairaperumal *et al.*, 2024). The GC–MS was conducted at the Physics and Chemistry laboratory at the Pietermaritzburg University of KwaZulu-Natal, where a Shimadzu GCMS-QP2010 SE instrumentation coupled with Zebron ZB-5MSplus (30m in length x 0.00025 m internal diameter 0.25 μm in thickness) was used. This method was used by Saikia *et al.* (2015); (Wang *et al.*, 2018); Kaur *et al.* (2024b) for bio-oil extracted from similar biomass. A mixture of 50 % chloroform and n-hexane was used as a solvent to ensure the solubility and volatility of bio-oil. Helium was used as a carrier gas, maintaining a flow rate of 1 $ml.\,min^{-1}$. The GC injector temperature was set at 200 °C with injector mode at spilled. The oven temperature was set at 40 °C and held for 1 min. It was then heated up from 200 °C, where the heating rate was 12 °C. min^{-1} and held for 20 min at the final temperature. In the Mass Spectrometry (MS), the source temperature was set at 200 °C with a scan from 50 to 700 m/z, which was broad to capture all compounds.

- High heating value

Due to limitations of direct HHV measurement, this study estimates its value based on similar woody and nonwoody IAPs that underwent pyrolysis under the same operational conditions using a fixed-bed reactor. The selected biomass species exhibited similar chemical compositions, as identified through GC-MS and FTIR analyses.

5.2.4 Data analysis

SPSS version 11 was utilised to conduct statistical analysis such as Pearson correlation coefficients (r), regression coefficients (R^2) and p-value with a significant level of 5 % to demonstrate the relationship between the factors and bio-oil yield of non-woody and woody IAPs.

5.3 Results and Discussion

Chapter 3 highlighted how structural, elemental, and proximate compositions affect bio-oil yield, while Chapter 4 focused on identifying IAPs most suitable for bio-oil production. This section builds upon those findings by validating them through discussions on thermogravimetric analysis (TGA), the pyrolysis process, and subsequent bio-oil characterisation.

5.3.1 Thermogravimetric analysis

The primary aim of the thermal analysis was to explore the thermal decomposition behaviour of IAPs and identify the most favourable temperature stages for achieving optimal bio-oil yield through pyrolysis. Figures 5.2 and 5.3 display the TGA and DTG curves for woody and nonwoody IAPs, respectively. The summary of data extracted in TGA and DTG is illustrated in Table 5.3, with m_{loss}, representing weight loss; T_i initial temperature; T_f, final temperature and T_p peak temperature.

Table 5.3 Thermogravimetric analysis and differential thermogravimetry for the woody and nonwoody IAPs

	Dehydration			Active pyrolysis				Passive pyrolysis	
Woody IAPs									
Sample	m_{loss} (%)	T_i (°C)	T_f (°C)	m_{loss} (%)	T_i (°C)	T_f (°C)	T_p (°C)	T_i (°C)	T_f (°C)
E. grandis	2.5	33	147	77.6	147	468	279	468	600
A. mearnsii	1.6	33	205	98.1	205	470	305	470	600

P. patula	3.4	34	155	75.5	155	446	286	446	600
Non-woody IAPs									
Sample	m_{loss} (%)	T_i (°C)	T_f (°C)	m_{loss} (%)	T_i (°C)	T_f (°C)	T_p (°C)	T_i (°C)	T_f (°C)
L. camara	5.1	35	176	58.5	176	476	315	476	600
C. odorata	6.2	33	177	59.5	177	474	308	474	600
S. mauritianum	5.3	33	180	59	180	480	326	480	600

All values are means of three replications

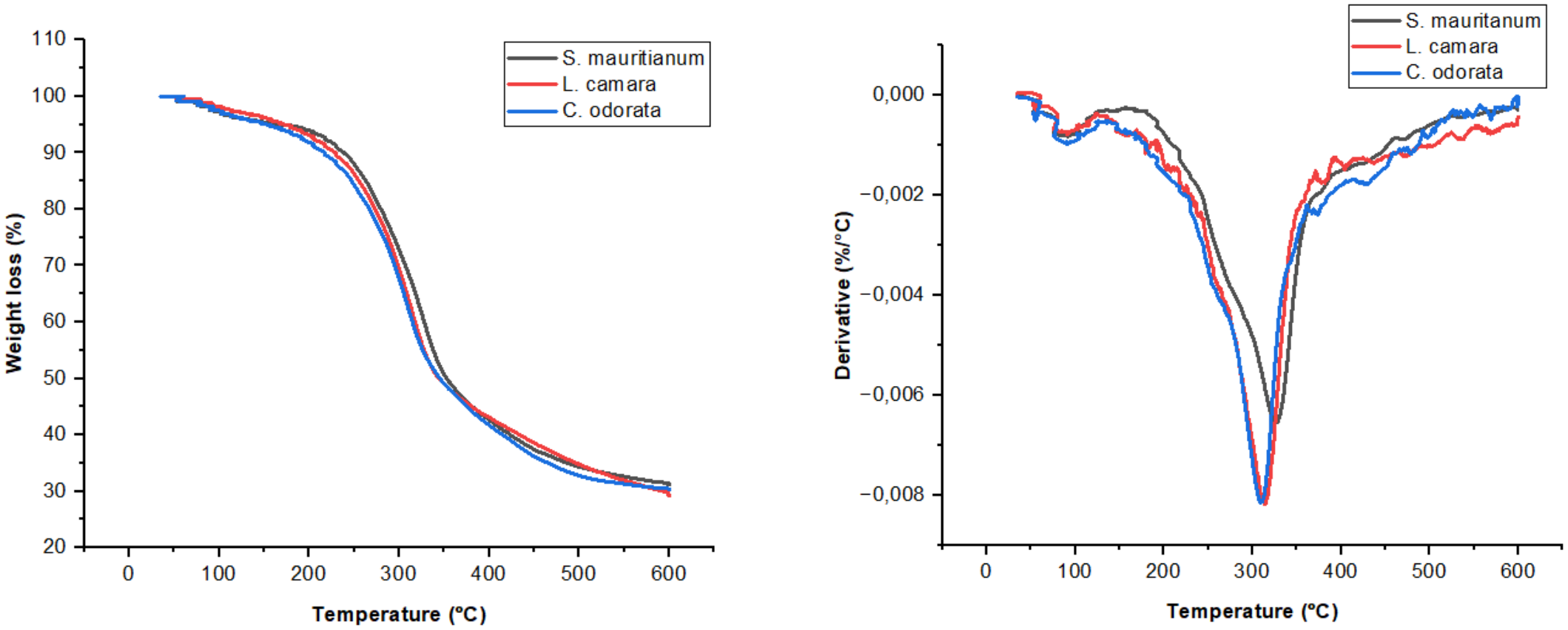
The thermogravimetric analysis results indicate that woody and nonwoody IAPs underwent three distinct thermal stages: dehydration, active, and passive pyrolysis. During the dehydration phase, moisture and volatile compounds were released following an increase in temperature from 33 to 205 °C in woody IAPs and 33 to 180 °C in nonwoody IAPs. The corresponding weight loss was 1.6 to 3.4 % in woody IAPs and 5.1 to 6.2 % in nonwoody IAPs, with a negative peak at 110 °C in DTG Figure 5.2 and Figure 5.3 (b). These results are consistent with previous studies (Havilah *et al.*, 2019; Ramesh and Somasundaram, 2022), showing the dehydration region at temperatures less than 200 °C and peak dehydration at 110 °C. The greater weight loss in nonwoody also observed in Section 3.3.3 is attributed to lower lignin content, which lowers the density of the tissues, allowing more available space for water retention than woody IAPs (Pasangulapati *et al.*, 2012). This stage is not designated for bio-oil production but rather biochar production, which enables an operator to implement pre-drying steps to remove excess moisture, reducing energy consumption during pyrolysis

The active pyrolysis stage occurs between 205 to 470 °C for woody IAPs and 180 to 480 °C for nonwoody IAPs, as indicated by the steep decreasing slope, suggesting weight reduction in TGA Figures 5.2 and 5.3 (a). The weight reduction is due to the thermal degradation of cellulose and hemicellulose into smaller compounds with the release of volatile compounds that can be condensed to bio-oil (Mishra and Mohanty, 2018). The two distinct peaks on *A. mearnsii* in Figure 5.3 (b) DTG are attributed to hemicellulose degradation (304 °C) and cellulose degradation (409 °C) because *A. mearnsii* has isolated cellulose and hemicellulose, while the two other IAPs have a complex mixture of cellulose and hemicellulose. This phenomenon is supported by Kosowska-Golachowska *et al.* (2018) with distinct peaks for

hemicellulose (319 °C) and cellulose (438 °C) on *A. mearnisii*. Active pyrolysis is explained as the temperature region where the maximum yield of bio-oil will occur, due to the degradation of cellulose and hemicellulose that release condensable volatile compounds. This is justified by Guedes *et al.* (2018), suggesting that temperatures between 450 to 550 °Care optimal for achieving a high yield of bio-oil.

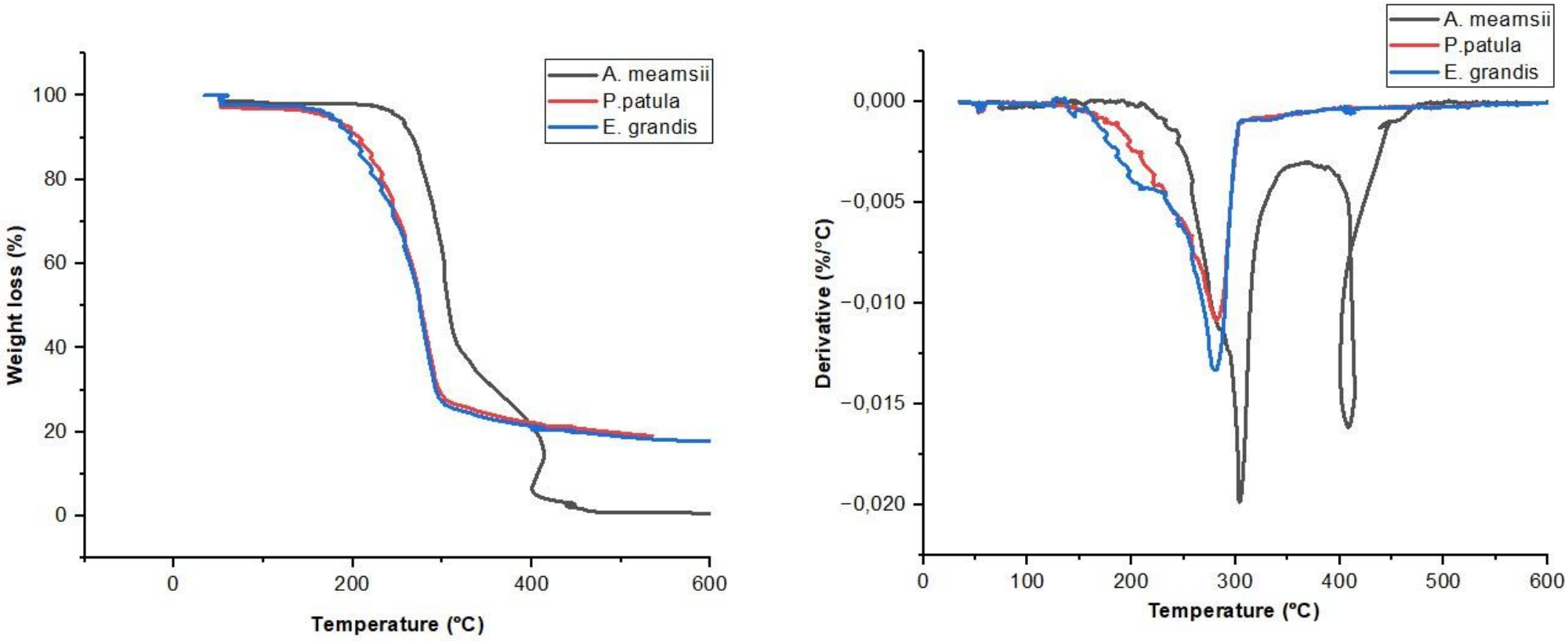
The passive pyrolysis stage occurs at 470 to 600 °C for woody IAPs and 480 to 600 °C for nonwoody IAPs, indicated by long-tailed slow decomposition with no significant peaks shown in Figure 5.2 and Figure 5.3 (a). This stage is attributed to lignin decomposition and char formation, due to the lignin complex's three-dimensional structure that requires higher temperature conditions to break down. Bio-oil from lignin typically ranges from 0.2 to 0.5 % between 500 to 700 °C, making this stage inefficient for bio-oil production (Zhong *et al.*, 2022b). These findings agree with Shafiq and Capareda (2021), where no bio-oil was obtained at 300 °C, and bio-oil yield was 6.2 % at 450 °C, which declined to 5.7 % at 600 °C.

The results suggest that the active pyrolysis phase plays a critical role in achieving optimal bio-oil yields. Conducting TGA provides valuable insights for enhancing reactor design and improving the regulation of temperature and reaction dynamics. However, one limitation of the method is its inability to distinguish the decomposition temperature ranges of cellulose and hemicellulose individually, which would be beneficial for assessing thermal stability and refining material analysis and processing. Additionally, the technique does not indicate the quantity of bio-oil generated at each stage or provide information on its chemical makeup.



