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Thermochemical conversion of underutilized lignocellulosic waste to syngas: Supercritical water gasification for value addition to corncob and sisal waste

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ABSTRACT

In the context of escalating global energy demands and environmental concerns associated with fossil fuels, this paper reports the conversion of underutilized agricultural residues in Tanzania, namely corncob and sisal waste, into syngas as sustainable biomass alternatives for energy production. Employing supercritical water gasification, the study evaluated the potential of corncob and sisal waste for syngas generation. Proximate analysis showed corncob as more suitable for energy conversion due to its lower moisture content (11.5%) and higher volatile matter (74.9%), compared to the higher moisture (14.9%) and ash content (17.2%) of sisal waste. However, the elemental analysis underscores both materials' feasibility for syngas production, with corncob and sisal waste showing substantial carbon and hydrogen contents, which are crucial for syngas. Despite the slight energy advantage of corncob indicated by its higher heating values (HHV: 25.44 MJ/kg, LHV: 24.40 MJ/kg) over sisal waste (HHV: 24.87 MJ/kg, LHV: 23.86 MJ/kg), reaction kinetics and syngas composition analysis suggested that both residues are viable feedstocks. Reaction kinetics analysis revealed temperature dependence in the conversion process, with higher temperatures favoring hydrogen production but increasing CO_2 emissions, underscoring the need for a balanced approach in syngas production. The syngas produced composes of H_2, CO, CH_4, CO_2, and light hydrocarbon gases. Moreover, the H_2/CO of the syngas gas was less than 1, suggesting that this syngas would be suitable for oxo-synthesis, aligning with existing literature. Regression analysis highlights temperature as the most influential factor on Total Syngas Yield, with significant R-square values (0.992 for corncob and 0.944 for sisal waste). However, a paired sample T-test indicated no significant yield difference between corncob and sisal waste (t-value = -0.518, *p*-value = 0.626). These values implied that both feedstocks are equally effective in syngas production under the examined conditions. This observation suggested that feedstock selection can be flexible based on other factors such as availability and environmental impact. The findings contribute new insights into biomass-to-energy conversion, emphasizing the viability of agricultural residues as sustainable energy sources. It informs feedstock selection, balancing environmental impact and cost factors, and advocates for a shift towards a more sustainable, circular energy economy.

Keywords: Corncob; Sisal waste; Supercritical water gasification; Syngas
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INTRODUCTION

The global shift towards green energy sources is largely driven by the detrimental effects of fossil fuel combustion, notably its significant contribution to greenhouse gas emissions and global warming (Park *et al.,* 2022; Tambunan *et al.,* 2023). Fossil fuels, the main culprits of these emissions, are depleting and causing severe environmental impacts (Omer, 2008; Raja and Iftikhar, 2021). This situation, coupled with an anticipated increase in global energy demand to around 19177 Million Tonnes of Oil Equivalent (MTOE) by 2040, underscores the urgent need for renewable energy alternatives (Moghaddam *et al.*, 2021). Among these, agricultural residues are emerging as a key solution (Uddin *et al.,* 2018).

Biomass, particularly agricultural residues, represents the largest renewable energy source worldwide (Sharma *et al.*, 2019). It is seen as a viable substitute for fossil fuels due to its energy-rich components (Hansson *et al.*, 2020). Agricultural residues, such as corncobs and sisal waste, are rich in carbohydrates like cellulose, hemicellulose, and lignin, making them ideal for bio-energy production, especially syngas. Precisely, agricultural residues are considered a promising alternative to renewable energy sources to meet future energy demand and reduce greenhouse gas emissions (Fraga *et al.*, 2019; Bilgili, 2022). However, despite the potential, there has been limited value addition to such waste, possibly due to inadequate government involvement, traditional farming practices, and a need for more technological advancement (Rogers *et al.*, 2022).

