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Experimental Biodiesel Derivation from Peanut and Bambara Groundnut Shells Pyrolysis Oils

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***Abstract*— This study investigated the potential of generating biodiesel from Bambara groundnut shells and peanut hulls, two abundant agricultural waste products. The primary aim was to expand energy sources and create value from plant waste. A two-step process was implemented: rapid pyrolysis to transform the husks into bio-oil, followed by transesterification to yield biodiesel. The results demonstrated that five liters of bio-oil could be derived from 8.62 kg of Bambara groundnut shells or 8.2 kg of peanut hulls. The subsequent transesterification process achieved high biodiesel conversion rates, reaching 95% and 96% for Bambara groundnut shells and peanut hulls, respectively. Although the biodiesels displayed comparable properties, a slight variation in calorific value was noted, with peanut hull-derived biodiesel showing a marginally higher heat content. These findings underscore the viability of producing biodiesel from these agricultural residues, presenting a promising pathway for waste valorization and energy diversification.**

***Keywords*—Bambara groundnut shells, Peanut hulls, Fast pyrolysis, Transesterification, Biodiesel, Bio-oil**

I. INTRODUCTION

The global energy transition, driven by the depletion of fossil resources and growing environmental concerns, has sparked increased interest in biofuels. Among these, biodiesel, produced from extractable lipids or "renewable fats", stands out as a promising alternative to petroleum-based fuels. By reducing dependence on fossil fuels and decreasing greenhouse gas emissions, biodiesel plays a crucial role in combating climate change and promoting energy sustainability ([16], [17], [21]).

This study focuses on the energy valorization of two often overlooked agricultural by-products: Bambara Groundnut Shells (BGS) and Peanut Hulls (PH). These lignocellulosic residues contain extractable lipids that can serve as potential feedstock for biodiesel production. The primary objective of this research is to assess the feasibility of converting the lipids derived from these shells into biodiesel. Preliminary literature reviews have shown that the lipids present in these types of materials can be converted into biodiesel ([5], [8], [13], [16], [18], [21], [22], [26]).

According to Mohammed, I. Y. (2016), previous studies in [10] and [13] have shown that BGS constitute a significant proportion of the total pod weight, ranging between 28.6% and 34.2%, and reaching up to 41% in some cases. This abundance, coupled with their lignocellulosic composition, makes them a potential feedstock for biofuel production [12].

PH, a byproduct of peanut production, constitute a significant portion of the total pod weight, ranging from 21% to 29% ([1], [24]). These shells are primarily composed of fiber (over 60%) and lignin (6-45%), with smaller amounts of protein (7%) and oil (2%) [6]. Given their abundance and composition, PH have emerged as a promising feedstock for various applications, including biofuel production. The high cellulose and lignin content makes them suitable for conversion into biofuels and other value-added products.

To achieve this objective, the following steps will be implemented:

- Lipid extraction: A solvent extraction method will be used to extract the renewable fats from the BGS and PH ([8], [14]).

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- Transesterification: The extracted renewable fats will be converted into biodiesel through a transesterification process, which involves reacting triglycerides with an alcohol (methanol) in the presence of a catalyst.
- Biodiesel characterization: The obtained biodiesel will be analyzed to verify its compliance with current standards and to evaluate its physicochemical properties (density, viscosity, higher heating value) [9].

This study will contribute to the assessment of the potential of BGS and PH as sources of renewable fats for biodiesel production, thus opening up new perspectives for the sustainable valorization of agricultural waste.

I. MATERIALS AND METHODS

A. *Substrates : Bambara Groundnut Shells (BGS) and Peanut hulls (PH)*

The bibliographic study informs us about the characteristics of GBS (Groundnut Bambara Shells) and PH (Peanut Hulls).

1. GBS

The hulls used in this study were sourced from the Bambara groundnut plant (Vigna subterranea), a legume belonging to the Fabaceae family. The hull, the hard outer part of the pod, serves to protect the seeds from external aggressions and environmental stresses throughout maturation.

The chemical composition of BGS was analyzed and found to be:

- 42.4% cellulose ;
- 27.8% hemicellulose ;
- 13.0% lignin ;
- 16.8% extractives ([7], [14]).

This analysis confirms that BGS belongs to the lignocellulosic biomass group. Further characterization revealed the following properties [14].

- Proximate analysis :
  - Volatile matter content : 69.1% ;
  - Moisture content : 4.4% ;
- Thermal properties :
  - Thermal stability : 178.5°C ;
  - Maximum degradation temperature : 305.7°C ;
  - Activation energy: 49.4 kJ/mol.