(a) TGA (b) DTG

Figure 5.2 Thermogravimetric analysis of nonwoody IAPs with TGA curve and DTG



(a) TGA (b) DTG

Figure 5.3 The TGA and DTG of woody IAPs to assess the thermal behaviour

5.3.2 Pyrolysis products from woody and nonwoody IAPs

This section aims to validate the MCDM approach discussed in Chapter 4 and assess the feasibility of IAPs for bio-oil production. The mean yield of bio-oil, biochar, and syngas derived from woody and nonwoody IAPs is presented in Table 5.4.

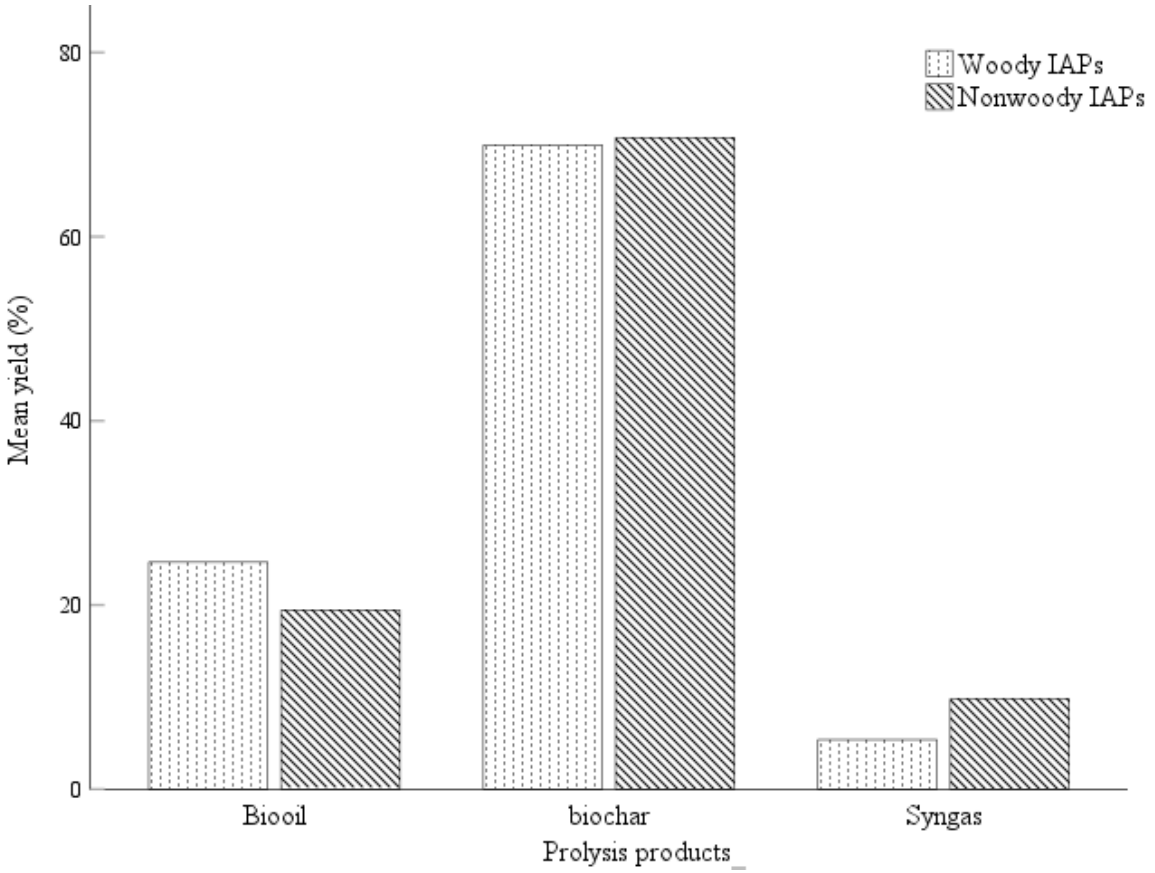
Table 5.4 Yield of bio-oil, biochar, and biogas in nonwoody and woody IAPs

IAPs	Bio-oil (%)	Biochar (%)	Syngas (%)
Woody IAPs			
A. mearnsii	23.51	73.13	3.36
E. grandis	27.55	65.66	6.79
P. patula	22.93	71.05	6.01
Non-woody IAPs			
L. camara	19.10	72.17	8.73
C. odorata	20.45	66.17	13.38
S. mauritianum	18.77	73.95	7.28

The statistical analysis of woody and nonwoody IAPs on pyrolysis products was further analysed, and the results are three values ± standard deviations with p values in Table 5.5. The graphical representation of these mean values and sample compositions is presented in Figure 5.4.

Table 5.5 Statistical analysis of woody and nonwoody IAPs on pyrolysis products

Pyrolysis product	Woody IAPs ± SD	Nonwoody IAPs ± SD	P value
Bio-oil	24.66 ± 2.52	19.44 ± 0.89	0.028
Biochar	69.95 ± 3.86	70.76 ± 4.07	0.813
Syngas	5.38 ± 1.80	9.59 ± 3.35	0.105







(a) Mean pyrolysis product from woody and nonwoody IAPs

(b) Bio-oil from *L. camara*

(c) Biochar from *L. camara*

Figure 5.4 The mean composition of pyrolysis products derived from woody and nonwoody IAPs

The results in Table 5.5 indicate that woody IAPs produce higher bio-oil yield (24.66%) compared to nonwoody IAPs (19.44%), with a significant difference ($p < 0.05$). These findings align with the integrated AHP and TOPSIS analysis in Chapter 4, reinforcing the suitability of woody IAPs for bio-oil production compared to biogas production. The variation in bio-oil production is attributed to the difference in biomass composition, as discussed in Chapter 3. Lower cellulose and hemicellulose in nonwoody IAPs reduce condensable vapours, and higher ash content hinders heat transfer, leading to incomplete combustion. Similar trends of bio-oil yield have been observed on nonwoody IAPs such as *Parthenium hysterophorus* (25.80%), *Arundo Donax L.* (20.13%), and *Miscanthus x giganteus* (21.2%) (Yorgun, 2003; Saikia *et al.*, 2015; Ramesh and Somasundaram, 2022). Likewise, woody IAPs such as acacia sawdust and eucalyptus yielded about 29.40 % and 20 % of bio-oil, similar to those found by (Ahmed *et al.*, 2020; Kashif *et al.*, 2024), aligning with the findings of this study.

Figure 5.4 reveals an unexpected outcome, where bio-oil yield is significantly lower compared to biochar, despite the biomass composition in Chapter 3 identifies these species as suitable for bio-oil production. This is because bio-oil production is influenced by several factors, including biomass composition, type of pyrolysis, reactor design, and operational conditions. By referring to Table 8.5, Appendix B, a strong negative correlation ($r = -0.91$, $p < 0.05$) between moisture content and bio-oil is observed, indicating that high moisture levels reduced bio-oil production. This is supported by (Eke *et al.*, 2020), where increasing moisture content (2.69%, 5.4%, and 9.29%) corresponded with a decline in bio-oil production (32.6%, 29.0%, and 22.9%), respectively. A weak positive correlation ($r = 0.41$, $p < 0.05$) between volatile content and bio-oil suggests that while volatile compounds contribute to bio-oil production, some are non-condensable, forming syngas instead. Elemental composition influences the quality of bio-oil and will be discussed in the characterisation section (Section 5.3.3). This emphasises the need to optimise feedstock properties to optimise bio-oil production.

The pyrolysis reactor orientation influences bio-oil production. This study utilised a vertical fixed bed reactor, where biomass remains stationary, inhibiting heat transfer and volatile compound formation, resulting in a lower yield of bio-oil (Lewandowski *et al.*, 2019). With a small diameter of 3 cm and external heating, closely packed particles experience inadequate heat distribution, leading to incomplete degradation (Gholizadeh *et al.*, 2020). Additionally, high vapour residence time (88s) in a fixed bed reactor enables secondary cracking, causing further degradation of volatile gases into biochar and syngas (Kan *et al.*, 2016). The type of

pyrolysis reactor plays a significant role in determining bio-oil yield. For instance, fluidised fixed-bed reactors have been reported to achieve yields as high as 71.1% (Heidari *et al.*, 2014), while microwave-assisted pyrolysis has demonstrated yields ranging from 19.8% to 39.25% (Kashif *et al.*, 2024). In this study, a conventional fixed-bed reactor yielded 27.55% bio-oil from Eucalyptus species. These variations highlight the critical impact of reactor configuration and process conditions on pyrolysis performance, emphasising the need for reactor selection to be tailored to the biomass feedstock and desired product outcomes to maximise efficiency and yield.

The bio-oil yield in this study is influenced by the key operational conditions shown in Table 5.1. The selected pyrolysis temperature of 450 ℃ proposed by Saikia *et al.* (2015) and supported by thermogravimetric analysis conducted in Section 3.2.1 was sufficient for optimal bio-oil production. The carrier gas flow rate of 200 $\mathrm{ml.\,m^{-1}}$ recommended by Aysu (2015) was optimal, as studies have shown a bio-oil yield of 34.62 % (100 $\mathrm{ml.\,m^{-1}}$), 35.75 % (200 $\mathrm{ml.\,m^{-1}}$) and 33.46 % (250 $\mathrm{ml.\,m^{-1}}$). However, the slow heating rate is 5 $\mathrm{℃.\,min^{-1}}$ was insufficient for efficient degradation. Research has shown that the highest yield was observed at 50 $\mathrm{℃.\,min^{-1}}$ and was reduced to 75 $\mathrm{℃.\,min^{-1}}$ (Yorgun, 2003). The longer vapour residence time of 88s and reaction time of 90 min contributed to secondary cracking, leading to higher biochar yields.

This study underscores the significance of biomass composition, reactor design, and operational conditions in bio-oil production, highlighting the importance of optimising these factors. A key limitation is the estimated vapour residence time, heating rate, and reaction time, which may produce slight variations in the experiment. The fixed bed reactor constraints highlight the need for control systems and alternative efficient reactor designs such as fluidised-bed, auger, or microwave pyrolysis. This study contributes toward advancing bio-oil research in South Africa by guiding process optimisation and reactor selection for optimal production.

5.3.3 Bio-oil characterisation

Bio-oil analysis for energy conversion is outlined in this section.

5.3.3.1 Fourier transform infrared spectroscopy (FTIR)

The results of the FTIR analysis are presented in Table 5.6 derived from FTIR spectra in Figure 8.1, Appendix B. The results from Table 5.8 indicated that bio-oil derived from both woody and nonwoody IAPs contains common functional groups such as N–H stretch, C–H stretch, –C≡C stretch, N–H bend, C–H bend, C–H wag (– CH^2X), and C–N stretch. Bio-oil derived from non-woody IAPs independently contains chemical compounds such as –C≡C–H: C–H stretch, C–C stretch (in–ring), and C–H rock, while bio-oil derived from woody IAPs has chemical compounds such as H–C=O: C–H stretch, and C=O stretch.

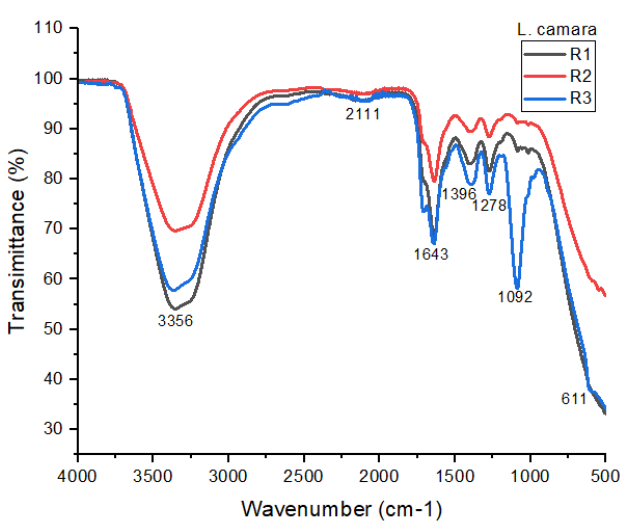
Table 5.6 The chemical composition derived from woody and nonwoody IAPs