Technologies like supercritical water (SCW) gasification have been developed to convert bio-waste into syngas. This process involves high temperatures and pressures ($T > 374$ °C, $P > 22.1$ MPa), resulting in a mix of hydrogen, carbon monoxide, carbon dioxide, and light hydrocarbons (Rana *et al*., 2019; Su *et al*., 2020). The presence of CO_2, however, can decrease the heating value of syngas (Bakari *et al.*, 2021; Bakari *et al.*, 2023). Additionally, this method produces by-products such as liquid tar and solid char (Okolie *et al.*, 2020; Okolie *et al.*, 2021). While the potential of biomass as a renewable energy source is widely recognized, the specific conversion of underutilized lignocellulosic materials like corncob and sisal waste into syngas represents a notable research gap, particularly in Tanzania. This gap stems from the limited exploration of these specific agricultural residues in existing studies despite their abundant availability and high energy content (Aslam *et al.*, 2021; Rogers *et al.*, 2022; Zhao *et al.*, 2022). Most existing research in biomass conversion focuses broadly on more common types of agricultural waste or does not delve into the nuanced differences in efficiency and output between different types of biomass. Furthermore, the process of biomass conversion is not without challenges. Difficulties include the heterogeneity of the biomass, structural variations, and the complexity of the pretreatment processes (Zhao *et al.* 2022). These factors contribute to lower conversion efficiency and high enzymatic costs, posing significant hurdles in the efficient and cost-effective utilization of biomass for renewable energy. These challenges underscore the need for more targeted research, particularly focusing on the unique characteristics and conversion potential of specific types of biomass, like corncob and sisal waste, to optimize the process and maximize the energy output. Paying heed to the above limitations, this study fills the gap by targeting specific, less-utilized forms of biomass in Tanzania, which are often overlooked due to a need for more understanding of their potential or the absence of tailored conversion technologies. By focusing on corncob and sisal waste, the research explores new materials for syngas production. It seeks to optimize the conversion process to enhance the efficiency and output quality of the syngas produced. Furthermore, the study's approach to supercritical water gasification (SCW) of these materials is innovative. SCW gasification, a process involving high temperatures and pressures, has been studied before. However, its application to specific underutilized agricultural residues like corncobs and sisal waste is less common in Tanzania. The research investigates how these specific materials react under SCW conditions to maximize syngas production. The results are important for bioenergy and, in particular, aid in extending the route of converting agricultural waste to energy. Converting corncob and sisal waste into syngas adds value to these underutilized resources and fosters the growth of bio-based industries. This approach promotes new market opportunities for bio-based products and supports the principles of a circular economy, moving away from the traditional "take-use-dispose" model. Ultimately, this research contributes significantly to achieving multiple United Nations Sustainable Development Goals, promoting sustainable energy solutions while addressing global environmental challenges.

MATERIALS AND METHODS

Biomass preparation and analysis

Sisal waste (SW) and corncobs (CC) were collected at Kwamdulu Sisal Estate in Korogwe-Tanga and Magara village in Babati-Manyara, Tanzania, respectively. After collection, the samples were placed in clean, dry plastic bags for safe transportation to the laboratory. Once in the laboratory, the samples underwent sun-drying, grinding into powder, and sieving. This process resulted in uniform particles with a 2 mm size. The choice of this particular particle size is based on literature as findings suggest that a particle size of around 2 mm is optimal for maximizing yield, minimizing energy consumption, and improving the conversion of biomass to valuable products (Chundawat *et al.*, 2007; Bağder Elmacı and Özçelik, 2018; Yang *et al.*, 2018).

In the experimental process, specific chemicals and reagents were utilized during the supercritical water gasification of these prepared biomass materials. Among these were Loctite N-5000, nitrogen gas, and distilled water. Loctite N-5000 was sourced from Henkel Corp in Rocky Hill, Canada. At the same time, the nitrogen gas and distilled water were procured from Tanzania Oxygen Limited and the Nelson Mandela African Institution of Science and Technology, respectively. The next critical step involved the detailed characterization of the powdered sisal waste and corncobs. Parameters such as elemental composition, higher heating value (HV), moisture content (MC), volatile matter (VM), ash content (AC), and fixed carbon (FC) were meticulously determined. This characterization was conducted using established ASTM standards and various analytical instruments: the elemental composition was analyzed according to ASTM D5373-16 using a Flash 2000 CHNS-O elemental analyzer, and the higher heating value was gauged according to ASTM D5865 using a Gallenkamp Auto bomb calorimeter. Additionally, the moisture content, volatile matter, ash content, and fixed carbon were determined in adherence to the relevant ASTM standards D 3173-78, D 3175-11, D 3174-89, and E711-87, respectively.

Experimental procedure of syngas production

Supercritical water gasification (SCWP) experiments were performed at the School of Materials, Energy, Water and Environmental Sciences (MEWES) - Nelson Mandela African Institution of Science and Technology using a 316 stainless steel batch autoclave reactor (Parr 4650 series, Parr Instrument Company Moline, Illinois, U.S.A) with an internal volume of 500 mL, and maximum temperature and pressure (600 °C and 35 MPa). The used reactor was coupled with a nitrogen gas cylinder, Berrcom communication software version 1.0.0.9 (Parr Instrument Company, Moline, Illinois), AC source, and master controller (Figure 1).