Fig. 1 Bambara groundnut

Fig.2 Peanuts in their shells

2. PH

Peanut plant (Arachis hypogaea), a legume native to South America but widely cultivated in tropical and subtropical regions, were used as substrates in this study. Specifically, we selected hulls, harvested in the Tsiroanomandidy region. These hulls, from conventional crops, were chosen for their local abundance. The hull, the lignified part of the pod, plays a crucial role in protecting the subterranean seeds from external aggressions and environmental stresses throughout their development.

After the plants are uprooted at maturity, the pods are dried, then shelled and dried again. The moisture content of the pods thus decreases from 30-40% at harvest to 6-8% before storage [15]. The density of the hull was determined to be in the range of 0.27 to 0.30 g/cm³. The chemical composition of the peanut hull was found to be:

- 48.2% cellulose and hemicellulose,
- 48.67% lignin,
- 3.13% extractives [25].

Peanut hulls also have the following properties:

- High volatile matter content : 70-85 ([3], [21]) ;
- Low moisture content : 5-10% ([3], [21]) ;
- Thermal stability :
  - Maximum degradation temperature: around 300°C [21];
  - Activation energy: 60-80 kJ/mol [3].

B. Bi-Oil Extraction

1. Pretreatments

a. Drying

Bambara groundnut husks were subjected to air drying in the sun to reduce their moisture content and optimize oil yield during extraction. Peanut shells, being already dry, did not require this preliminary step.

To assess the drying efficiency, we weighed the husks before and after the 4-day sun exposure.

The initial and final weights of the raw materials were measured.

For Bambara Groundnut Shells (BGS), the weight decreased by 71.4%, from an initial weight of 3.5 kg to a final weight of 1.0 kg after processing.

For Peanut Hulls (PH), the weight decreased by 33.3%, from an initial weight of 1.5 kg to a final weight of 1.0 kg after drying.

b. Grinding

Manual comminution was performed using a mortar and pestle to reduce the particle size. This operation aims to increase the specific surface area of the materials, thus improving mass and heat transfer during subsequent steps.

The particle size reduction was significant for both materials. BGS were reduced from an initial size range of 10-20 mm to a final average size of 1.5 mm. PH underwent a more substantial reduction, from an initial size range of 20-30 mm to a final average size of 1.8 mm.

C. Rapid Pyrolysis Process

Hulls, as lignocellulosic biomass, are subjected to a pyrolysis process to produce a crude oil rich in aromatic compounds.

Rapid pyrolysis is a thermal conversion process that transforms biomass into valuable products. This process occurs in several key stages within a specialized reactor.

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1. Pyrolysis Reactor

A rapid pyrolysis reactor is designed to optimize the conversion of biomass. It typically consists of several distinct zones :

- Feed zone: Biomass, such as fruit shells, is introduced intermittently into the upper part of the reactor. This method allows for better control of the flow rate and reaction temperature.
- Heating zone: A wood-fired burner heats the reactor. The generated heat initiates and sustains the pyrolysis reaction.
- Reaction zone: This is the core of the reactor where pyrolysis takes place. Under high temperatures (above 500°C) and in the absence of oxygen, the biomass decomposes into three main fractions:
    - Pyrolysis oil: A liquid rich in organic compounds.
    - Biochar: A carbonized solid.
    - Pyrolysis gas: A mixture of combustible gases (hydrogen, methane, etc.).
- Cooling zone: Located downstream of the reaction zone, this zone cools the gases produced by pyrolysis. A water circulation cooling system is typically used to condense oil vapors and recover pyrolysis oil.
- Recovery zone: The condensed pyrolysis oil is collected in this zone.

Fig. 3 Pyrolysis reactor

2. Stages of Rapid Pyrolysis

a. Reactor Preheating

The reactor is preheated to approximately 300°C before the introduction of biomass. This initial heating significantly accelerates the pyrolysis process once the biomass is added.

b. Biomass Introduction and Inert Atmosphere

Biomass is then introduced into the preheated reactor. To prevent combustion, the reactor atmosphere is purged and replaced with an inert gas, such as nitrogen or argon.

c. Pyrolysis

Under the influence of heat and in an oxygen-free environment, the biomass undergoes pyrolysis, decomposing into biochar, pyrolysis oil, and pyrolysis gas.

d. Cooling and Condensation

The hot gases produced during pyrolysis are cooled in a condenser. This cooling process causes the oil vapors to condense, forming liquid pyrolysis oil.

D. Biodiesel Production

1. Purification of pyrolysis bi-oil

Prior to transesterification, crude pyrolysis oil undergoes a purification process. First, the oil is allowed to settle, allowing solid particles to sediment. This step removes insoluble impurities denser than the oil. Next, free fatty acids in the oil are neutralized by adding a sodium hydroxide solution, producing water-soluble soaps. The mixture is then allowed to settle to separate the aqueous and organic phases. Finally, the organic phase is finally filtered through a fine-pore sieve to remove the last solid particles and obtain purified pyrolysis oil.

