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A Combination of Hydrothermal Carbonization under CO_2 and High-Temperature Steam Gasification of Bagasse

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ABSTRACT

This research explored the combined process of hydrothermal carbonization under CO_2 atmosphere and high-temperature steam gasification of bagasse, a plentiful biomass in Vietnam. The bagasse underwent HTC at 200°C in a 100% N_2 and CO_2 atmosphere, with a bagasse-to-water ratio of 1:8 and a residence time of 7200 s. The resulting hydrochar was then used for steam gasification at 900°C under 100% steam. A comparative experiment using untreated bagasse was served as a baseline. The findings reveal significant improvements in fixed carbon content and higher heating value of the hydrochar compared to the original biomass. Hydrochar also demonstrated faster conversion compared to that of raw bagasse, enhancing the efficiency of gasification. Furthermore, the syngas produced from the hydrochar resulted in 5% higher concentrations of both H_2 and CO. These enhancements in gasification performance suggest promising possibilities for the more efficient and sustainable use of bagasse in energy production.

Introduction

Vietnam's sugar industry produces a massive amount of bagasse waste each year, around 8 million tons, but only a handful of factories use it for power [1]. Most of this bagasse goes unused, creating a missed opportunity, especially considering the global push for renewable energy [2]. In this context, gasification offers a way to utilize bagasse. Gasification is a thermochemical process that transforms carbon-based materials into syngas, rich in H_2 and CO, which can be applied for power generation, heating, or can be refined into transportation fuels. Currently, woody feedstock dominates biomass gasification processes [3,4]. However, reliance on wood faces challenges such as deforestation or competition with other wood-dependent industries. Diversifying feedstock types to include non-woody biomass, agricultural residues, or organic wastes requires innovative approaches and technological adaptations. Bagasse possesses a high heating value thanks to its significant content of cellulosic components and soluble substances like sugar [5]. However, using bagasse directly for gasification encounters limitations due to the relatively

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high moisture content and the inherent heterogeneity, with the outer section of the bagasse stem being denser and more rigid, while the inner portion is porous and softer, leading to difficulties in controlling the gasification process [1,2]. Thus, pretreating bagasse before gasification is essential to enhance biomass quality and enable effective utilization as a feedstock.

Hydrothermal carbonization (HTC) is a promising technique for pretreating biomass, involving subjecting it to high temperatures and pressures in a water-based environment. This process breaks down complex organic compounds in the biomass, changing its structure and improving its properties for subsequent processes like gasification. HTC offers several advantages, including enhancing biomass uniformity, calorific value, and energy density [5,6]. It also reduces ash content by dissolving inorganic constituents, making the biomass easier to grind and store. Various studies have explored this, with one indicating that HTC improves biomass compatibility with entrained flow gasification. Additionally, experiments under different atmospheres have shown that CO_2 presence increases both liquid and gas yields compared to inert atmospheres, with CO_2 also enhancing hydrochar crystallinity [7]. Gasification parameters, including the choice of gasifying agents like oxygen, steam, air, and carbon dioxide, significantly affect gasification products [8]. Our focus is on steam gasification, widely used to enhance syngas quality, as evidenced by several studies. Research indicates that supercritical steam gasification of bagasse yields higher conversion rates compared to other agents [7]. Steam gasification of hydrochar derived from fruit waste through HTC has shown changes in syngas composition, indicating the influence of HTC on gasification outcomes [9].

In short, combining hydrothermal pretreatment under a CO_2 atmosphere with steam gasification shows great potential for converting agricultural wastes into high-quality syngas. However, research on this process is currently scarce. To our knowledge, there hasn't been a comprehensive study investigating HTC under a CO_2 atmosphere followed by high-temperature gasification using supercritical steam. Nonetheless, encouraging results from existing literature indicate that integrating these steps could significantly improve the syngas quality.

Therefore, the research aimed to investigate the combined process of hydrothermal carbonization (HTC) under CO_2 atmosphere and high-temperature steam gasification applied to bagasse in Vietnam.

Experimental

Bagasse

The bagasse waste was gathered directly from a processing facility in the Mekong Delta following the ISO 18135:2017 standard for sampling solid biofuels. To prepare it for analysis, the biomass undergoes cutting, grinding, sieving, and meticulous blending to achieve uniform particles with a diameter of less than 1mm.