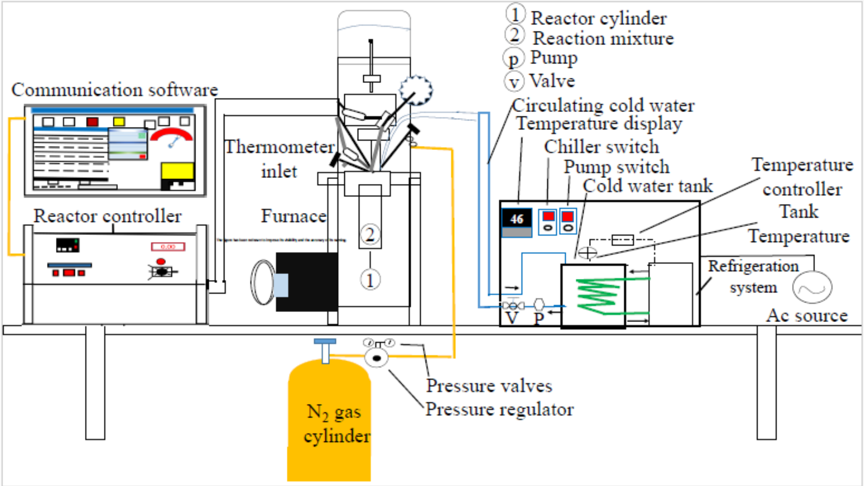


Figure 1. Schematic diagram of the reactor assembly

Before the experimental process, the raw feedstock, once dried, was accurately measured and thoroughly blended with distilled water to create a specific concentration of biomass feedstock. In aligning with the methodology outlined by Bakari *et al*. in both 2021 and 2023, the feed concentration used was 3%. To elaborate, the production of syngas through thermochemical processes is influenced by feed concentration (Bai *et al*., 2019; Mtili *et al*., 2021). Specifically, Bakari *et al*. (2021) reported that lower feed concentrations, such as 3% wt, enhance mass transfer between raw feedstock particles and water, which is crucial for the reaction. This concentration leads to a higher yield of syngas. Conversely, when the feed concentration exceeds 3% wt, the mass transfer rate decreases, reducing syngas production. Considering the feed concentration and the autoclave's maximum water capacity of 150 mL, the biomass amount was maintained below 4.6 grams, as calculated using Equation 1.

$$\text{Feed concentration}\,(\%\text{wt}) = \left(\frac{\text{B}}{\text{B}+\text{V}}\right) \times 100 \qquad (1)$$

Where: B = Biomass weight (g); V = Volume of distilled water (mL)

The reactor's bolts were also meticulously cleaned and lubricated with Loctite N-5000. The prepared biomass feedstock was then loaded into the reactor, which was sealed using a flexible virgin graphite gasket (model 457 HC3KL REV: R2, from Parr Instrument Company, Moline, Illinois, U.S.A). To prevent any pressure or gas leaks from the reactor, a torque wrench was employed incrementally at 20 Nm, 40 Nm, and 50 Nm. Moreover, it was purged with nitrogen gas at a pressure of 2 MPa to evacuate oxygen from the reactor system. After each purge, the pressurized reactor was monitored for 30 minutes to check for any pressure drops indicating leaks. The reactor system's settings, including temperature, residence time, and heating rate for each experimental run, were programmed using Berrcom controller communication software. The heating rate was set to approximately 4 °C/min to reach and maintain the desired operating temperature for the specified residence time.

A comprehensive experimental matrix comprising 12 tests was designed to facilitate syngas production from CC and SW. This matrix was structured to investigate the effects at two residence times, specifically 60 and 120 minutes, as outlined in Table 1. This approach allowed for a detailed exploration of the time-dependent variables in syngas production from these biomass sources. Subsequently, syngas production was carried out under the programmed temperature and residence time conditions. Following this, rapid cooling of the reactor vessel was achieved using a Makita UB 1100 wind blower from Japan, bringing the temperature down to 300 °C. The reactor underwent a quenching process in a cold water bath to reduce the temperature to ambient levels further. The syngas thus generated was captured in a Tedlar gas sampling bag (Tedlar PVF bag & PTFE valve, Model TDL31_1 L, Hedetech, Canada) for preservation. These bags containing the syngas were then stored in a cool box, ensuring their stability for subsequent analysis.

Table 1. Test matrix of experiments for syngas production from CC and SW

Residence time(min)	CC Sample	SW Sample	Temperature (°C)	Biomass weight (g)	Distilled water (mL)	Feed conc. (% wt)	Pressure (MPa)
60	1	1	400	4.60	150	2.98	28.45
	2	2	450	2.16	70	2.99	28.90
	3	3	500	1.91	60	3.09	29.37
120	4	4	400	4.60	150	2.98	28.45
	5	5	450	2.16	70	3.00	28.90
	6	6	500	1.92	60	3.10	29.37

Characterization of syngas using gas chromatography

Syngas analysis was conducted using a gas chromatograph with a thermal conductivity detector (GC-TDC) model Shimadzu GC-8A and a gas chromatography flame ionization detector (GC-FID) model Shimadzu GC-9A. An isocratic mode was employed since the temperature remained constant during the analysis process. Gas standards were used to calibrate the apparatus, and the gases were identified using the retention time and concentrations estimated from the peak areas. The composition of syngas was determined using a thermal conductivity detector (TCD) for permanent gases, and using a flame ionization detector (FID) for lighter hydrocarbon gases. The total syngas yield (TSY) was calculated using Equation 2 (Hantoko *et al.*, 2019; Maniscalco *et al.*, 2021).

$$\mathrm{TSY}\,(\frac{\mathrm{mol}}{\mathrm{kg}}) = \frac{\text{total moles in syngas (mol)}}{\text{total mass of feedstock}\left(\mathrm{kg}\right)} \tag{2}$$

Multiple linear regression and t-test analysis

The multiple linear regression and T-test were performed using IBM Statistical Package for Social Science (SPSS) version 20. Multiple linear regressions were conducted to determine the correlations between the independent and dependent parameters during SCW gasification. Furthermore, a paired-sample T-test was used to compare the means of two sets of observed syngas yield from corncobs and sisal waste and to find to what extent such difference is by chance.