2. Transesterification

a. Reactants

Transesterification is a chemical process that transforms the triglycerides found in oil into methyl esters, better known as biodiesel, and glycerol. To achieve this transformation, purified pyrolysis oil is used. Methanol serves as the alcohol reactant, while sodium hydroxide (NaOH) acts as a catalyst to increase the reaction rate and promote the formation of methyl esters.

b. Biodiesel manufacturing process

The transesterification process involves mixing oil, methanol, and a catalyst in a reactor. The mixture is then heated to approximately 60°C to accelerate the chemical reaction. Continuous stirring ensures proper mixing of the reactants.

c. Separation

Once the reaction is complete, after approximately 30 minutes, the reaction mixture is transferred to a separatory funnel. Upon standing, the two liquid phases, differing in density, separate due to gravity. The less dense biodiesel forms the top layer, while the denser glycerol and excess methanol form the bottom layer.

3. Biodiesel cleaning

The biodiesel obtained is subsequently washed with distilled water to eliminate residual glycerol and catalyst. A final drying process may be required to ensure the biodiesel meets quality standards. To enhance the energy efficiency of the transesterification process, various parameters can be modified.

II. RESULTS AND DISCUSSION

A. Products of Fast Pyrolysis

Fast pyrolysis experiments were conducted on 1 kg samples of both BGS and PH The product distribution was analyzed for three main components: bio-oil, biochar, and gas. The results are presented in Table I.

Table I.

	Bio-oil (L)	Biochar (kg)	Gas (L)*
BGS (1 kg)	0.58	0.31	120
PH (1 kg)	0.61	0.29	100

*Gas volume measured at standard temperature and pressure conditions

When considering potential scale-up applications, our experimental yields can be translated into practical production scenarios. A comparison of feedstock requirements for both materials reveals interesting insights. To achieve a target production of 5 liters of bio-oil, BGS would require 8.62 kg of raw material (based on its yield ratio of 0.58 L/kg), while PH would need 8.20 kg (with its yield ratio of 0.61 L/kg). This slight difference in conversion efficiency (approximately 5%) favoring PH could become significant in larger-scale operations, potentially influencing feedstock selection when both materials are available.

B. Characteristics of Pyrolysis Bi-Oils

1. Hydrogen potential (pH)

Both pyrolysis bi-oils exhibited a pH of 3 and a reddish-brown hue, with similar viscosities due to their high water content. Their physicochemical properties are compared to heavy fuel oil in Table II.

Table II. Physicochemical Properties of Pyrolysis Oil

Property	BGS Pyrolysis Bi-Oil	PH Pyrolysis Bi-Oil	Heavy Fuel Oil
Water Content (%)	22	18	10
pH	3	3	-
Density (g/cm³)	1.2	1.3	0.94
Higher Heating Value (MJ/kg)	17	18	~40
Viscosity (cSt)	23	26	1500

The physicochemical properties of pyrolysis oils derived from BGS and PH were analyzed and compared to conventional heavy fuel oil. This comparison reveals both promising features and certain limitations:

2. Water Content and Acidity:

- The BGS and PH pyrolysis oil shows a relatively high water content (18-22%), significantly higher than heavy fuel oil (10%). This higher moisture content could affect combustion efficiency and stability during storage.
- Both BGS and PH pyrolysis oils exhibit acidic properties (pH= 3), which could raise concerns about corrosion in storage and handling equipment.

3. Density and Viscosity :

- The pyrolysis oils from both feedstocks show higher densities (BGS: 1.2 g/cm³, PH: 1.3 g/cm³) compared to heavy fuel oil (0.94 g/cm³). This could affect fuel handling and atomization characteristics.
- Interestingly, both bio-oils demonstrate significantly lower viscosities (BGS: 23 cSt, PH: 26 cSt) compared to heavy fuel oil (1500 cSt). This lower viscosity could be advantageous for pumping and atomization processes, potentially requiring less energy for handling and combustion.

4. Energy Content :

- The Higher Heating Values (HHV) of both pyrolysis oils (BGS: 17 MJ/kg, PH: 18 MJ/kg) are notably lower than heavy fuel oil (~40 MJ/kg). This represents a significant limitation, as approximately twice the volume would be needed to achieve the same energy output.
- The slightly higher HHV of PH pyrolysis oil suggests marginally better energy efficiency compared to BGS oil.

