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Comparative Analysis and Characterisation of Amine-Local Solvent Blends for Natural Gas Sweetening

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ABSTRACT

This study compared and characterised hybrid amine-local solvent blends for sustainable natural gas sweetening. The study designed and evaluated an absorption process using blends of monoethanolamine (MEA) with solvents derived from agricultural waste Plantain Peel Ash Extract (PPAE) and Coconut Shell Ash Extract (CSAE). The comprehensive characterisationprovided fundamental insights into the viability of using agricultural waste for gas sweetening. Plantain peels' high volatile matter (74.3%) yields ash rich in active alkaline compounds during calcination, while coconut shells' higher fixed carbon (19.5%) produces more stable char with lower alkaline content. The ultimate analysis showed that coconut shells' higher carbon content (49.5%) aligns with its lignocellulosic nature, while plantain peels' higher oxygen content (47.5%) indicates more carbohydrate-rich material that decomposes to yield higher ash alkalinity.The electrolyte properties further confirm PPAE's superiority, with higher pH (12.1), conductivity (28.5 mS/cm), and ionic strength (0.42 mol/L), all contributing to better absorption performance while influencing corrosion behavior.

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INTRODUCTION

The main component of natural gas, methane (CH4), is usually 70-90% by volume and is the most fundamental alkane structure (Kohl, A. L., & Nielsen, R. B. (1997). A colourless and odourless chemical, methane (CH4) is sometimes called natural gas because of how effectively it burns with little byproducts.Its low ignition threshold gives it several names, such as marsh gas or methyl hydride. comparison to other non-renewable energy sources, such as coal, natural gas have long been championed as leading contenders in the shift towards renewable energy. This is primarily due to the fact that when natural gas is burned, it emits approximately half the amount of carbon dioxide (CO_2) as coal does. Furthermore, the combustion of natural gas results in significantly fewer pollutants, making it a more appealing option with a reduced environmental impact. However, raw natural gas extracted from geological reservoirs is rarely pure. It often contains significant quantities of acid gases, primarily hydrogen sulfide (H2S) and carbon dioxide (CO2), along with other sulfur compounds like mercaptans and carbonyl sulfide (Khan et al., 2017). The process of removing these impurities, known as gas sweetening, is an indispensable step in natural gas processing (Bae, H. K., Kim, S. Y., & Lee, B. 2011). The search for and acquisition of alternate solvents for natural gas sweetening is mostly driven by the recognised energy intensity of conventional alkanolamine techniques, particularly monoethanolamine (MEA). Extensive research, shown in techno-economic evaluations, has consistently revealed the significant regeneration energy need as the primary cost factor, hence creating a strong motivation for the development of solvents with lower energy needs (Gutierrez et al., 2017;Driessen 2018; Aissaoui et al., 2017). Concurrently, the field of green chemistry has explored the use of bio-based and waste-derived alkalines, such as wood ash leachates, for CO2 capture, demonstrating the critical viability of these substances (Verma & Dubey 2024; Sheldon 2024). Zhu et al. (2021) proposed a multiple gas feeds process to optimize temperature and concentration distribution in the absorber, strengthening mass transfer. Reduced energy consumption by 6.5% and exergy loss by 18.75%.Darani et al. (2021)Used Taguchi method and HYSYS simulation to optimize DEA-based CO_2 removal. Found amine concentration to be the most effective parameter. Noted deviations between simulation and plant data.

The theoretical foundation is based on the assumption that the electrolyte properties of agricultural waste ashes, namely plantain peel and coconut shell, may be systematically characterised and integrated into a hybrid solvent system. This technique seeks to use the inherent alkalinity from waste to modify the thermodynamics and kinetics of absorption in a conventional MEA system, so creating a novel pathway for energy reduction that aligns with circular economy concepts.

MATERIALS AND METHODS

Tel experimental phase involves the collection, preparation, and comprehensive chemical characterisation of the local solvents (Plantain Peel Ash Extract - PPAE and Coconut Shell Ash Extract - CSAE) to derive critical electrolyte properties for simulation.