Measurement accuracy and reliability

To ensure reliability and accuracy in the results, three strategies were employed to account for potential measurement errors. Firstly, the experiments were conducted in triplicate, which ensured consistency in the results and identified any anomalous readings that may have occurred due to instrument errors. This approach provided a solid check against one-off discrepancies in data. Secondly, standard reference materials were used to cross-verify the measurements (e.g., in gas chromatography), which validated the accuracy of the instrument against known benchmarks and reinforced the credibility of the measurement techniques. Lastly, a comprehensive error analysis was performed, where standard deviations were calculated for each measurement and diligently reported in the results. This provided a clear perspective on the potential variability in the data and was pivotal in understanding and communicating the precision of the findings.

RESULTS AND DISCUSSION

Proximate analysis results

The proximate analysis (MC, VM, AC, and FC) results of CC and SW are shown in Table 2. The proximate analysis of CC and SW shows distinct differences in their compositions, which are critical for their potential applications, particularly in energy production or material recovery. Moisture Content (MC) is notably different between the two biomasses. Corncobs have a moisture content of 11.45 ± 0.23%, whereas sisal wastes are higher at 14.91 ± 2.15%. This higher moisture content in sisal wastes suggests a need for more energy to dry the biomass before it can be efficiently used for energy purposes, affecting thermal efficiency during processes like combustion or gasification.

Table 2. Proximate analysis results of corncobs (CC) and sisal wastes (SW)

Parameter	**% composition**	
	CC	**SW**
MC	11.45 ± 0.23	14.91 ± 2.15
VM	74.90 ± 3.80	64.46 ± 1.76
AC	1.16 ± 0.28	17.16 ± 1.12
FC	12.49 ± 4.01	3.47 ± 2.45

Regarding Volatile Matter (VM), corncobs have a higher content of 74.90 ± 3.80% compared to sisal wastes at 64.46 ± 1.76%. Volatile matter is essential for combustion and gasification as it contributes to the flame. Like corncobs, biomass with higher volatile matter is typically more suitable for direct combustion or gasification, offering better combustibility.

The moisture content (MC) for corncob (CC) in this study, recorded at 11.45% wt, aligns closely with the findings of Danish *et al.* (2015), Biagini *et al.* (2014), and Suhartono *et al.* (2017), who reported MC values of 11.74%, 10.1%, and 10.97% wt, respectively, in their thermal analyses of corncob samples (Suhartono and Azizah, 2006; Biagini *et al.*, 2014; Danish *et al.*, 2015). However, it is slightly lower than the 12.70% wt reported by Biswas *et al.* (2017) and higher than García *et al.*'s (2012) finding of 7.0% wt (García *et al.*, 2012; Biswas *et al.*, 2017). In contrast, the sisal waste (SW) MC in this study was found to be 14.91% wt, which is considerably higher than the 6.11% wt reported by Jambeiro *et al*. (2018) for Brazilian sisal residues (Jambeiro *et al.*, 2018). Bridgwater (2012) also noted that for effective conversion of sisal waste to biofuel, the optimal MC should be above 10% wt (Bridgwater, 2012).

Ash content (AC) in corncobs is significantly lower (1.16 ± 0.28%) than in sisal wastes (17.16 ± 1.12%). The observed difference in ash content between CC and SW can be attributed to a combination of factors, including plant species, growth environment, plant structure, and processing methods. High ash content can lead to operational challenges, such as slagging and fouling in combustion systems. The lower ash content in corncobs suggests they would produce less residue after combustion, making them a cleaner and more efficient option for energy production. In the current study, the ash content (AC) of the corncob (CC) sample was found to be in line with the 1.53% wt reported by Suhartono *et al*. (2017) from their thermal assessment for syngas production using corncobs. However, this figure is lower compared to the AC values reported in other studies: 2.12% wt by Biagini *et al*. (2014), 2.30% wt by Biswas *et al*. (2017), 2.70% wt by Sulaiman *et al*. (2019), 2.72% wt by Martínez *et al*. (2019), and 2.40% wt by Arun *et al*. (2020), all of whom examined corncob samples for thermal conversion processes (Sulaiman *et al.*, 2019; Arun *et al.*, 2020; Martínez *et al.*, 2020). For sisal waste (SW), the current study found a higher AC compared to both the CC sample of this study and the 12.70% wt AC reported by Guerra *et al*. (2019) in their study on the chemical and physicochemical characterization of Brazilian natural sisal waste (Guerra *et al.* 2019). However, this value was similar to the 16.28% wt AC reported by Jambeiro *et al*. (2018) during their study on the fast pyrolysis of sisal residues for bio-oil production.