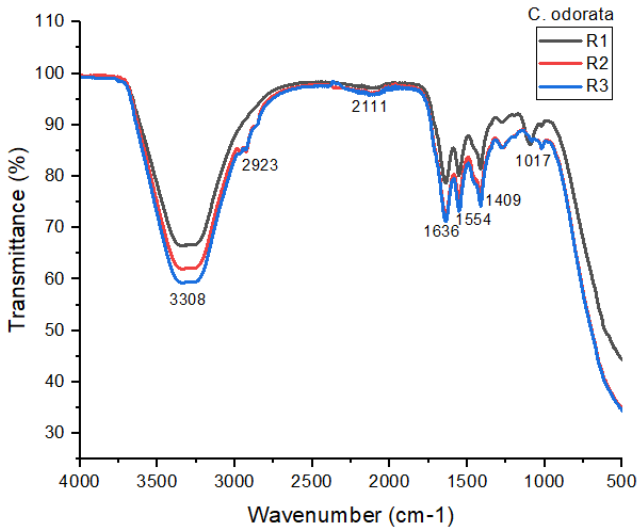
Wavenumber (cm-1)	Bonds	Functional group	Origin of functional group	Nonwoody IAPs	Woody IAPs
3400–3250	N–H stretch	1˚, 2˚ amines, amides	Degradation of proteins from high nitrogen (Alvarez *et al.*, 2016)	✓	✓
3330–3270	–C≡C–H: C–H stretch	alkynes (terminal)	Degradation of carbohydrates to form char polymeric network (Mosonik *et al.*, 2018)	✓	×
3000–2850	C–H stretch	alkanes	Presence of methyl and methylene groups CH2 (Mosonik *et al.*, 2018)	✓	✓
2260–2100	–C≡C– stretch	alkynes	Degradation of carbohydrates to form char polymeric network (Mosonik *et al.*, 2018)	✓	✓
1730–1715	C=O stretch	α, β–unsaturated esters	Presence of carbohydrate and dehydration reaction (Lv *et al.*, 2017)	×	✓
1650–1580	N–H bend	1˚ amines	Degradation of proteins from high nitrogen (Alvarez *et al.*, 2016)	✓	✓
1600–1585	C–C stretch (in–ring)	aromatics	Lignin and protein concentration (Mishra and Mohanty, 2018; Bhattacharjee and Biswas, 2020)	✓	×
1470–1450	C–H bend	alkanes	Degradation of cellulose and polar compounds (Baloyi and Marx, 2021)	✓	✓

1370–1350	C–H rock	alkanes	Alkanes: methyl (-CH3) methyl C-H asym./sym. Bend (AlDayyat *et al.*, 2021)	✓	×
1300–1150	C–H wag (–CH^2X)	alkyl halides	Organic nitrates (AlDayyat *et al.*, 2021)	✓	✓
1250–1020	C–N stretch	aliphatic amines	Associated with fractions from peptide linkages (Baloyi and Marx, 2021)	✓	✓

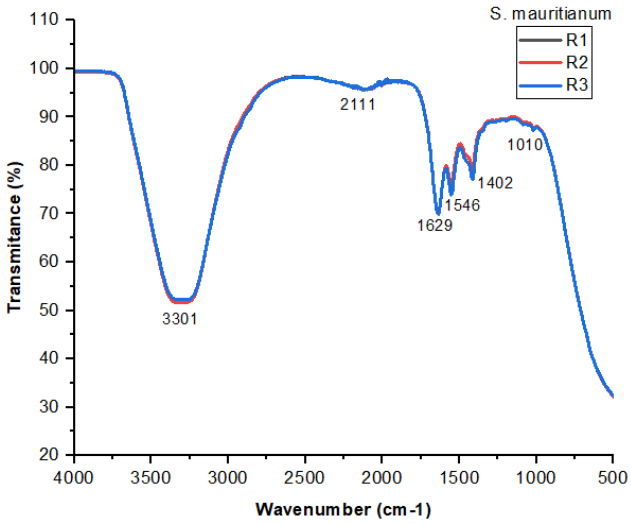
× = Not present functional group, ✓ = Present functional group

From a common functional group within bio-oil derived from woody and nonwoody IAPs, the presence of N–H stretch, N–H bend, and C–N stretch is associated with the presence of 1˚, 2˚ amines, amides, and aliphatic amines due to decomposition of protein with nitrogen content as presented in Table 5.6 (Alvarez *et al.*, 2016). The higher concentration of these compounds illustrated by the transmittance of 50% in Figure 5.5 (a to f), indicates that bio-oil can be utilised as a plasticiser and oil additive lubricant to reduce wear, corrosion, and rust in turbines or engines (Drese *et al.*, 2011; Alvarez *et al.*, 2016). The presence of C–H stretch, C–H bend, and C–H wag (–CH^2X) suggests that bio-oil contains alkanes and alkyl halides due to degradation of cellulose and polar compounds, and the presence of methyl and methylene groups CH^2 (Mosonik *et al.*, 2018; Baloyi and Marx, 2021). Alkanes and alkyl halides are known to provide high energy density and stability characteristics of fuel to increase the efficiency and performance of fuel (Chen *et al.*, 2024).

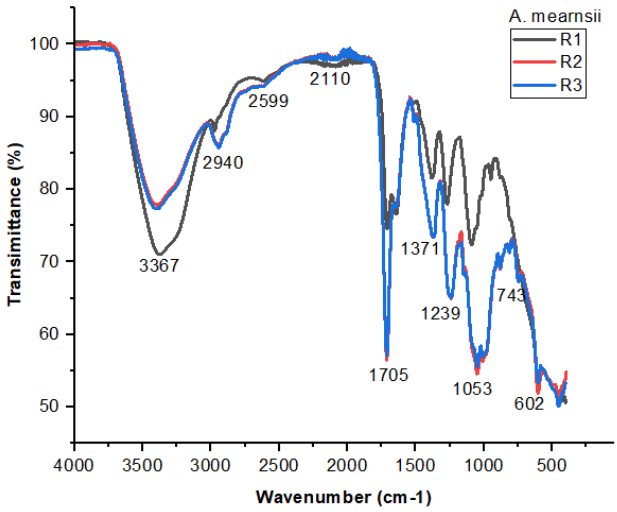




(a) FTIR spectra of *L. camara*

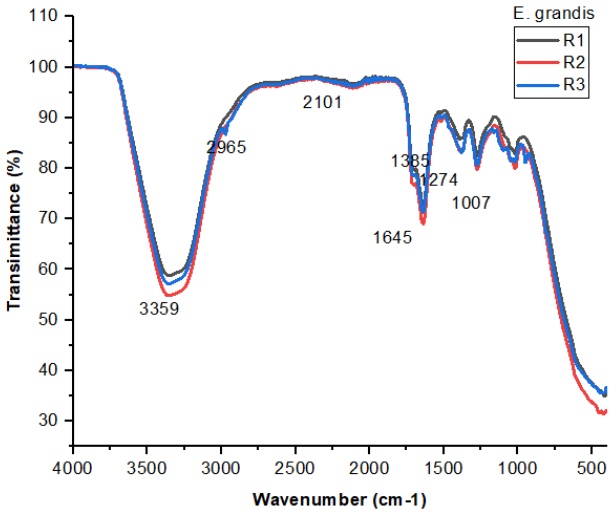


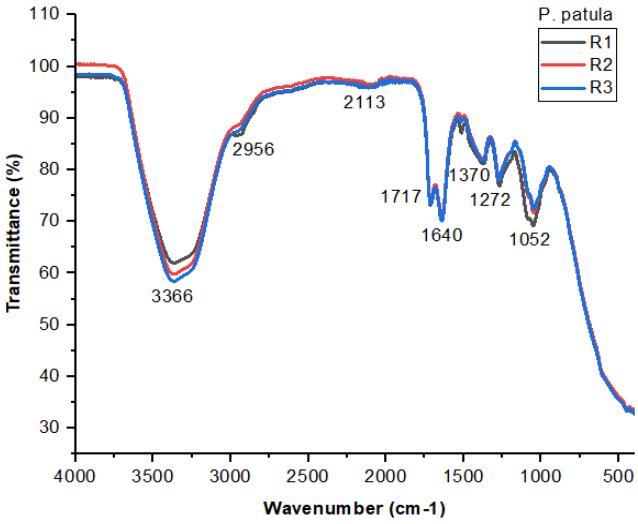
(b) FTIR spectra of *C. odorata*



(c) FTIR spectra of *S. mauritianum*

(d) FTIR spectra of *A. mearnsii*





(e) FTIR spectra of *E. grandis*

(f) FTIR spectra of *P. patuala*

Figure 5.5 The FTIR spectra of nonwoody and woody IAPs

The carbon-carbon triple bond (–C≡C stretch) is associated with the presence of alkynes due to the degradation of carbohydrates (cellulose, hemicellulose, and lignin) (Mosonik *et al.*, 2018). The alkynes suggest oxidation stability, further chemical reaction of bio-oil with oxygen affecting higher heating value (Balakrishnan *et al.*, 2016). Common functional groups on bio-oil derived from woody and nonwoody IAPs were also observed in the study conducted by Baloyi and Marx (2021) for bio-oil production using *Scenedesmus acutus* plants. The presence

of –C≡C–H: C–H stretch, C–C stretch (in–ring), and C–H rock suggest that bio-oil derived from nonwoody IAPs contains alkanes and aromatic compounds due to the degradation of carbohydrates to form char polymeric network (Mosonik *et al.*, 2018). Aromatic compounds present in bio-oil enhance its stability, reduce its chemical reactivity, and contribute to a higher-octane number, thereby improving the overall efficiency of the biofuel (Yang and Koel, 2018).

The presence of H–C=O: C–H stretch, and C=O stretch in bio-oil derived from woody IAPs is associated with aldehydes and α, β–β-β-unsaturated esters, respectively, due to the presence of carbohydrate and dehydration reaction (Lv *et al.*, 2017). The presence of aldehydes promotes combustion, which influences the ignition quality of bio-oil (Salooja, 1965). The α, β unsaturated esters, such as methyl ester, have lower ignition quality, less stability, and result in the emission of NOx (Connely and Tao, 2006). Bio-oil derived from the pyrolysis of softwood has similar functional groups (Lozano *et al.*, 2020).

Both bio-oil derived from woody and nonwoody IAPs contain energy-rich compounds that enhance combustion efficiency. The toxic compounds, such as alkynes, are present at lower transmittance (< 5%), posing minimal impact on the energy content of bio-oil. A limitation of the FTIR method is that it does not quantify the exact concentration of compounds in bio-oil. The transmittance peaks can overlap with each other, making it difficult to accurately quantify other compounds. To complement the FTIR methods, other methods such as Gas Chromatography-Mass Spectrometry (GC-MS) provide a detailed quantitative analysis of chemical compositions, providing standard methods for accuracy and consistent preparation of the sample, utilising advanced software for data analysis, and establishing calibration will increase the accuracy of the result.

5.3.3.2 Gas chromatography-mass spectrometry (GC-MS)

The objective of conducting GC-MS analysis on bio-oil was to understand the quantity of chemical composition and their influence on bio-oil as a renewable fuel. A total of 37 chemical compounds with peak area exceeding 4% were identified in bio-oil from woody and nonwoody IAPs, as shown in Table 5.7. The chemical compounds included ketones, phenols, aldehydes, acids, alkoxybenzenes, and nitrogen-containing compounds, with their respective intensities illustrated in Figure 5.6

Table 5.7 The GC-MS chemical compounds derived from woody and nonwoody IAPs with peak area percentage greater than 4%

Retention time (min)	Compound name	Compound group (Lu *et al.*, 2012)	Peak Area (%)					
			Non-woody IAPs			Woody IAPs		
			L. camara	*C. odorata*	*S. mauritianum*	*A. mearnsii*	*E. grandis*	*P. patula*
5.52	3-Hexen-2-one	Ketones	20.54	-	8.95	-	-	-
8.52	Catechol	Phenols	8.08	-	-	-	-	-
9.51	Phenol, 2,6-dimethoxy-	Phenolss	7.54	2.74	1.32	3.23	3.65	4.74
5.02	Ethanone, 1-(3-ethyloxiranyl)-	Ketones	6.77	-	1.96	3.68	2.93	5.79
4.55	Butanoic acid, 3-methyl-	Carboxylic acid	-	12.44	2.5	1.52	2.76	-
4.92	Butyrolactone	Ketones	-	8.84	8.97	4.08	2.04	2.99
4.32	2-Acetyl-2-methyl-succinonitrile	Nitrile group	-	8.34	-	-	-	
7.08	2-Amino-5,6-dihydro-4,4,6-trimethyl-4H-1,3-oxazine	Nitrogen-containing compounds	1.83	5.11	10.96	-	-	3.9
4.27	2-Furanmethanol	Alcohols	-	4.68	11.04	-	-	1.67

6.25	1,2-Cyclopentanedione, 3-methyl-	Ketones	2.31	4.29	2.75	3.92	5.82	6.33
5.90	Formic acid phenyl	Carboxylic acid	-	-	11.04	-	-	-
4.47	N, N-Dimethylacetamide	Nitrogen-containing compounds	-	-	7.33	-	-	-
10.21	4-Hydroxy-2-methoxybenaldehyde	Aldehydes	-	-	-	5.52	-	-
8.37	3,4-Dimethoxytoluene	Alkoxybenzenes	-	-	-	5.44	-	-
6.64	Phenol, 3-methyl-	Phenols	-	-	-	4.65	5.18	4.37
10.57	2-Isopropyl-5-methyl-6-oxabicyclo [3.1.0] hexane-1-carboxaldehyde	Aldehydes	-	-	-	4.49	-	-
7.24	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	Ketones	-	2.23	-	4.47	4.99	5.52
11.40	2,2,3,3-Tetramethylcyclopropanecarboxylic acid, 4-methylphenyl ester	Acids	-	1.01	1.01	4.18	-	-
6.87	Phenol, 2-methoxy-	Phenols	-	-	-	4.16	4.37	4.21
10.87	Apocynin	ketones	1.12	-	-	4.16	3.63	-
22.31	1,5-Bis[veratrylaminomethyl]-2,6-dihydroxynaphthalene	Alkoxy benzenes					6.17	
23.16	4-Methyl-2,5-dimethoxybenzaldehyde	Aldehydes	-	-	-	-	5.84	-