Sample Collection and Preparation

a. Plantain Peels: Fresh plantain peels were sourced from local markets in Port Harcourt, Rivers State, Nigeria. The peels were thoroughly washed with deionized water to remove dirt and soluble impurities.
b. Coconut Shells: Mature coconut shells were collected from the same geographical region. They were broken into smaller pieces and cleaned to remove any coir and contaminants.

Preparation of Ash and Extract

The preparation followed a strict protocol of drying, ashing, extraction, and filtration to produce consistent PPAE and CSAE samples for analysis.

1. Drying: The cleaned plantain peels and coconut shells were sun-dried for 48 hours followed by oven-drying at 105°C for 24 hours to achieve a constant weight.
2. Ashing: The dried samples were placed in a muffle furnace (Model: Nabertherm LVT 15/12) and calcined. The controlled ashing procedure was as follows:
   a. Heating rate: 10°C/min
   b. Final temperature: 600°C
   c. Holding time: 4 hours
   This temperature was selected to ensure complete carbon burnout while minimizing the volatilisation of alkaline compounds.
3. Extraction: The resulting ash was ground into a fine powder. A solid-to-liquid ratio of 1:10 (w/v) was used for extraction by dissolving the ash in deionized water and stirring magnetically at 60°C for 2 hours.
4. Filtration: The mixture was vacuum filtered using Whatman No. 1 filter paper to obtain a clear, aqueous extract, designated as PPAE and CSAE, respectively (Figure 1). The extracts were stored in airtight containers for analysis.

Fig. 1: Extracts from plantain peels and coconut shells

Experimental Procedures for Solvent Characterization

This section outlined the methods used to characterize PPAE and CSAE to define their electrolyte properties.

Proximate and Ultimate Analysis

1. Proximate Analysis: The moisture, volatile matter, ash content, and fixed carbon of the raw biomass were determined according to ASTM standards (D3172-D3175).
2. Ultimate Analysis: The carbon, hydrogen, nitrogen, and sulphur content of the raw biomass were determined using an Elemental Analyzer (Model: Elementar Vario EL Cube) (Fig. 2).

Fig. 2: Elemental Analyzer (Model: Elementar Vario EL Cube)

Chemical Composition Analysis

a. X-Ray Fluorescence (XRF): The elemental composition (Na, K, Ca, Mg, Si, P, etc.) of the ash samples was determined using an Olympus Vanta L Series XRF Analyzer (Fig. 3).
b. Inductively Coupled Plasma Mass Spectrometry (ICP-MS): This technique was used to quantify the concentration of specific metal cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) in the aqueous extracts (PPAE, CSAE) with high precision.

Determination of Electrolyte Properties

1. Alkalinity and Hydroxide Content: The total alkalinity of the extracts was determined by potentiometric titration with 0.1M HCl using an automated titrator (Model: Metrohm 902 Titrando). The hydroxide (OH^-) concentration was estimated from the titration curve.
2. pH and Conductivity**:** The pH and electrical conductivity of the extracts were measured using a calibrated multi-parameter meter (Model: Hach HQ40d).

Fig.3: Olympus Vanta L Series XRF Analyzer

RESULTS AND DISCUSSIONS

Characterization of Raw Biomass and Solvent Extracts

Proximate and Ultimate Analysis of Raw Biomass

The analysis of the raw biomass materials (Table1) provided insight into their energy content and expected ash yield. The high volatile matter in plantain peel indicates a high reactivity, while the higher fixed carbon in coconut shell suggests it would yield a more stable, porous char during ashing.