Furthermore, Fixed Carbon (FC) content is higher in corncobs (12.49 ± 4.01%) compared to sisal wastes (3.47 ± 2.45%). Fixed carbon is important for sustained burning in combustion processes, with higher content indicating a longer, more stable burn. This makes corncobs potentially more advantageous for certain thermal processes. The fixed carbon (FC) content of the corncob (CC) sample was found to be similar to the values reported in other research: Suhartono *et al*. (2017) and Arun *et al*. (2020) observed FC contents of 14.51% wt and 16.6% wt, respectively, in their thermal assessments of Indonesian and Indian corncobs. For sisal waste (SW), the FC content in this study was higher than the 1.31% wt reported by Jambeiro *et al*. (2018) in their study on the fast pyrolysis of sisal residues into bio-oil. However, both CC and SW in this study had lower FC contents when compared to the 21% wt found in South African corncobs, as Anukam *et al*. (2017) reported in their thermal characterization study (Anukam *et al.*, 2017). The analysis highlights that corncob, due to its higher volatile matter, fixed carbon content, and lower moisture and ash content, seems more favorable for energy production methods like combustion and gasification. Conversely, sisal wastes require additional processing, such as drying and ash removal, to be effectively utilized in similar applications. These attributes are key considerations for determining these biomasses' most efficient and sustainable uses.

Elemental composition and heat values of agricultural residues

The elemental composition and heat values of the corncobs (CC) and sisal wastes (SW) are shown in Table 3. The elemental composition and heating values of CC and SW play a significant role in determining their suitability for syngas production. Both CC and SW possess substantial carbon contents, with CC at 33% and SW at 30.4%, which is beneficial since carbon is a primary component of syngas. The hydrogen content is slightly higher in CC (4.8%) compared to SW (4.6%), which is advantageous as hydrogen is another key element in syngas. However, SW has a higher nitrogen content (2.4%) than CC (1.4%), which could impact the combustion process and potentially lead to the formation of nitrogen oxides. Fortunately, the sulfur content in both materials is below the detection limit, which is favorable due to the undesirable nature of sulfur compounds in syngas. Oxygen content is also a notable factor, with CC and SW having 48.2% and 44.2% respectively. This oxygen can contribute to partial oxidation during gasification, which is essential in syngas production. The H/C and O/C ratios in both CC and SW are similar, indicating the potential for similar reactions during gasification, with CC having a slightly more hydrogen-rich composition.

Table 3. Elemental composition and heat values of corncobs (CC) and sisal wastes (SW)

Parameter	**% composition**	
	CC	**SW**
C	33.00 ± 0.80	30.43 ± 0.41
H	4.76 ± 0.30	4.61 ± 0.06
N	1.43 ± 0.14	2.43 ± 0.13
S	Below detection limit	Below detection limit
O*	48.21 ± 1.76	44.16 ± 3.86
H/C (mole ratio)	1.82 ± 0.066	1.73 ± 0.001
O/C (mole ratio)	1.09 ± 0.027	1.10 ± 0.013
HHV (MJ/kg)	25.44 ± 0.127	24.87 ± 0.389
LHV (MJ/kg)	24.40 ± 0.127	23.86 ± 0.389

Note: * = calculated amount of oxygen (Equation 3).

$$O(\%) = 100 - (C + N + H + S + AC + MC) \quad \text{(Klaas } et\ al. \text{ 2020)} \qquad (3)$$

Where: AC and MC are ash content and moisture content.

Furthermore, the higher heating values (HHV) and lower heating values (LHV) indicate the energy content of the biomass. CC exhibits slightly higher values (HHV: 25.44 MJ/kg, LHV: 24.40 MJ/kg) compared to SW (HHV: 24.87 MJ/kg, LHV: 23.86 MJ/kg), implying that it may be a more energy-rich feedstock for syngas production. These values are crucial as they determine how much energy can be extracted from the biomass. The elemental compositions and heating values suggest that both CC and SW are suitable for syngas production. CC, however, appears to have a slight edge due to its higher energy content and hydrogen richness. The low sulfur and comparable nitrogen content, particularly in CC, also make them environmentally friendly options for syngas production. The oxygen content and H/C, O/C ratios further imply efficient gasification for both types of biomass.