10.58	Borane, tributyl-	Alkanes					5,82	
22.88	3-Cyclobutene-1,2-dicarboxylic acid,3-methyl-4-propyl-, dimethyl trans-	Acids					5,42	
23.63	Acetamide, 3-ethyl-2-hydroxy-	Nitrogen containing	-	-	-	-	5.09	3.97
5.95	Phenol	Phenols	1.41	2.44	-	-	4.88	6.84
8.98	2-Acetylcyclopentanone	Ketones	2.22	-	-	-	4.66	-
19.33	5-Phosphatricyclo [6.1.1.0(2,6)]dec-2(6)-ene, 5,9,9-trimethyl-	Phenols					4.53	
6.70	1,2-Ethanediol, 1-(2-furyl)-2-phenyl-	Phenols	-	-	-	-	4.37	3.27
6.88	Phenol, 2-methoxy-	Phenols	-	-	-	-	4.37	-
5.16	Cyclohexanone	Cyclic ketones	-	-	-	1,91	4.35	-
21.51	2-Hydroxy-4-isopropyl-7-methoxytropone	ketones	-	-	-	-	4.31	-
4.12	3-Hepten-2-one, 4-methyl-	Ketones	-	-	-	-	4.12	-
6.29	2(5H)-Furanone	Ketones	-	-	-	-	2.54	6.08
9.01	Ethanone, 1-(2-ethyl-5-ethynyl-4-methyl-1,3,2-dioxaborolan-4-yl)-	Ketones						5.79

13.01	3,5-Dimethoxy-4-hydroxyphenylacetic	Phenylacetic acid	-	-	-	3.95	-	5,23
12.30	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	Aldehydes	-	-	-	3.52	3.42	4.82

- Means not detected

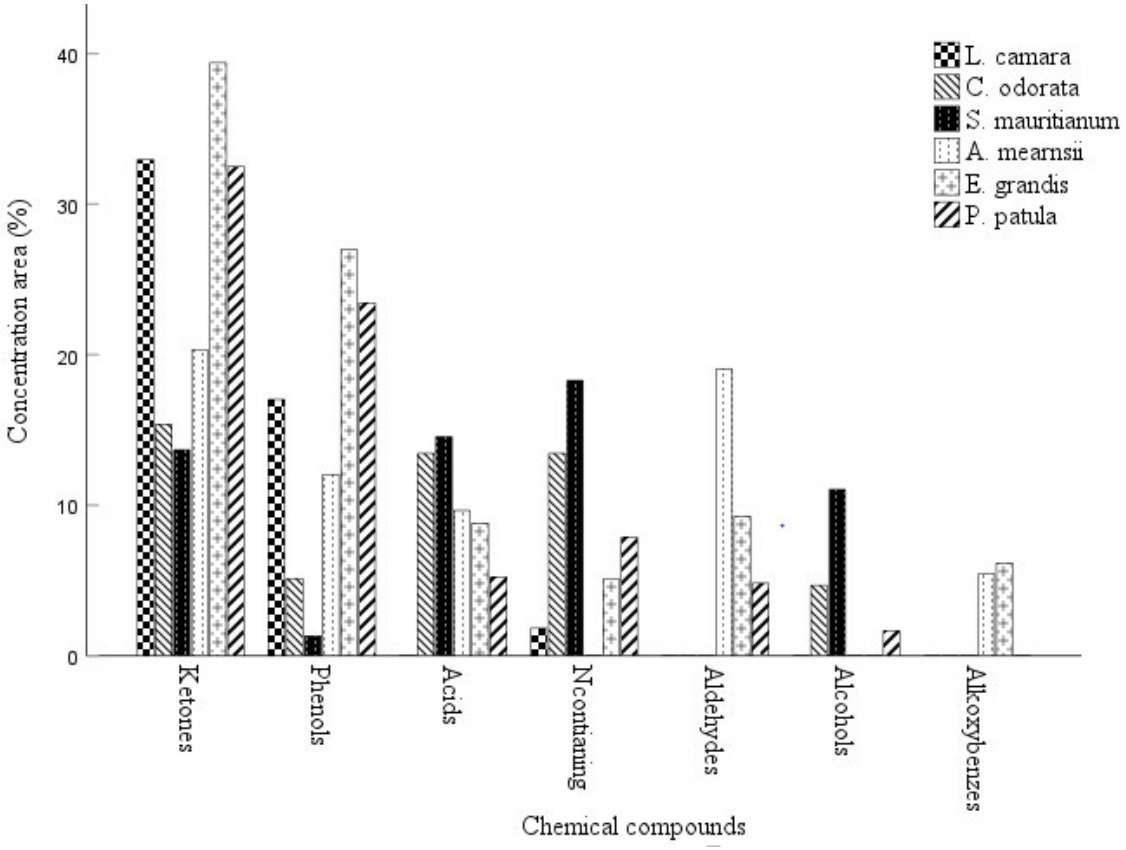


Figure 5.6 The distribution of chemical compounds in bio-oil derived from woody and nonwoody IAPs

The predominant chemical compounds in bio-oil from woody and nonwoody IAPs were Phenol, 2,6-dimethoxy- and 1,2-Cyclopentanedione, 3-methyl-. These compounds indicate the presence of phenols and ketones derived from the degradation of lignin macromolecules, respectively (Lu *et al.*, 2012; Kaur *et al.*, 2024b). Phenols characterised by a hydroxyl group bonded to the benzene ring ranged from x ee12.04 to 26.98% in woody IAPs and 1.32 to 17.03% in nonwoody IAPs. Ketones with a carbonyl group attached to carbon atoms within the carbon chain ranged from 20.31 to 39.39 % in woody IAPs and 13.68 to 32.92% in nonwoody IAPs. Their concentration contributes to oxidation reactions leading to residue formation, increased viscosity, poor atomisation, and potential corrosion of fuel systems (Deng *et al.*, 2009).

Bio-oil from woody and nonwoody IAPs contained about 7.68% and 9.33% of acids, respectively, as shown in Figure 5.6. These acids (formic, butanoic, pentadecanoic acid) are organic compounds with a carboxyl group attached to the alkyl group derived from the degradation of cellulose and hemicellulose (Lu *et al.*, 2012). Their concentration contributes to the corrosiveness of fuel systems and acts as a catalyst for polymerisation, affecting bio-oil stability (Hu *et al.*, 2017). The nitrogen-containing compounds (amides, amine), also detected in FTIR from protein decomposition, act as a plasticiser and oil additive lubricant to reduce wear, corrosion, and rust in turbines or engines (Drese *et al.*, 2011; Alvarez *et al.*, 2016). However, their combustion produces nitrogen oxide emissions, impacting the environment. Aldehydes, found in bio-oil derived from woody IAPs are by-products of incomplete combustion, posing risks to respiratory health and environmental pollution (Guo *et al.*, 2023).

Bio-oil from woody and nonwoody IAPs contained small concentrations of alcohols, Alkoxybenzenes, alkane, and alkenes. Alcohols (Furan methanol, pentanol, propanol) are derived from cellulose and hemicellulose degradation, improve fuel stability, and enhance higher heating value (Omar *et al.*, 2019). Alkane and alkenes (nonane, hexane, decene, octadiene) derived from waxes increase the combustion efficiency of the fuel (Chen *et al.*, 2024). Similar compounds, such as phenols with a concentration of 36.26%, were observed in eucalyptus biomass (Kaur *et al.*, 2024b).

The findings imply that bio-oil from woody and nonwoody IAPs is unsuitable for energy generation due to its high concentration of phenols, ketones, and acids, which promote oxidation, reducing heating value while increasing viscosity and corrosiveness in fuel systems.

These compounds require further upgrading through solvent addition (alcohol addition, esterification) to reduce fuel acidity. One of the limitations of GC-MS is that it is quite sensitive, so detecting chemical compounds in lower concentrations can be quite challenging. Other compounds degrade at higher temperatures, and higher temperatures in GC-MS lead to decomposition rather than detection. It is recommended to employ advanced GC-MS methods to improve the accuracy of compound identification and quantification.

5.3.3.3 Estimation of higher heating value (HHV) of bio-oil derived from woody and nonwoody IAPs using literature approaches

The HHV indicates the amount of energy that can be obtained from bio-oil for applications such as heat production, electricity generation, and transportation fuel. Due to the limitation of direct HHV measurement, this study estimates its value based on similar woody and nonwoody IAPs that underwent pyrolysis under the same operational conditions (as detailed in Table 5.1) using a fixed-bed reactor. The selected biomass species exhibited similar chemical compositions, as identified through GC-MS and FTIR analyses. The estimated HHV values are presented in Table 5.8.

Table 5.8 Estimated HHV of bio-oil derived from woody and nonwoody IAPs using a literature-based approach

IAPs	HHV ($MJ.kg^{-1}$)	Operational	FTIR	GCMS	Literature
Nonwoody IAPs					
Eucalyptus wood	24.26	Temperature: 500 °C Particle size: 2 mm Fixed bed reactor Bio-oil yield: 17.75%	O-H stretching C–H stretch C–H bending	Phenols, Aromatic acids	(Sakhakarmy *et al.*, 2024)
Acacia mangium wild	24.32	Temperature: 440 °C Particle size: 2 mm Fixed bed reactor Bio-oil yield: 17.3%	C-H stretching OH group C=O stretching	Phenols, ketones aldehydes alcohols	(Charusiri and Numcharoenpinij, 2017)

Pine wood	24.27	Temperature: 500 °C Particle size: 0.3mm Fixed bed reactor	C–O bond C–H bond O–H bond	phenolic, aromatic, acidic, furan, ketone, and aldehyde	(Rahman *et al.*, 2020)
Nonwoody IAPs					
Arundo Donax L	24.7	Fixed bed Temperature: 450 °C Gas flow rate: 200 $ml.\,m^{-1}$ Bio-oil yield: 26%	O-H stretching C=C stretching C-H stretching	Phenolic, aromatic, ketones, esters, acids	(Saikia *et al.*, 2015)
Heracleum persicum Desf. w	19.75	Fixed bed Temperature: 400 °C Gas flow rate: 100 $ml.\,m^{-1}$ Bio-oil yield: 33.0%	O-H stretching C-H stretch C-C stretching	furans, ketones, benzenes, amine, amides	(Aysu, 2013)
Glycyrrhiza glabra L	22.46	Fixed bed Temperature: 550 °C Gas flow rate: 100 $ml.\,m^{-1}$ Bio-oil yield: 26%	O-H stretching C≡C stretch C-C stretching	aldehydes, ketones, esters, amines, and carboxylic acids	(Aysu and Durak, 2015)
Fossil fuels					
Fossil fuels	HHV ($MJ.kg^{-1}$) (Sánchez-Borrego *et al.*, 2021)				
Heavy fuel oil Diesel Gasoline	42.9 47.0 45.6				

The estimated HHV of bio-oil from woody and nonwoody IAPs based on literature sources in Table 5.8 was 24.28 $MJ.kg^{-1}$ and 22.16 $MJ.kg^{-1}$, respectively. While woody IAPs exhibited slightly higher HHV compared to nonwoody IAPs, both were significantly lower than fossil fuels such as heavy fuel oil (42.9 $MJ.kg^{-1}$) used for heating and power generation, as well as diesel (47 $MJ.kg^{-1}$) and gasoline (45.6 $MJ.kg^{-1}$) used in transportation (Sánchez-Borrego *et al.*, 2021). The HHVs were derived in research studies using biomass similar to that in this research, pyrolysed in a fixed-bed reactor under comparable operational conditions. The fixed-

bed reactor's limited heat transfer restricts lignin degradation, which contains high-energy compounds, thereby contributing to the lower HHV compared to fossil fuels (Lewandowski *et al.*, 2019), (Butler *et al.*, 2011).

Literature-based studies on IAPs in Table 5.8, identified key chemical compounds such as O-H stretching, C=C stretching, and C-H stretching, representing oxygen-containing compounds, alkynes, and alkanes, respectively. These compounds, derived from the degradation of cellulose, hemicellulose, and lignin, closely align with those identified in this study through FTIR analysis in Section 5.3.3.1. The GC-MS results further confirmed the presence of phenols, with concentrations ranging from 12.04% to 26.98% in woody IAPs and 1.32% to 17.03% in nonwoody IAPs. The presence of alkynes and phenols contributes to oxidation reactions, lowering HHV, and increasing viscosity, all of which affect combustion efficiency and storage stability (Balakrishnan *et al.*, 2016). On the other hand, presence of alkane could offset the toxic compounds by providing high energy density and stability characteristics of fuel to increase the efficiency and performance of fuel (Chen *et al.*, 2024).