Table 1: Proximate and Ultimate Analysis of Raw Biomass

Analysis	Parameter	Plantain Peel	Coconut Shell
Proximate (wt. %, dry basis)	Moisture	11.5	8.2
	Volatile Matter	74.3	70.1
	Fixed Carbon	11.0	19.5
	Ash Content	3.2	2.2
Ultimate (wt. %, dry basis)	Carbon	45.1	49.5
	Hydrogen	5.8	5.5
	Nitrogen	1.2	0.3
	Sulphur	0.4	0.1
	Oxygen (by difference)	47.5	44.6

Major Elemental Composition of Biomass Ash and Extracts

XRF analysis of the ashes (Table 2) confirmed they are rich in alkali and alkaline earth metals. PPAE showed a higher concentration of potassium (K) and calcium (Ca), while CSAE had a significantly higher silicon (Si) content, which is inert in the absorption process. ICP-MS analysis of the aqueous extracts quantified the soluble ions, with K^+ being the dominant cation in both extracts.

Table 2: Major Elemental Composition of Biomass Ash and Extracts

Component	Plantain Peel Ash (XRF, wt.%)	Coconut Shell Ash (XRF, wt.%)	PPAE (ICP-MS, mg/L)	CSAE (ICP-MS, mg/L)
K_2O / K^+	35.2	25.8	12,450	8,950
CaO / Ca^{2+}	15.5	8.3	4,120	2,250
MgO / Mg^{2+}	7.1	3.5	1,850	920
Na_2O / Na^+	2.1	1.8	890	750
SiO_2	18.3	35.1	-	-
P_2O_5	9.5	4.2	-	-
Others	12.3	21.3	-	-

Electrolyte Properties of the Aqueous Extracts

The electrolyte properties (Table 3) confirmed the strong alkaline nature of both extracts, with PPAE exhibiting higher values across all parameters due to its greater concentration of soluble alkaline compounds. The calculated ionic strength for PPAE was 35% higher than for CSAE, indicating a more significant electrolyte effect.

Table 3: Electrolyte Properties of PPAE and CSAE

Property	PPAE	CSAE	Test Method
pH	12.1	11.8	Potentiometric
Conductivity (mS/cm)	28.5	19.2	Conductometric
Total Alkalinity (M as $CaCO_3$)	1.8	1.4	Potentiometric Titration
Density at 25°C (kg/m^3)	1050	1030	Pycnometer
Viscosity at 25°C (cP)	1.25	1.15	Viscometer
Calculated Ionic Strength, I (mol/L)	0.42	0.31	Derived from ICP-MS

The comprehensive characterisation (Tables 1-3) provides fundamental insights into the viability of using agricultural waste for gas sweetening. Plantain peels' high volatile matter (74.3%) yields ash rich in active alkaline compounds during calcination, while coconut shells' higher fixed carbon (19.5%) produces more stable char with lower alkaline content. The ultimate analysis shows coconut shells' higher carbon content (49.5%) aligns with its lignocellulosic nature, while plantain peels' higher oxygen content (47.5%) indicates more carbohydrate-rich material that decomposes to yield higher ash alkalinity.

PPAE's significantly higher potassium content (35.2% K_2O vs 25.8% in CSAE) is crucial because potassium carbonate/bicarbonate systems enhance CO_2 absorption capacity through the bicarbonate formation pathway (Mandal & Bandyopadhyay, 2006). Conversely, CSAE's substantial silica content (35.1% SiO_2) represents inert material that dilutes active components and may cause operational issues including fouling and reduced mass transfer efficiency. The electrolyte properties further confirm PPAE's superiority, with higher pH (12.1), conductivity (28.5 mS/cm), and ionic strength (0.42 mol/L), all contributing to better absorption performance while influencing corrosion behavior (Kittel et al., 2009).

CONCLUSION

The characterisation studies revealed that PPAE possessed superior alkaline properties with higher potassium concentration (12,450 mg/L) (35.2% K_2O) , pH (12.1), and ionic strength (0.42 mol/L) compared to CSAE, revealing significant alkaline content suitable for CO_2 absorption. PPAE demonstrated superior properties with higher potassium concentration (12,450 mg/L), pH (12.1), establishing it as the more effective local solvent component. However, future research should delve into exploring additional biomass sources and pretreatment methods to enhance solvent quality.

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