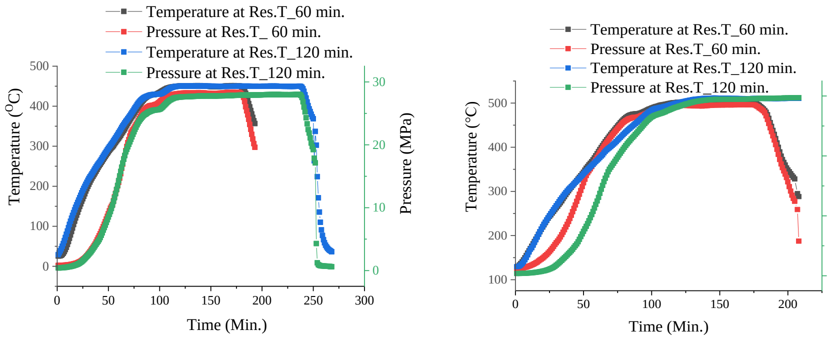
Reaction progress during syngas production

Figure 2 illustrates the reaction progress during syngas production under supercritical water gasification. The data depicted in the graphs indicate that the reactions are exothermic, as evidenced by the concurrent rise in both temperature and pressure. Such an increase points to a reaction that generates heat and possibly gas, contributing to the increase in pressure. A distinct feature in these reactions is the dependency of the reaction rate on temperature; a rapid rise in both temperature and pressure is observed at 500 °C when compared to 450 °C, underscoring that higher temperatures accelerate the reaction rate. This observation aligns with the Arrhenius equation, which suggests that an increase in temperature reduces the activation energy barrier, allowing more molecules to participate in the reaction.

As the reactions progress, a deceleration in the rate of temperature increase is noticeable, leading to a flattening of the temperature curves. This pattern is characteristic of chemical reactions where decreased reactant concentration over time results in a slower reaction due to fewer collisions between molecules. Moreover, the graphs suggest the presence of a cooling phase where, after reaching a peak, the temperature starts to drop. This could be due to heat dissipation to the surroundings or the slowing down of the exothermic reaction as the reactants are being used up. Furthermore, the declining trend observed in temperature and pressure at later times could indicate that the reactions are approaching a state of equilibrium or that the reactants are nearing depletion. At equilibrium, the forward and reverse reactions occur at the same rate. Consequently, there is no net change in the concentrations of reactants and products, which can stabilize temperature and pressure.

The pressure profiles across all graphs show a consistent upward trend, hinting at gas production, and suggest that the reaction is moving toward completion, with the reactants gradually transforming into products. These insights collectively suggest that as the reactions advance toward equilibrium or the reactants are exhausted, the observed rate changes reflect the reactions' progress toward completion. In general, the reaction kinetics observed from these graphs indicate temperature-dependent exothermic reactions that slow down as the reactants are consumed, potentially reaching a state of equilibrium or completion, as demonstrated by the changing rates of temperature and pressure over time.

(a) Corn cobs



(b) Sisal waste

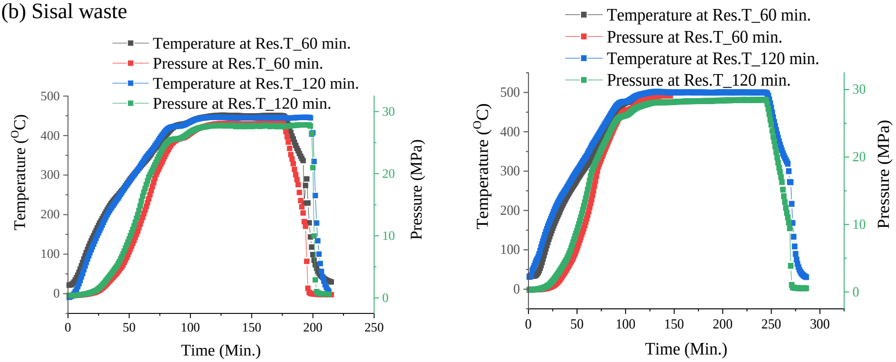


Figure 2. Reaction progress under supercritical water pyrolysis for corn cobs and sisal waste

Syngas yield and composition

The results of syngas composition are shown in Table 4. GC was able to detect H_2, CO, CH_4, CO_2, C_2H_6, C_2H_4, C_3H_8, cyclopropane, *n*-butane, and *t*-2- butane. At a 60-minute residence time (CC1-CC3), increasing the temperature from 400 °C to 500 °C results in a notable increase in hydrogen content, a desirable outcome for syngas production due to hydrogen's value as a fuel and chemical synthesis. The peak in CO_2 content at 450 °C suggests enhanced release or less effective conversion at this intermediate temperature. In contrast, the decreasing H_2/CO ratio with increasing temperature indicates a relatively more efficient hydrogen production than carbon monoxide generation at higher temperatures. Extending the residence time to 120 minutes (CC4-CC6) presents a shift in the syngas composition. At 400 °C, there is an increase in methane content compared to the 60-minute residence time, which may imply different reaction dynamics over a longer period. However, the total synthesis yield is lower, suggesting that a longer residence time at this temperature may not be beneficial. At elevated temperatures of 450 °C and 500 °C, we see a decrease in CO_2 alongside an increase in hydrogen, indicating that a longer residence time could lead to more effective conversion processes.