The HHV of woody IAPs was higher than that of nonwoody IAPs due to higher lignin content and carbon and hydrogen content, as discussed in Chapter 3. These compositions contain C-C and C-H bonds that release significant energy during the combustion process (Yao and Wang, 2019) (Butler *et al.*, 2011). In contrast, conventional fossil fuels have a significantly higher carbon content (86 to 88.1%) and lower oxygen content (0.35 to 0.64%), enhancing their energy density (Sánchez-Borrego *et al.*, 2021) compared to IAP-derived bio-oil, which contains 44.58 to 50.8% carbon and 42.97 to 48.79% oxygen. Given these variations, bio-oil from woody and nonwoody IAPs might need to be upgraded using methods such as hydrodeoxygenation and catalytic cracking in order to eliminate excess oxygen and increase stability. The improved bio-oil can be mixed with diesel to improve its combustion characteristics after it has been refined, making it a more attractive option for energy applications.

5.4 Conclusion

The objective of this section was to assess the suitability of woody and nonwoody IAPs for bio-oil production and to validate the multi-criteria decision-making process described in Chapter 4. Fixed-bed reactor experiments showed that woody IAPs achieved a bio-oil yield of

24.7%, whereas nonwoody IAPs produced 19.4%. The higher yield from woody IAPs supported the multi-criteria decision-making results, which ranked most woody species higher in terms of bio-oil potential. However, the bio-oil yields obtained in this study were lower than those reported in previous research. The findings highlighted the limitations of the fixed-bed reactor, revealing that factors such as operating parameters and feedstock characteristics significantly influenced bio-oil production. This underscores the need for selecting appropriate conversion technologies and optimising process conditions to enhance production efficiency.

With respect to bio-oil quality and energy potential, FTIR and GC-MS analyses of bio-oil from invasive plant species revealed the presence of oxygenated compounds, including phenols and ketones, which contributed to lower heating values and reduced fuel quality. This work demonstrated the novel application of detailed molecular characterisation to identify limitations of bio-oil for direct energy use and highlighted the need for upgrading processes such as hydrodeoxygenation or thermal cracking. While these techniques can improve quality, they may also increase processing costs.

This study provides a novel, comprehensive evaluation of woody and non-woody invasive alien plant species (IAPs) as feedstocks for bio-oil production in South Africa, integrating thermogravimetric analysis, fixed-bed pyrolysis, and advanced characterization techniques (FTIR, GC-MS). Findings indicate that both feedstock types are unsuitable for efficient bio-oil production under the investigated conditions. Limitations include high capital requirements for IAP eradication, preprocessing, pyrolysis, and upgrading. These results highlight the need for further research on the techno-economic feasibility of large-scale bio-oil production in South Africa.

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6. EVALUATING THE POTENTIAL OF WOODY AND NONWOODY INVASIVE ALIEN PLANT SPECIES FOR BIOGAS PRODUCTION

This chapter evaluates the yield and quality of biogas derived from woody and nonwoody invasive alien plants species (IAPs) as sources of renewable energy. It further examines and validates the findings from Chapter 4, on the selection of IAPs suitable for optimal biogas.

Abstract

Biogas plays a crucial role in generating bioheat and biopower, while its by-products serve as valuable fertilisers in agriculture. However, because of unavailable energy substrates, these benefits are limited in South Africa. To address these challenges, this study evaluates the potential of woody IAPs *(Acacia Mearnsii*, *Eucalyptus Grandis*, and *Pinus Patula)* and nonwoody IAPs (*Lantana Camara*, *Chromolaena odorata*, and *Solanum mauritianum)* as a biogas energy substrate. To do this, an automatic methane potential test system (AMPTS) was utilised to evaluate methane potential, and the Buswell equation was used to determine the biodegradability of woody and nonwoody IAPs. Furthermore, the methane potential of IAPs was compared to biogas substrate in South Africa.

The results of this study indicated that the average methane potential of nonwoody IAPs was 162.62 Nml. g^{-1}VS with a biodegradability of 35.81%, while woody IAPs produced an average yield of 117.49 Nml. g^{-1}VS with biodegradability of 26.41%. This suggests a higher yield in nonwoody, thus strong potential for biogas production. However, these are quite low concentrations, especially when compared with the theoretical methane potential ranging between 407.02 to 498.08 Nml/ g VS. This is attributed to higher lignin content, which forms a rigid, complex, and insoluble structure around cellulose and hemicellulose, reducing microbial access to organic compounds. To reduce the amount of lignin, pre-treatment techniques such as acid, enzymes, and heat are advised.

6.1 Introduction

Anaerobic digestion is the degradation of organic biomass derived from plants or animal origin to produce value biofuels such as biogas/biomethane (Soldano *et al.*, 2012). These biofuels

provide sustainable, long-term renewable energy solutions, addressing environmental, economic, and social crises (Sawyerr *et al.*, 2017). This includes environmental advantages such as carbon neutrality and versatile energy sources used for heating, electricity generation, and transport fuel (Kadam and Panwar, 2017). Furthermore, the anaerobic digestion process results in digestate rich in nitrogen compounds that can be utilised as biofertiliser for sustainable agricultural production (Edith *et al.*, 2019). These address South African challenges such as energy security, climate change, and agricultural production.

A wide range of biomass, such as plant, animal, food, and municipal waste, has been adopted in South Africa for biogas production (Sawyerr *et al.*, 2017). Some of these biomass sources are staple food crops with higher capital input requirements, creating the need to seek low-cost energy substrates. There is less investment in research and development toward utilising IAPs as a potential energy substrate for biogas production (Melane *et al.*, 2017). Utilising IAPs for biogas production diversifies biomass substrate while minimising competition for energy and food crops (Akinbami *et al.*, 2021). Furthermore, clearing IAPs helps to control and manage infestations, reducing their impact on biodiversity, water systems, and the economy while also providing work opportunities (Mugido *et al.*, 2014).

Therefore, this study aims to evaluate the potential of IAPs as biomass feedstock for biogas production. Utilising three woody IAPs, *Acacia Mearnsii*, *Eucalyptus Grandis*, and *Pinus Patula*, as well as three nonwoody species, *Lantana Camara*, *Chromolaena Odorata*, and *Solanum mauritianum.* A Biochemical Methane Potential (BMP) test is used to evaluate the methane potential and degradability of IAPs while minimising large-scale economic losses. Furthermore, the methane potential of IAPs is compared to South Africa's biogas substrate to assess its viability for biogas production. By investigating IAPs for biogas production, this research work contributes toward sustainable energy solutions, supports biodiversity conservation, and encourages policies that integrate invasive species management with renewable energy goals, ultimately fostering a more sustainable future.

6.2 Materials and Methods

The BMP test is an automatic laboratory method used to determine the optimal methane potential of the substrate under controlled anaerobic conditions (Cabrita and Santos, 2023).

This section utilises the automatic methane potential test system (AMPTS) to evaluate the biogas and biodegradability of woody and nonwoody IAPs as sustainable bioenergy sources.

6.2.1 IAPs, inoculum, and cellulose preparation

The preparation of woody and non-woody IAPs, using freshly harvested and processed plant material, is explained in Section 3.2.2, Chapter 3. To establish the first microbial environment, the inoculum (liquid digestate) was taken from a commercial biogas facility located in Bronkhorstspruit, Pretoria. The inoculum was collected in 20-litre bucket five days prior to the experiment. It was then left open for five days at 25 ℃ to degas and remove oxygen that inhabits microbial activities and growth (Wang, 2016). A monocrystalline cellulose with a known methane potential was used to assess the effectiveness of the microbial community and BMP test essay (Filer *et al.*, 2019). The cellulose was sampled from the Agricultural Research Council Bioenergy laboratory in Pretoria.

Furthermore, the BMP test utilised the anaerobic reactor bottle, with feeding based on the number of volatile solids and total solids of both IAPs and inoculum. The determination of volatile solids and total solids is presented in Section 3.2.3, Chapter 3, and Section 4.2.1, Chapter 4, respectively. The summary of woody, nonwoody IAPs, inoculum, and cellulose characterisation is presented in Table 6.1

Table 6.1 Initial characteristics of IAPs, inoculum, and cellulose

IAPs	Total solids (%)	Volatile solids (%)
Woody IAPs		
A. mearnsii	96.08	87.20
E. grandis	98.14	87.90
P. patula	97.14	86.8
Nonwoody IAPs		
L. camara	95.77	83.96
C. odorata	96.72	85.34

S. mauritianum	96.43	82.89
Inoculum and cellulose		
Inoculum	6.49	4.01
Monocrystalline cellulose	96.26	96.22

6.2.2 Biochemical methane potential test

The experimental setup, design, and procedure are outlined in this section.

- Automatic methane potential test system (AMPTS)

This research study utilised the Bioprocess Control (AMPTS) instrument for measuring the biochemical methane potential of woody and nonwoody IAPs as presented in Figure 6.1. The system was equipped with 15 × 500 mL reactor bottles for substrate, inoculum, and cellulose as shown in Figure 6.1. (2). The reactor bottles were housed in a thermostatic water bath for microbial mobilisation fitted with an electric motor that powers the rotating shaft to facilitate mixing, as depicted in Figure 6.1 (1). The reactor bottle was connected to a carbon dioxide scrubbing unit that absorbed carbon dioxide, leaving purified methane gas. The scrubbing solution was made up of 80 mL of 3 M NaOH and 0.4 % Thymolphthalein pH indicator and fitted in a 15 × 100 mL glass bottle as shown in Figure 6.1 (3). The amount of methane gas generated in each reactor bottle was measured by the flow cell gas using liquid displacement (Figure 6.1 (4)). The Bioprocess Control program, which records the data on gas generation and manages the experiment, was connected to a laptop via the gas counter.



Figure 6.11 Biochemical methane potential (BMP) setup, (1) thermostatic water bath, (2) glass bottle reactor (biodigester), (3) CO_2 scrubbing unit, and (4) gas volume measuring device (Matheri *et al.*, 2018)

- Experimental design

The experimental design is illustrated in Figure 6.2. Initially, a batch of three nonwoody IAPs (*Lantana camara, Chromolaena odorata, and Solanum mauritianum*), combined with inoculum and cellulose, was processed for 30 days using 15 reactor bottles, with each setup run in triplicate to ensure reliability. Following this, a second batch comprising woody species (*Acacia mearnsii, Eucalyptus grandis, and Pinus patula*) was similarly run for another 30 days. To analyse biogas composition, a 10 ml gas-tight syringe was connected to the pipeline before the carbon dioxide scrubbing unit, with samples taken every seven days (Arrhenius *et al.*, 2019).

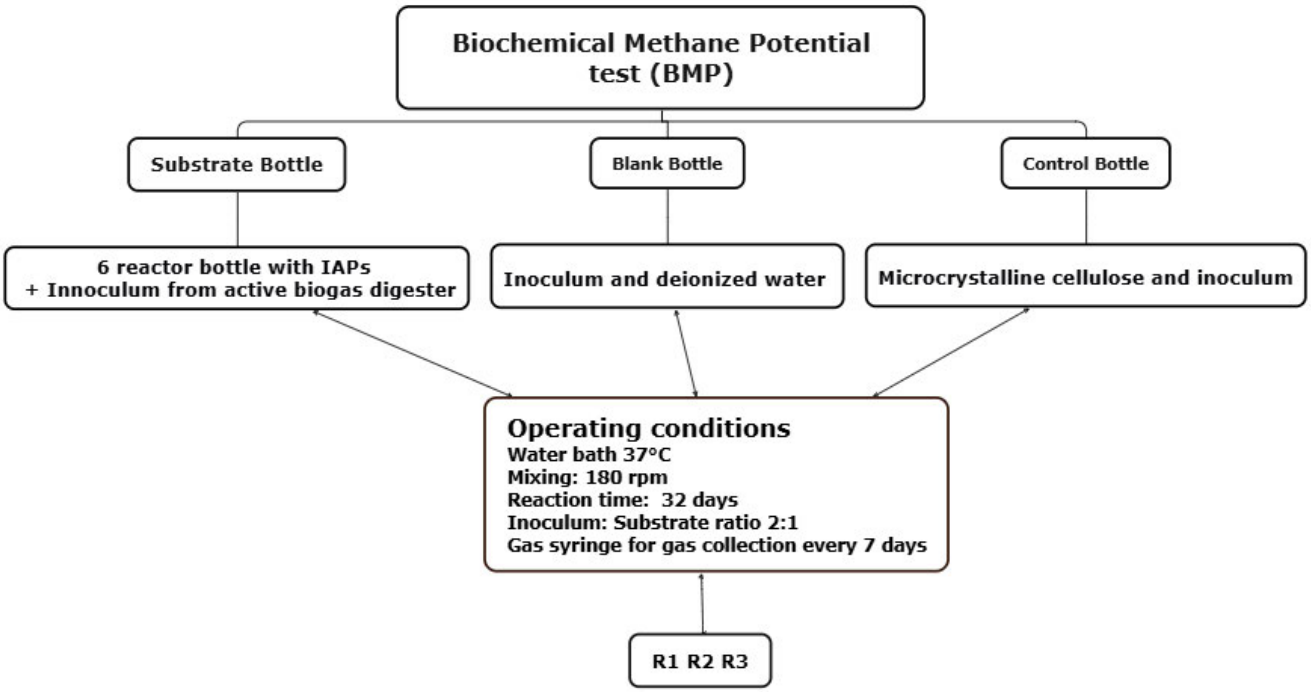


Figure 6.2 BMP test experimental design

- Experimental procedure

After preparing and characterising the IAPs, inoculum, and cellulose, each of the 15 × 500 ml reactor bottles was filled with 400 g of the prepared mixture (equivalent to 400 ml, assuming a density of 1 g/ml) comprising the inoculum, substrate, and cellulose, as outlined in the experimental layout (Figure 6.2). According to Bioprocess Control (2016), a 400 g loading limit is advised to minimise the risk of foaming. This setup resulted in a working volume of 400 ml and a headspace of 200 ml, comprising 100 ml from the reactor's headspace and 100 ml from the connecting tubing. The AMPTS software calculated the required quantities of substrate and inoculum based on a volatile solids (VS) ratio of 2:1 (substrate VS to inoculum VS). Table 6.2 presents the specific amounts loaded into each reactor. Once filled, the reactors were placed in a thermostatic water bath maintained at 37 °C to simulate mesophilic conditions. Each reactor was sealed with a gas-tight rubber stopper equipped with three outlet ports. An aluminium cap containing power cables was used to secure the setup. To establish anaerobic conditions, the headspace of each reactor was purged with a gas mixture of 20% CO_2 and 80% N_2 for one minute at a flow rate of 1 m^3. min and a pressure of 0.1 bar, eliminating residual oxygen. The experiment was initiated through the AMPTS software once the water bath reached the target temperature.