5. Implications and Recommandations :

   a. The lower viscosity could be advantageous for handling and processing, potentially reducing energy requirements for pumping and atomization.

   b. The high water content and acidity necessitate careful material selection for storage and handling equipment to prevent corrosion.

   c. The lower energy content suggests these bio-oils might be better suited for:

- Blending with conventional fuels rather than direct replacement
- Applications where lower energy density is acceptable
- Scenarios where environmental benefits outweigh energy density considerations

6. Future development efforts should focus on:
   - Reducing water content through improved processing techniques
   - Investigating methods to increase energy density
   - Developing suitable storage and handling solutions to address the acidity issue
   - Exploring potential applications that can capitalize on the lower viscosity while accommodating the lower energy content

C. *Products of Transesterification*

1. Diesel Yield

Transesterification of bio-oils produced by rapid pyrolysis of BGS and PH resulted in diesel yields of 95% and 96%, respectively. This indicates the potential for using these shells as a feedstock for biofuel production.

2. Comparative Analysis of Biodiesel and Diesel Fuel Properties and Performance Characteristics

This table presents a comparative analysis of biodiesel and diesel fuel, highlighting their key properties and performance characteristics.

Table III: Comparison of Biodiesel and Diesel

	Higher Heating Value (HHV)(MJ/kg)	Energy Density (kg/dm³)	References
BGS Biodiesel	38	0.91	This study
PH Biodiesel	39	0.93	This study
Diesel	43-44	0.83	[4]

To the best of our knowledge, transesterification of Bambara groundnut and peanut shell pyrolysis oil has not been reported in the literature.

A comparative analysis of the energy properties between biodiesels produced from BGS and PH versus conventional diesel reveals interesting insights:

a. Higher Heating Value (HHV)

The HHV analysis shows that both biodiesels demonstrate promising energy content:

- They achieve approximately 88-90% of conventional diesel's heating value;
- PH biodiesel shows a slightly higher energy content (39 MJ/kg) compared to BGS biodiesel (38 MJ/kg);
- This relatively small difference in energy content (approximately 11-13% lower than diesel) suggests both biodiesels could be viable fuel alternatives.

b. Energy Density:

Interestingly, both biodiesels exhibit higher energy densities than conventional diesel:

- BGS biodiesel is 9.6% denser than conventional diesel;

- PH biodiesel is 12% denser than conventional diesel;
- This higher density could potentially compensate for the slightly lower heating values in terms of energy content per volume.

c. Practical Implications:

- Fuel Tank Capacity and Range:
  - The higher energy density might partially offset the lower heating values;
  - Vehicles might achieve comparable ranges despite the lower HHV.
- Engine Performance Considerations:
  - The similar properties between both biodiesels suggest they could be interchangeable in most applications;
  - The slightly higher performance characteristics of PH biodiesel might make it marginally preferable in high-performance applications.
- Economic and Environmental Perspectives:
  - Both biodiesels represent viable sustainable alternatives to conventional diesel;
  - The minimal performance differences between them suggest feedstock availability and production costs might be more relevant factors in choosing between them.

d. Recommendations

Both biodiesels could be suitable for:

- Direct use in diesel engines with minimal modifications;
- Blending with conventional diesel to optimize performance characteristics.

Future research could focus on:

- Long-term engine performance studies;
- Cold-weather performance characteristics;
- Economic analysis of production scaling;
- Environmental impact assessment of the complete production cycle.

III. CONCLUSION

The valorization of pyrolysis oils derived from the thermal conversion of residual biomass, such as BGS and PH, presents a promising avenue for the production of sustainable biofuels. These oils, rich in complex organic compounds, offer significant potential to reduce our reliance on fossil fuels and mitigate greenhouse gas emissions.

However, transforming these crude oils into biodiesel poses several challenges. Their heterogeneous composition, characterized by a wide variety of molecules, necessitates tailored purification and conversion processes. The traditional transesterification reactions used to produce biodiesel from vegetable oils must be optimized to accommodate the unique characteristics of pyrolysis oils. Catalyst selection, reaction conditions, and separation processes are critical parameters that must be carefully controlled to obtain high-quality biodiesel that meets industry standards.

Current research is focused on developing novel technologies for processing pyrolysis oils, such as hydroprocessing, heterogeneous catalysis, and combined processes. These approaches aim to improve oil stability, reduce the content of undesirable compounds, and promote the formation of methyl esters. Furthermore, the investigation of new, more efficient, and selective catalysts is a promising research area.

Although significant progress has been made, the production of biodiesel from pyrolysis oils remains at a pre-industrial development stage. Larger-scale studies are needed to assess the technical and economic feasibility of these processes. Moreover, integrating these new value chains into the existing energy landscape requires a comprehensive consideration of environmental, economic, and social aspects.

Ultimately, the valorization of pyrolysis oils derived from bambara groundnut and peanut shells into biodiesel offers exciting prospects for the energy transition. However, the complexity of these oils and the technological challenges associated with their conversion require sustained research efforts to develop efficient and economically viable industrial processes. The outcomes of this research could contribute significantly to the sustainable valorization of residual biomass and the production of biofuels.

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