At a 60-minute residence time (SW1-SW3), there is a substantial amount of methane at 400 °C, which decreases with rising temperatures, aligning with the notion that higher temperatures favor methane decomposition. CO_2 levels stay relatively constant, while hydrogen increases with temperature, again advantageous for syngas quality. With a residence time of 120 minutes (SW4-SW6), the trend in methane content mirrors that of the CC samples, with higher levels at 400 °C and a reduction at increased temperatures. The total synthesis yield and H_2/CO ratios generally show an upward trend with temperature, suggesting that syngas production's efficiency improves with higher temperatures and extended reaction times.

The reason for the increase in TSY is likely due to the domination of free radical reactions caused by the powerful oxidizing agents of supercritical water (Acelas *et al.*, 2014; Klaas *et al.*, 2020; Wang *et al.*, 2021). In the process, temperature promotes steam reforming (Equations 4a and 4b) and water-gas shift reaction (Equation 4c), which facilitate production of H_2; the other syngas components including CO_2, CH_4, CO and other lower hydrocarbon gases occur due to intermediate reactions like decarboxylation reaction (Equation 4d, 4e and 4f) (Salimi *et al.*, 2016; Pinto *et al.*, 2017; Adar *et al.*, 2020). At lower temperatures, about 400 °C, decarboxylation reaction was dominant; hence, the main product was CO_2 compared to other syngas components. At higher temperatures (450 and 500 °C), the supercritical water became a more powerful oxidizing agent; hence, free radical reactions dominated.

The calculated H_2/CO was less than 1, suggesting that this syngas would suit the oxo-synthesis process (Kantarelis and Zabaniotou, 2009). This ratio aligns with existing literature, which mentions that syngas produced from biomass gasification typically has a low H_2/CO ratio, necessitating modifications for certain uses, such as the Fischer Tropsch synthesis (Tijmensen *et al.*, 2002). Current methods to modify the H_2/CO ratio in syngas from gasification include syngas reforming, tar cracking, and the water gas shift reaction (Wang *et al.*, 2011; Chianese *et al.*, 2015).

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (4a)$$

$$C_nH_m + H_2O \longrightarrow nCO + (n + m/_2)H_2 \qquad (4b)$$

$$H_2O + CO \longrightarrow H_2 + CO_2 \qquad (4c)$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad (4d)$$

$$C_nH_m + nCO_2 \longrightarrow 2nCO + m/_2H_2 \qquad (4e)$$

$$C_nH_m + nCO_2 \longrightarrow C_{n-x}O_{m-y} + H_2 + CH_4 + C \qquad (4f)$$

Both CC and SW samples generally exhibit higher temperatures conducive to hydrogen production, a key component of high-quality syngas. Nevertheless, this often coincides with increased CO_2 production, which poses environmental concerns. The H_2/CO ratio, a critical indicator of syngas quality, shows that higher ratios are typically achieved at higher temperatures. The residence time also plays a pivotal role, with longer times generally leading to higher hydrogen yields, though the effects on methane and CO_2 vary. These findings highlight the importance of optimizing temperature and residence time to tailor the syngas composition for specific applications, balancing efficiency and environmental impact. Differences between the CC and SW processes suggest distinct reaction mechanisms, potentially influenced by catalytic effects in CC or the steam reforming in SW and underscore the need for tailored approaches in optimizing syngas production processes.

Table 4. Syngas composition obtained from gas chromatography

Sample No	**Temperature (°C)**	**Residence time (min)**	**Syngas composition (% mol)**					**TSY (mol/kg)**	**H_2/CO Ratio**
			CH_4	**CO_2**	**CO**	**H_2**	**C_2-C_4**		
CC1	400	60	2.38	1.52	0.66	0.31	0.55	28.44	0.46
CC2	450	60	4.59	7.64	0.70	0.30	2.56	34.31	0.43
CC3	500	60	4.65	2.87	0.71	0.29	1.39	45.86	0.41
CC4	400	120	2.03	4.07	0.76	0.24	0.95	17.47	0.32
CC5	450	120	2.28	2.24	0.72	0.28	0.78	29.12	0.38
CC6	500	120	4.08	2.00	0.71	0.29	1.09	42.57	0.41
SW1	400	60	5.00	3.24	0.69	0.31	0.49	21.12	0.45
SW2	450	60	1.92	2.02	0.70	0.32	1.42	33.33	0.45
SW3	500	60	3.39	3.10	0.72	0.28	0.82	38.43	0.39
SW4	400	120	4.76	2.37	0.72	0.28	2.60	23.29	0.39
SW5	450	120	2.94	1.92	0.67	0.33	1.20	32.62	0.50
SW6	500	120	1.94	2.81	0.65	0.35	1.41	37.23	0.54

TSY= Total Syngas Yield; C_2-C_4 includes ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), cyclopropane (C_3H_6), *n*- butane (C_4H_{10}) and *t*-2- butene (C_4H_8)