Table 6.2 The amount of substrate, cellulose, and inoculum added in each reactor bottle based on volatile solids

IAPs	Inoculum (g VS/ inoculum g)	Substrate (g VS/ substrate g)
Woody IAPs		
A. mearnsii	15.66 g VS/ 391.86 g	7.83 g VS/ 8.52 g
E. grandis	15.48 g VS/ 386.96 g	7.74 g VS/ 13.04 g
P. patula	15.60g VS/ 389.96 g	7.80 g VS/ 10.04 g
Nonwoody IAPs		
L. camara	15.63 g VS/ 390.81 g	7.82 g VS/ 9.19 g
C. odorata	15.63 g VS/ 390.67 g	7.81 g VS/ 9.33 g
S. mauritianum	15.62 g VS/ 390. 41 g	7.81 g VS/ 9.59 g
Inoculum and cellulose		
Inoculum	16 g VS/ 400 g	0
Monocrystalline cellulose	15.67 g VS/ 391. 86 g	7.84 g VS/ 8.14 g

6.2.3 Biomass biodegradability

The biodegradability of substrate refers to the ability of organic materials to be degraded by microorganisms during anaerobic digestion Sawyerr *et al.*, 2017). This is evaluated by the cumulative methane yield from the BMP test and theoretical methane yield from the Buswell equation using the elemental composition adopted by Galván-Arzola *et al.* (2021) and by Sawyerr *et al.* (2017). The Buswell equation is a chemical formula ($C_aH_bO_cN_d$) used to evaluate the potential biogas from the substrate. The chemical formula is presented in Equation 6.1 and simplified stoichiometric Equation 6.2. The values a, b, c, and d are the coefficients of carbon, hydrogen, oxygen, and nitrogen, respectively, calculated using the mass number of the element and elemental composition in Table 3.3, Chapter 3, and the equations are presented in 6.3 to 6.6. Lastly, the biodegradability of the substrate is calculated using Equation 6.7.

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right)CO_2 + dN \quad (6.1)$$

$$CH_4{}^{theo} = 22.4 \times \frac{(4a + b - 2c - 3d - 2e)/8}{12a + b + 16c + 14d + 16e} \times 1000 \quad (6.2)$$

$$a = \frac{C_{elemental\ value}}{12} \quad (6.3)$$

$$b = \frac{H_{elemental\ value}}{1} \quad (6.4)$$

$$c = \frac{O_{elemental\ value}}{16} \quad (6.5)$$

$$d = \frac{N_{elemental\ value}}{14} \quad (6.6)$$

Where

$C, H, O, N =$ Carbon, hydrogen, oxygen, and nitrogen are presented in Table 3.3 (%)

$a, b, c, d =$ Coefficient of carbon, hydrogen, oxygen, and nitrogen (g/mol)

$H_2O =$ Water

$CH_4 =$ Methane

$CO_2 =$ Carbon dioxide

$CH_4{}^{Theo} =$ Theoretical methane (Nml CH_4/g VS)

$$\text{Biodegradability} = \frac{\text{Cumulative methane yield}}{\text{Theoretical methane yield}} \times 100 \quad (6.7)$$

6.2.4 Biogas characterisation

Due to limitations in biogas direct characterisation, this study compares the methane potential of woody and nonwoody IAPs with other South African biogas energy substrates. Previous studies, such as (Sawyerr *et al.*, 2019a), have evaluated the theoretical methane potential of substrates such as cassava peels, cattle manure, cassava tubers, and fruit and vegetable waste. This is motivated by their availability, with cattle manure production reaching approximately 136,161 tons per year, fruit and vegetable waste amounting to 1,387 tons annually, and cassava production exceeding 263 million tons per year (Sawyerr *et al.*, 2019a). Furthermore, the

residues of these feedstocks are discarded in landfills, which contributes to environmental pollution and health risks through the release of harmful compounds (Whiting *et al.*, 2004). Given the infestation of invasive species with inadequate methods, this method will assess the feasibility of IAPs compared to conventional substrates.

6.2.5 Data analysis

Data analysis was performed using SPSS version 11 to compare the difference between woody and nonwoody IAPs. The analysis of variance (ANOVA) was used to test for differences.

6.3 Results and Discussion

Chapter 3 has outlined the impact of proximal, elemental, and structural composition on the yield of biogas. Chapter 4 has selected IAPs suitable for biogas production. This chapter further validates the results from these two chapters through a discussion on methane potential, biodegradability, and biogas characterisation.

6.3.1 Biogas and methane potential of woody and nonwoody IAPs

The primary aim of this section is to assess the suitability of IAPs for biogas production, especially methane content. The quantity of biogas produced with methane potential derived from woody and nonwoody IAPs is presented in Table 6.3 with a visual comparison in Figure 6.3. Furthermore, a cumulative methane yield over the space of 30 days to assess the ease of degradation is presented in Figure 6.4.

Table 6.3 Biogas and methane production of woody and nonwoody IAPs with statistical analysis

Parameters	Units	Woody IAPs			Nonwoody IAPs			
		A. mearnsii	*E. grandis*	*P. patula*	*L. camara*	*C. odorata*	S. mauritianum	Monocrystalline cellulose
Methane potential	Nml $CH_4.g^{-1}$ VS	164.00	96.84	78.70	160.86	195.33	142.58	355.58
Theoretical methane	Nml $CH_4.g^{-1}$ VS	407.02	498.08	490.88	458.03	435.00	468.40	400
Biodegradability	%	40.29	19.44	16.03	35.12	44.90	30.44	89

Statistical analysis

Parameters	Nonwoody IAPs					Woody IAPs					P-value (t-test)
	Mean	Median	SD	Min	Max	Mean	Median	SD	Min	Max	
Methane potential	162.62	177.10	61.96	75.66	269.01	117.49	98.27	36.77	76.90	166.56	< 0.001
Biodegradability	35.81	39.62	13.74	16.15	57.43	26.41	19.73	10.84	15.67	40.92	< 0.001

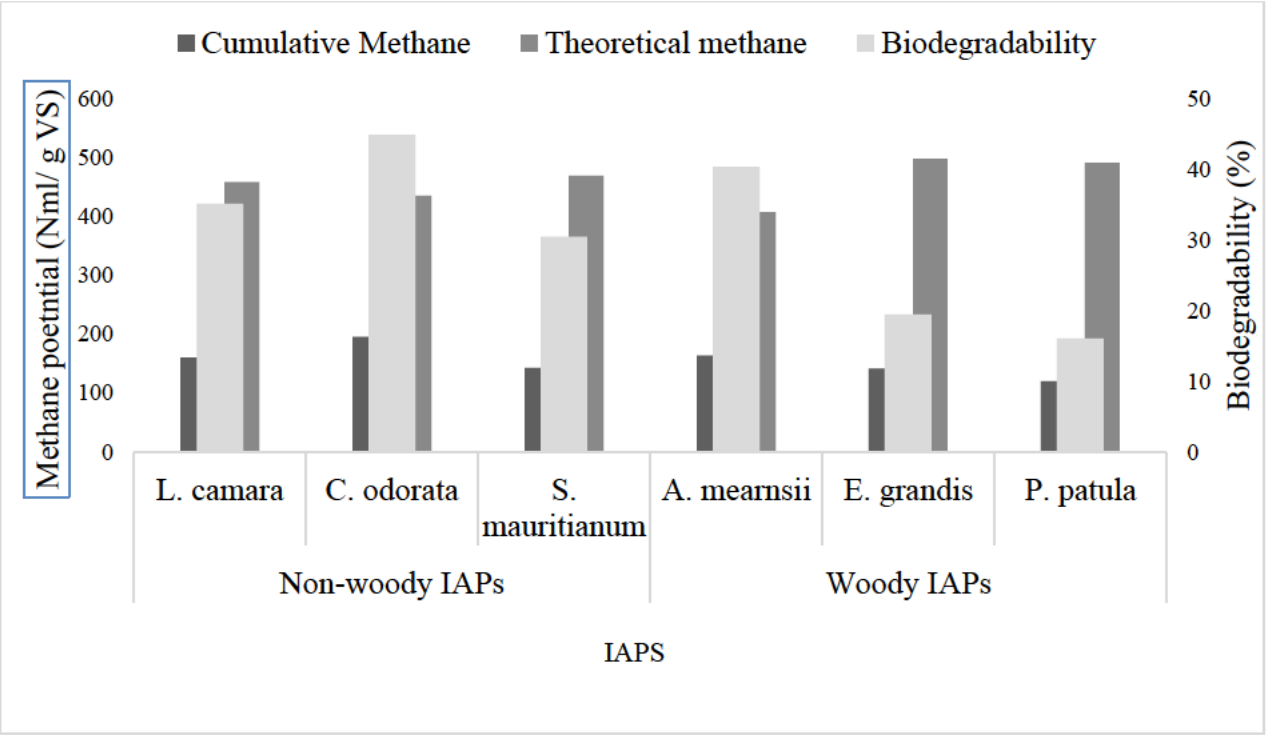
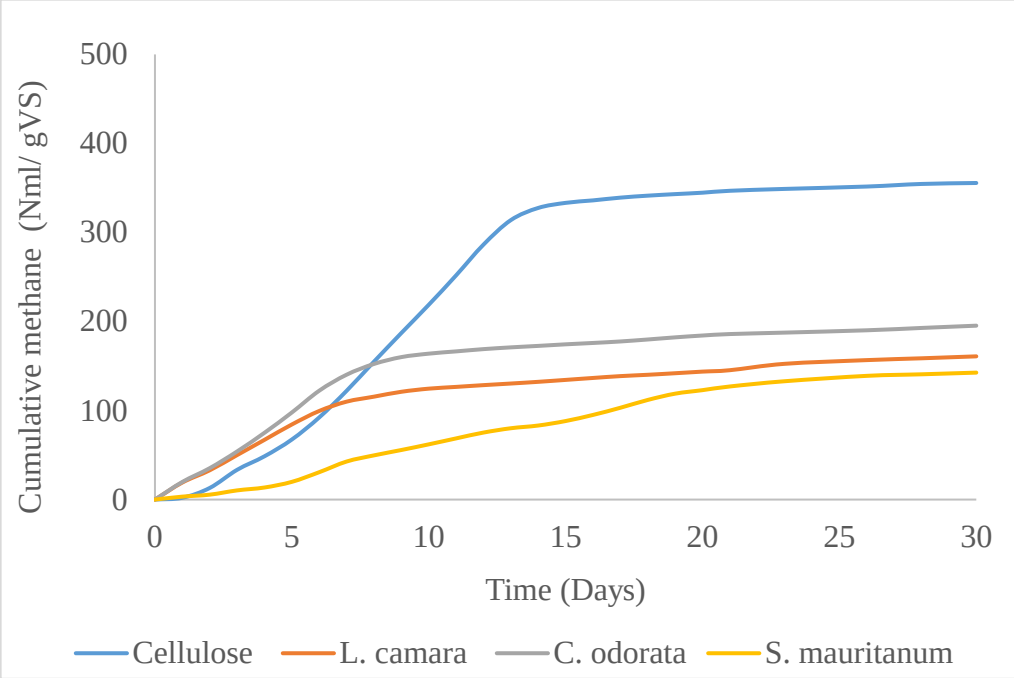
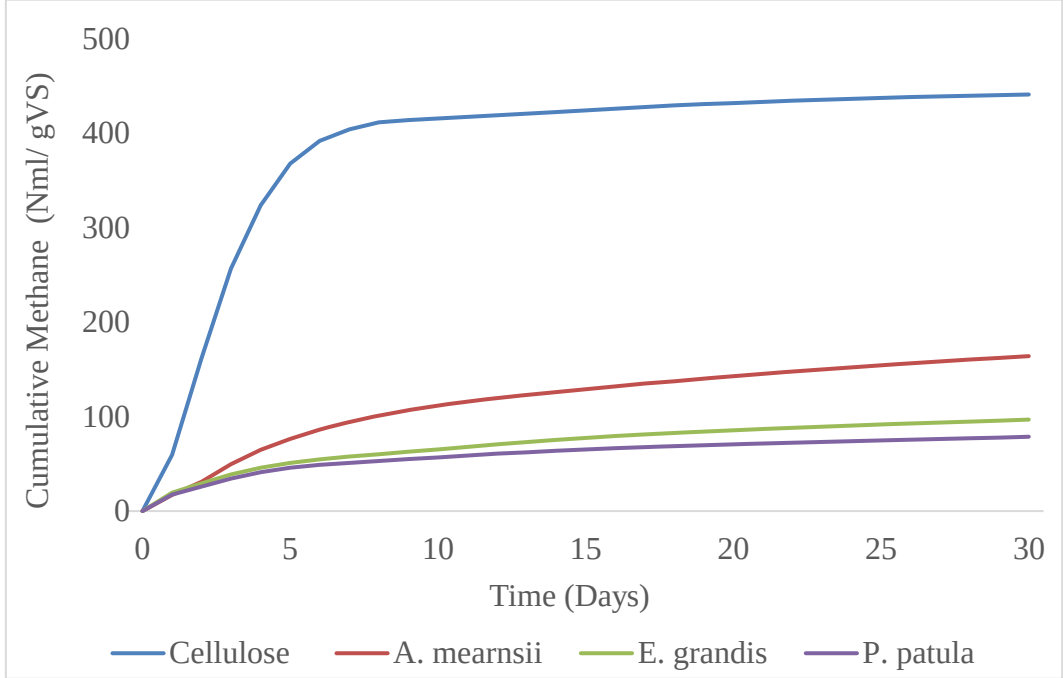


Figure 6.3 A visual comparison between woody and nonwoody on cumulative, theoretical methane potential, and biodegradability

Table 6.3 indicated nonwoody IAPs had higher methane potential (162.62 Nml $CH_4.g^{-1}$ VS compared to woody IAPs (117.49 Nml $CH_4.g^{-1}$ VS) with a significant difference ($p < 0.001$). The variation is attributed to the absence of nitrogen content in woody IAPs, which affects the C: N ratio crucial for the growth and activities of micro-organisms for methane production (Yan *et al.*, 2015). Nitrogen was not detected because the CHNS element analyser used was unable to measure concentrations below 1% (Darvell *et al.*, 2012). Among nonwoody IAPs in Figure 6.3, *S. mauritianum* had the lowest yield due to a lower C/N ratio (10.65) outside the recommended ratio of 20 to 30 (Singhal *et al.*, 2017). In contrast, *L. camara* has the highest yield due to a C/N ratio of 20.67 and a higher yield of volatile compounds, cellulose, and moisture content that contain higher sugar moieties that induce microbial growth and can be degraded into biomethane (Yadav *et al.*, 2017; Avinash and Mishra, 2023). A study conducted by Triolo *et al.* (2012) observed a higher methane yield of 332.7 CH_4 NL.kg^{-1} VS in herbaceous plants and less methane yield of 172. 0 CH_4 $NL.kg^{-1}$ VS in non-herbaceous plants such as woody cuttings. These results are coherent to the results obtained in this study



(a) Nonwoody IAPs



(b) Woody IAPs

Nonwoody IAPs	Trendline equation	R^2
Cellulose	y = 142.68ln(x) – 97.366	R^2 = 0.8968
L. camara	y = 44.653ln(x) + 13.554	R^2 = 0.9747
C. odorata	y = 58.347ln(x) + 12.477	R^2 = 0.9423
S. mauritinaum	y = 50.801ln(x) – 41.964	R^2 = 0.8888

Woody IAPs	Trendline equation	R^2
Cellulose	y = 103.62ln(x) + 124.6	R^2 = 0.7452
A. mearnsii	y = 54.292ln(x) – 21.594	R^2 = 0.997
E. grandis	y = 45.748ln(x) – 15.545	R^2 = 0.9985
P. patula	y = 37.327ln(x) – 7.5717	R^2 = 0.9991

Figure 6.4 Cumulative methane yield of nonwoody and woody IAPs.

Figure 6.4 illustrates the total methane production over time. The cumulative methane potential started immediately after filling and peaked early on nonwoody IAPs, particularly on day 5 (100 Nml $CH_4.\,g^{-1}$ VS) while the methane potential of woody IAPs gradually peaks with day 5 (60 Nml $CH_4.\,g^{-1}$ VS). The cumulative methane potential of nonwoody IAPs is not steadily continuous, with fluctuations, especially in *S. mauritianum*, decreasing around day 15. The highest cumulative methane potential and early peak in nonwoody IAPs indicate their greater biodegradability (35.81%), as shown in Table 6.3. In contrast, woody IAPs exhibited a gradual methane peak due to lower biodegradability (26.41%), attributed to high lignin that acts as a barrier for microbial access to cellulose and hemicellulose, ultimately lowering methane yield. The fluctuation in *S. mauritianum* is due to the presence of alkaloids such as solasodine that alter the plant cell, making other parts of cellulose crystalline (Mokgehle *et al.*, 2022). Overall, the biodegradability of both woody and nonwoody IAPs remained below 50% due to due to their lignified structure and high crystallinity, particularly in cellulose, hemicellulose, and lignin, which hinder microbial degradation.

The monocrystalline cellulose was used to assess the effectiveness of micro-organisms and the efficiency of the BMP test. The observed methane yield was 355.58 Nml $CH_4.\,g^{-1}$ VS aligning with the expected range of 340 to 395 Nml $CH_4.\,g^{-1}$ VS. With a biodegradability of 89%, the analysis confirmed the presence of sufficient micro-organisms and higher degradation efficiency, validating the methane potential. Overall, nonwoody IAPs exhibited a comparatively higher methane yield, aligning with the MDCM model presented in Chapter 4. However, both woody and nonwoody IAPs produced lower methane concentrations, which can be attributed to lower C/N ratios, insufficient moisture content, and high lignin levels that inhibit microbial degradation. A notable limitation in this study was the potential overdrying of biomass, likely resulting from the absence of standardised preparation protocols, which may have affected microbial activity and methane output.

To address these limitations, future research should focus on developing and validating standardised biomass handling and preparation procedures. Additionally, investigating various pre-treatment techniques such as alkaline, acid, and enzymatic processes may enhance methane yields by lowering cellulose crystallinity and increasing substrate digestibility. Implementing such strategies could improve the overall efficiency and viability of IAPs as substrates for biogas production.

Overall, nonwoody IAPs demonstrated higher methane yield, supporting the MDCM in Chapter 4. However, both woody and nonwoody IAPs had lower methane concentration due to lower C/N ratio and water content, lignin content. One of the limitations could be overdrying the biomass due to no standard prescribed methods. More research on methods. Pre-treatment strategies, such as alkaline, acid, or enzymatic treatments, should be explored to further break down lignin and reduce cellulose crystallinity, improving methane production.

6.3.2 Biogas characterisation

The theoretical methane of woody and nonwoody IAPs is compared to South African biomass substrate in a study conducted by Sawyerr *et al.* (2019a). The results are illustrated in Table 6.4.

Table 6.4 The theoretical methane of woody and nonwoody IAPs compared to other biogas substrates

South African biomass substrate	Theoretical methane potential (Nml $CH_4.g^{-1}$ VS)
Cassava Peel	496
Cattle Manure	575
Cassava Tuber	499
Fruit and Vegetable waste	533
Woody IAPs	453
Nonwoody IAPs	465

The results in Table 6.4 show that both woody and nonwoody IAPs exhibited the lowest theoretical methane potential compared to other biomass substrates. This is primarily due to their lower moisture content (1.86% to 4.23%) compared to other biomass sources, which range between 58.40% and 83.50% (Sawyerr *et al.*, 2019a). Higher moisture levels enhance nutrient solute transport, facilitate microbial mobility, and dilute system inhibitors, thereby improving anaerobic digestion efficiency (Pantini *et al.*, 2015). Although the C/N ratio of other biomass feedstock is significantly higher (18.50 to 75.12) compared to IAPs (10.65 to 20.71),

excessively high values can lead to rapid nitrogen depletion, ultimately reducing gas production (Sawyerr *et al.*, 2019a).

While cassava peels, cassava tubers, cattle manure, and fruit and vegetable waste generate higher methane yields, they present several drawbacks. Their elevated moisture levels increase handling and transportation costs due to their weight and the need for additional drying processes (Melane *et al.*, 2017). Cassava-based feedstocks, despite their high methane potential, contain cyanogenic glycosides that require pre-treatment to prevent inhibition of microbial activity (Cuzin and Labat, 1992). Similarly, cattle manure, while abundant, has relatively low energy content per unit mass and often requires co-digestion with other substrates to enhance methane production efficiency (Moreroa and Motshekga, 2024).

In contrast, IAPs, despite their lower theoretical methane yield, have advantages in terms of availability and cost-effectiveness, as they are widely regarded as waste material that requires removal to mitigate their ecological impact. However, their high lignin content limits biodegradability, necessitating pre-treatment methods to enhance microbial access to fermentable components. Overall, while conventional biomass substrates may yield higher methane volumes, their limitations in cost, handling, and sustainability highlight the potential of IAPs as an alternative substrate for biogas production, especially with appropriate pre-treatment strategies.

6.3.3 Conclusion

The objective of this section was to assess both the yield of biogas produced from woody and nonwoody IAPs as a renewable energy source. Biogas was generated through a biochemical methane potential test instead of constructing a full biogas digester to ensure a cost-effective and accurate method of evaluating the methane potential of IAPs without operational complexity and financial demands. Results demonstrated an average methane yield of 162.62 Nml/g VS for nonwoody IAPs and 117.69 Nml/g VS for woody IAPs, indicating significant comparative analysis within the species. Additionally, the incorporation of theoretical methane potential (TMP) analyses provided both empirical validation and predictive insights, thereby enhancing the reliability of substrate evaluation.

The study also determined biodegradability, with woody IAPs achieving an average of 35.81%, compared to 26.41% in nonwoody IAPs. This information offers valuable understanding of substrate digestibility and conversion efficiency, creating a scientific basis to recommend pretreatment strategies such as catalyst addition to lignin. By comparing IAPs with conventional substrates such as cassava peels, cattle manure, cassava tubers, and fruit and vegetable waste, the study positions IAPs as a viable, sustainable, and cost-effective alternative feedstock. Overall, this addresses environmental challenges through the valorisation of problematic invasive species, adding a dual benefit of energy production and ecological management. Future research should therefore focus on scaling up promising IAPs substrates, exploring pretreatment methods, and assessing long-term process stability to ensure successful practical implementation.

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7. CONCLUSION, RECOMMENDATIONS, AND FUTURE RESEARCH OPPORTUNITIES

This chapter will draw the conclusion of this research, make recommendations, and identify future research opportunities.

7.1 Conclusion

This research evaluated the potential of invasive alien plant species (IAPs) as renewable energy sources for biogas and bio-oil production. The literature review highlighted the diverse applications of these biofuels, including bioheat, biopower, and transport fuel. However, bioenergy development in South Africa faces challenges such as food security concerns, land conversion, and limited expertise in optimising conversion processes. The review also underscored the widespread infestation of IAPs, which negatively impacts ecosystems and economies, with no effective control measures. The review categorised the species into three woody IAPs (*Acacia mearnsii, Eucalyptus grandis,* and *Pinus patula*) and three nonwoody IAPs (*Lantana camara*, *Chromolaena odorata*, and *Solanum mauritianum*), suggesting them as an energy substrate for biofuel production. Additionally, emphasised the importance of characterisation, as their properties vary based on growth conditions, affecting conversion efficiency and costs. While characterisation methods such as proximate, elemental, structural, and thermal analysis provide essential data, they do not directly determine the most suitable feedstocks for specific biofuels. The literature review assessed the multi-criteria decision-making (MCDM) techniques, given usage for optimal materials selection in engineering and energy. Overall, the review revealed a gap in South Africa's bioenergy sector, emphasising the need to assess IAPs as alternative feedstocks, improve characterisation for targeted biofuel production, and enhance conversion processes for higher efficiency and quality.

Chapter 3 focused on assessing the physical and chemical characteristics of woody and nonwoody IAPs for bio-oil and biogas production. This included conducting proximate, elemental, structural, and thermal analysis. The results revealed that structural composition influences yield and efficiency of degradation, with woody IAPs, especially *Pinus patula,* having significantly higher structural composition ($p < 0.05$), improving biogas and bio-oil yield. Elemental analysis influences the quality of biofuels, with higher carbon and hydrogen

contents in both IAPs, indicating enhanced HHV and combustion, while lower nitrogen and sulphur levels reduced emissions. The highest HHV was observed from elemental analysis estimation equations, with woody at 19.5 MJ/kg, and nonwoody IAPs was 19.1 MJ/kg, sharing similarities with peat coal (17.4 to 22.4 MJ/kg), which is low-energy rank coal but can still be utilised for heat and electricity generation. This section addressed the research question regarding the influence of the physical and chemical properties of invasive plants on the yield and quality of bio-oil and biogas. Additionally, it enabled the strategic identification of high-performing biomass feedstocks, thereby reducing the need for extensive post-processing and enhancing the cost-efficiency of bio-oil and biogas production.