Multiple linear regressions

In the analysis, the Total Syngas Yield (TSY) was the primary variable of interest, impacted by three key factors: temperature, residence time, and pressure, each acting as an independent variable. The R-square value for TSY derived from CC was a notable 0.992. This value, close to 1, underscored a robust correlation between the independent variables (temperature, residence time, and pressure) and TSY, suggesting these factors significantly influence syngas yield. Temperature was identified as the most impactful factor, as evidenced by the coefficients in Equation 5. This implies that adjustments in temperature could lead to more pronounced changes in TSY compared to alterations in residence time or pressure. Furthermore, the high R-square value indicates the model's reliability in predicting

TSY based on these variables, reinforcing the importance of precise control over these conditions in syngas production processes.

$$TSY\ (mol/kg) = 5.512 + 0.306X_1 + 0.234X_2 - 4.819X_3 \quad (5)$$

Where X_1 is the temperature (°C), X_2 is the residence time (min) and X_3 is the pressure (MPa).

The R-square value for Total Syngas Yield (TSY) derived from Solid Waste (SW) was reported as 0.944. This indicates a solid correlation between the variables under study. However, the p-value associated with this correlation was 0.083, exceeding the standard threshold of 0.05. This suggests that, statistically, the observed correlation might not be significant. Analyzing the coefficient values presented in Equation 6, it becomes evident that temperature plays a more substantial role in affecting TSY when compared to other parameters. This highlights the critical influence of temperature in the process, although the statistical significance of its impact might be less certain due to the higher p-value.

$$TSY\ (mol/kg) = 50.686 + 0.114X_1 + 0.091X_2 - 2.844X_3 \quad (6)$$

Where X_1 is the temperature (^{o}C), X_2 is the residence time (min), and X_3 is the pressure (MPa)

Paired sample T-test

The results of the Paired T-test indicated that there was no statistically significant difference in the syngas yield between the two feedstocks. The calculated value ($T_{0.05\ (2),\ 5}$ = -0.518) and the corresponding *p*-value of 0.626 reinforced this finding. In statistical terms, the critical p-value is typically set at 0.05. A *p*-value higher than this threshold, as observed in this study (0.626), suggests that the difference in TSY between CC and SW is not significant enough to be considered more than a chance occurrence. This outcome is crucial in understanding the efficiency and effectiveness of the two feedstock sources for syngas production. From a statistical standpoint, it implies that both CC and SW are equally effective in producing syngas, as there is no significant variance in the yield from these sources. This can inform decisions on feedstock selection, indicating that factors other than syngas yields, such as availability, cost, and environmental impact, may be more critical in choosing between CC and SW for syngas production.

CONCLUSION

This paper provides findings on the evaluation of the potential of corncob (CC) and sisal waste (SW) as feedstocks for syngas production through supercritical water gasification (SCW). Both CC and SW are shown to be viable for syngas production, each exhibiting unique characteristics that influence their gasification efficiency. With its higher volatile matter, fixed carbon content, and lower moisture and ash content, CC stands out as more favorable for energy production methods like combustion and gasification. While effective, SW may require additional processing like drying and ash removal for optimal use. Elemental analysis and heat values of CC and SW underscore their suitability for syngas production. CC has a slight edge due to its higher energy content and hydrogen richness, supporting its potential as a renewable energy source. Statistical analyses, including multiple linear regressions and paired sample T-tests, highlight temperature as the most significant factor affecting Total Syngas Yield (TSY). Interestingly, no significant statistical difference in syngas yield was observed between CC and SW, indicating their comparable effectiveness as feedstocks for syngas production. These findings confirm the importance of biomass composition in determining the efficiency and output of the gasification process. Moreover, these findings align with existing literature on the importance of temperature and residence time in optimizing syngas production. Higher temperatures enhance hydrogen production, a vital component of high-quality syngas, while extended residence times influence the composition of syngas, offering a balance between efficiency and environmental impact. This study contributes significantly to the field by highlighting the efficient and sustainable utilization of less-utilized forms of biomass in Tanzania. It emphasizes the importance of targeted research on specific biomass types and their unique characteristics for optimizing the syngas production process. The results can guide decisions on feedstock selection, focusing on factors such as availability, cost, and environmental impact. More importantly, the findings fuel the alleviation of the "take-use-dispose" approach and promote a circular economy. Further, the findings hold particular promise for achieving multiple SDGs, including SDGs 8, 11, 12, 13, 14 and 15. Future research should explore the development of tailored conversion technologies for specific biomass types, considering their unique characteristics. Addressing challenges like the heterogeneity of biomass and the complexity of pretreatment processes could enhance the efficiency and cost-effectiveness of biomass utilization for renewable energy. The study also suggests that further exploration of strategies to optimize the gasification process, particularly in managing CO2 emissions and improving syngas quality, is needed. Investigating additional biomass sources and scaling the process for industrial applications could contribute greatly to renewable energy development.

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