Chapter 4 aimed to determine which of the woody and nonwoody IAPs are suitable for biogas and bio-oil production based on their physicochemical features from Chapter 3. Multi-criteria decision-making (MCDM) techniques such as the analytic hierarchical process (AHP) and the technique for order of preference by similarity to ideal solution (TOPSIS) were employed. The results indicated that criteria such as hydrogen, carbon, and volatile content are ideal for bio-oil production, while criteria such as Carbon/Nitrogen ratio, volatile content, and moisture content were suitable for biogas production. The acceptable consistency ratio of 0.079 and 0.081 illustrates the accuracy and uniformity of the pairwise comparison matrix, respectively. Woody invasive species were most suitable for bio-oil production with *E. grandis* ranking 1 due to the highest relative closeness of 0.774, while nonwoody IAPs were most suitable for biogas with *L. camara* ranking 1 due to the highest relative closeness of 0.874. The utilisation of AHP-TOPSIS models serves as a practical tool to simplify complex laboratory data and biomass characterisation results into clear, ranked recommendations for implementation in energy and engineering productions.

Chapter 5 aimed to evaluate the quantity and quality of bio-oil derived from IAPs to verify the results obtained from Chapter 4. The study employed a pyrolysis process with analytical methods such as TGA, FTIR, GCMS, and higher heating values. The results demonstrated a bio-oil yield ranging from 18.77 to 20.45 %, and 22.93 to 27.55 % for nonwoody and woody IAPs, respectively. The yield of bio-oil was lower compared to what was achieved by other researchers in literature studies. This was attributed to the orientation of the fixed bed reactor design, altering operating conditions for maximum yield of bio-oil. Furthermore, a quantitative analysis using GC-MS indicated the highest concentration of phenols, ketones, and acids that induce oxidation reactions that form oxygen compounds affecting the higher heating value,

stability and reactivity, pH, viscosity, and corrosiveness. The estimated HHV of bio-oil based on literature sources was 24.28 MJ/kg and 22.16 MJ/kg, respectively, which was considerably lower than fossil fuels, between 42.9 to 47 MJ/kg. This section responded to the research question by highlighting that woody and nonwoody IAPs, in their raw form, may not be ideal substrates for efficient bio-oil production. However, it recommends the use of advanced reactor systems such as auger or fluidised bed reactors to enhance conversion efficiency. Additionally, the adoption of bio-oil upgrading techniques such as catalytic cracking, hydrodeoxygenation, or emulsification is suggested to improve the fuel quality.

Chapter 6 aimed to evaluate the quantity and quality of biogas derived from IAPs to verify the selection method from Chapter 4. The study employed the biochemical methane potential test. The results on methane potential showed an average yield of 162.62 Nml/ g VS in nonwoody IAPs and 117.69 Nml/ g VS in woody IAPs. These results illustrated a lower yield in both woody and nonwoody IAPs, especially when compared with the theoretical methane potential ranging between 407.02 to 498.08 Nml/ g VS. The lower methane concentrations are primarily due to insufficient pre-treatment methods, such as the lack of enzymatic or acid-based processes needed to break down lignified tissues. Therefore, future research should focus on optimising and applying these pre-treatment strategies to enhance methane production.

Overall, the study demonstrated that both woody and nonwoody IAPs possess characteristics with potential for energy generation. However, their suitability for efficient biogas and bio-oil production remains limited. These limitations primarily arise from factors such as the lack of effective pre-treatment methods, efficient reactor design, and inadequate operational conditions. As a result, targeted improvements in processing technologies and system configurations are necessary to fully harness the energy potential of IAPs. The following section provides recommendations aimed at addressing these gaps and enhancing the feasibility of utilising IAPs as sustainable bioenergy feedstocks.

7.2 Recommendations

Based on the findings of this study, the following recommendations can be made:

1. For detecting lower element concentrations such as nitrogen and sulphur, an elemental analyser with no limit detection should be incorporated.

2. Utilising equations for higher heating value is accurate, but for more reliability, an adiabatic bomb calorimeter should be incorporated.
3. An auger or another pyrolysis reactor with efficient heat transfer instead of a fixed bed reactor should be adopted for optimal bio-oil yield.
4. The bio-oil concentration was lower to determine physical composition, such as water level, viscosity, and pH; more physical analysis should be adopted.
5. Pre-treatment methods acid, alkaline, and enzymatic, are recommended to break down lignified tissues for ease of degradation.

7.3 Future Research Opportunities

The following research opportunities can be explored in the future:

1. Assessing how environmental conditions influence the physicochemical characteristics of biomass for energy purposes.
2. Research on standardising testing methods for proximate, elemental and structural analysis.
3. Studies on evaluating the supply chain of biomass energy to assess economic feasibility on a large scale.
4. Designing a pyrolysis reactor and anaerobic digester for IAPs.
5. Incorporating artificial intelligence in the characterisation of IAPs.
6. Optimising operational conditions.
7. Exploring pre-treatment and upgrading techniques.
8. Instead of biofuel production, utilising IAPs for cofiring.

8. APPENDICES

8.1 Appendix A: Multi-criteria decision making to evaluate and prioritise IAPs suitable for bio-oil and biogas production

- Summary of physicochemical properties of IAPs to be utilised for the selection process

Table 8.1 IAPs physicochemical properties to prioritise species for maximum bio-oil yield

IAPs	Cellulose	Hemicellulose	Lignin	Carbon	Hydrogen	Oxygen	Moisture Content	Volatile Content	Ash Content	Fixed Carbon
Non-woody IAPs										
L. *camara*	26.73	19.25	8.74	48.10	6.10	43.51	4.23	83.96	8.56	3.25
C. odorata	24.05	16.19	9.92	46.11	6.18	44.85	3.28	85.34	8.08	3.30
S. *mauritianum*	20.41	12.15	7.42	48. 51	6.29	40.65	3.57	82.89	9.66	3.88
Woody IAPs										
A. mearnsii	43.69	23.6	22,86	44.58	5.63	48.79	3.92	87.20	0.88	8.0
E. grandis	53.49	20.27	15.93	50.83	6.22	42.97	1.86	87.90	3.82	6.42
P. patula	45.28	23.92	29.67	50.52	6.11	43.36	2.86	86.8	1.88	8.46

Table 8.2 The physicochemical properties of IAPs to prioritise optimal biogas production

IAPs	Cellulose	Hemicellulose	Lignin	C/N	Hydrogen	Oxygen	Moisture Content	Total solids	Volatile Content	Ash Content
Non-woody IAPs										
L. *camara*	26.73	19.25	8.74	20.71	6.10	43.51	4.23	95.77	83.96	8.56
C. odorata	24.05	16.19	9.92	16.13	6.18	44.85	3.28	96.72	85.34	8.08
S. *mauritianum*	20.41	12.15	7.42	10.65	6.29	40.65	3.57	96.43	82.89	9.66
Woody IAPs										
A. mearnsii	43.69	23.6	22.86	ND	5.63	48.79	3.92	96.08	87.20	0.88
E. grandis	53.49	20.27	15.93	ND	6.22	42.97	1.86	98.14	87.90	3.82
P. patula	45.28	23.92	29.67	ND	6.11	43.36	2.86	97.14	86.8	1.88

Table 8.3 Normalised pairwise comparison matrix from AHP for bio-oil

	Cellulose	Hemicellulose	Lignin	Moisture content	Volatile content	Ash content	Fixed	Carbon	Hydrogen	Oxygen	Sum of Weightage	Weightage	Ranks
Cellulose	0,107	0,143	0,132	0,165	0,066	0,157	0,129	0,125	0,074	0,143	1,241	0,124	4,000
Hemicellulose	0,053	0,072	0,132	0,147	0,044	0,157	0,103	0,084	0,055	0,125	0,972	0,097	5,000
Lignin	0,036	0,024	0,044	0,092	0,027	0,105	0,129	0,050	0,044	0,107	0,657	0,066	6,000

Moisture content	0,012	0,009	0,009	0,018	0,017	0,017	0,006	0,028	0,025	0,036	0,177	0,018	8,000
Volatile content	0,213	0,215	0,220	0,147	0,133	0,157	0,206	0,251	0,055	0,143	1,740	0,174	3,000
Ash content	0,012	0,008	0,007	0,018	0,015	0,017	0,006	0,028	0,025	0,054	0,190	0,019	8,000
Fixed carbon	0,021	0,018	0,009	0,073	0,017	0,070	0,026	0,031	0,032	0,054	0,350	0,035	7,000
Carbon	0,213	0,215	0,220	0,165	0,133	0,157	0,206	0,251	0,444	0,161	2,164	0,216	2,000
Hydrogen	0,320	0,286	0,220	0,165	0,532	0,157	0,180	0,125	0,222	0,161	2,368	0,237	10

Table 8.4 Normalised pairwise comparison matrix in AHP for biogas

	Cellulose	Hemicellulose	Lignin	C/N	Oxygen	Total solids	Moisture Content	Volatile Content	Ash Content	Fixed carbon	Sum	Weightage	Rank
Cellulose	0,070	0,101	0,089	0,106	0,137	0,044	0,038	0,054	0,136	0,126	0,901	0,090	5,000
Hemicellulose	0,035	0,050	0,089	0,080	0,120	0,029	0,029	0,043	0,136	0,101	0,712	0,071	6,000
Lignin	0,023	0,017	0,030	0,040	0,103	0,017	0,019	0,031	0,106	0,076	0,461	0,046	7,000
C/N	0,210	0,202	0,238	0,319	0,154	0,349	0,345	0,432	0,136	0,202	2,587	0,259	1,000
Oxygen	0,009	0,007	0,005	0,035	0,017	0,012	0,014	0,024	0,030	0,008	0,163	0,016	9,000

Total solids	0,140	0,151	0,149	0,080	0,120	0,087	0,058	0,072	0,121	0,151	1,129	0,113	4,000
Moisture Content	0,210	0,202	0,178	0,106	0,137	0,174	0,115	0,072	0,136	0,126	1,457	0,146	3,000
Volatile Content	0,280	0,252	0,208	0,159	0,154	0,262	0,345	0,216	0,136	0,176	2,190	0,219	2,000
Ash Content	0,008	0,006	0,004	0,035	0,009	0,011	0,013	0,024	0,015	0,008	0,133	0,013	10,000
Fixed Carbon	0,014	0,013	0,010	0,040	0,051	0,015	0,023	0,031	0,045	0,025	0,267	0,027	8,000

8.2 Appendix B: Evaluation of woody and nonwoody IAPs for bio-oil production

Table of Characteristic IR Absorptions

frequency, cm^{-1}	*bond*	*functional group*
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH_2X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Figure 8.1 Table of Characteristic IR Absorptions

Table 8.5 Correlation coefficient and p-value of proximate composition with bio-oil

Proximate composition	Moisture content			Volatile content			Fixed carbon			Ash content		
Non-woody IAPs												
Statistical analysis	r	R^2	p	r	R^2	p	r	R^2	p	r	R^2	p
	-0.91	0.86	< 0.001	0.41	0.17	< 0.001	-0.75	0.56	< 0.001	0.94	0.88	< 0.001
Regression equation	Bio-oil = 24.54 - 1.09 ×MC			Bio-oil = -11.78+0.36×VC			Bio-oil = 20.7 - 0.37 × FC			Bio-oil = 16.58 +0.49 ×AC		
Interpretation	Negative strong correlation, Negative slope with 1.09 unit decreases in bio-oil as MC increases, $p < 0.05$ statistically significant.			Positive weak correlation, Positive slope with 0.36 unit increases in bio-oil as VC increases, $p < 0.05$ statistically significant			Negative moderate correlation Negative slope with 0.37 unit decreases in bio-oil as FC increases, $p < 0.05$ statistically significant.			Positive strong correlation, positive slope with 0.49 increase in bio-oil as AC increases, $p < 0.05$ statistically significant		
Woody IAPs												
Statistical analysis	r	R^2	p	r	R^2	p	r	R^2	p	r	R^2	p
	-0.51	0.26	< 0.001	0.24	0.056	< 0.001	0.65	0.66	< 0.001	-0.38	0.15	< 0.001
Regression equation	Bio-oil = 26.2 – 0.51 ×MC			Bio-oil = 19.13 + 0.08×VC			Bio-oil = 11.01 + 0.95 × FC			Bio-oil = 26.49 – 0.2 ×AC		
Interpretation	Negative moderate correlation, Negative slope with 0.51 unit decrease in bio-			Positive weak correlation, Positive slope with 0.08 unit increases in bio-oil as VC			Positive moderate correlation			Negative weak correlation, positive slope with 0.2 decreases in bio-oil as		

	oil as MC increases, $p < 0.05$ statistically significant	increases, $p < 0.05$ statistically significant	Negative slope with 0.95 unit increases in bio-oil as FC increases, $p < 0.05$ statistically significant.	AC increases, $p < 0.05$ statistically significant