HTC treatment

For each HTC treatment, bagasse was introduced into an autoclave reactor (500 ml) with a biomass-to-water ratio of 1:8. The reactor was then charged with an atmosphere of 100% N_2 (purity: 99.99%) or 100% CO_2 (purity: 99.99%) and sealed before being inserted into the Nabertherm LT 24/12/P300 muffle furnace. The two contrasting atmospheres helped highlight the role of CO_2 in the HTC process. The HTC was introduced at a temperature of 200 °C and a residence time of 7200 s. Following the HTC treatment, the reactor was removed from the furnace and allowed to cool. Once it reached room temperature, the pretreated solid was separated from water through filtration and subsequently dried in a Memmert Model 800 Class B Incubator for use in further gasification experiments.

Analysis of raw and HTC samples

The raw and HTC-treated bagasse samples were taken to perform the proximate analysis, determining their moisture content (M) following the ASTM D4442, volatile matter (V) following the ASTM D-3175 standard, ash content (A) following the ASTM D-3174 standard, and fixed carbon content (FC) (FCdb = 100 – V – A). The higher heating value was determined using the Parr 6200 Calorimeter, following the procedure described in the NREL protocol. All measurements were repeated 3 times to ensure the accuracy of the result.

Gasification experiment

A lab-scale gasification reactor, installed at the Vietnam – France University, has been used for this study (Figure 1). The system comprises a ceramic tube with specific dimensions (length x internal diameter = 111 × 7.5 cm) placed within an electric furnace equipped with three distinct heating zones to ensure consistent and uniform temperature distribution throughout the reactor. In each experiment, the reactor initially reaches a temperature of 900°C. Subsequently, 25 grams of each sample is raised from its initial position to the intended location and maintained in an environment consisting of 100% steam. The selection of these

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gasifying conditions is based on prior studies for supercritical steam gasification . The sample undergoes gradual mass decrease due to gasification reactions, monitored continuously via a data acquisition system.

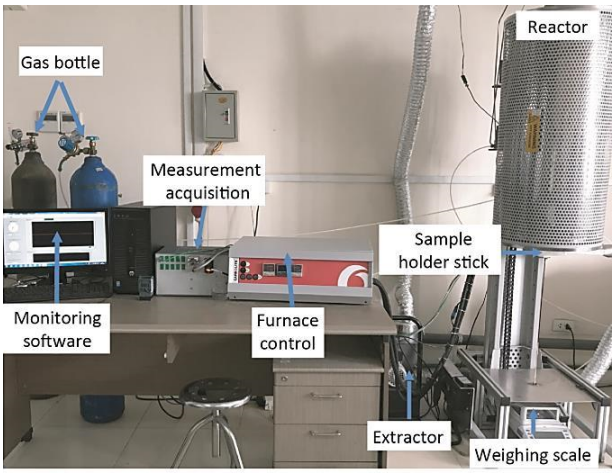

Fig. 1: Setup of the lab-scale gasification system

Syngas composition analysis is carried out by collecting and filtering gas samples every 300 s over 1800 s during the gasification process (when the system stabilizes) using an Agilent 990 Micro GC analyzer (Figure 2).

Fig. 2: Setup of the Macro-GC 900 for syngas analysis

To ensure more accurate comparisons of changes in each gas component, the experiments are repeated 3 times, with mean results reported. Prior to the analysis, the gas sampling tubes were purged with Argon gas to eliminate any residual gases. In this research, nitrogen gas flow was utilized as a tracer to determine the mass flow rates.

Results and discussion

Physical characteristics of raw and HTC-treated bagasse

The bagasse presents a relatively high moisture content of around 18.5%, which poses challenges for direct use in the gasification process but proves advantageous for the HTC process. Following the HTC treatment under both N_2 and CO_2, a noticeable reduction is observed in both the volatile matter and ash content of the bagasse. This reduction is likely due to the breakdown of certain weak bonds within the biomass during the HTC process, coupled with the removal of inorganic constituents [7,9]. Additionally, there is an increase in both the higher heating value (HHV) of the biomass. The elevation in HHV may be explained by the higher carbon content and lower oxygen content in the HTC-treated bagasse, indicating increased energy content [5].

Table 1. Proximate analysis of raw and HTC-treated bagasse

	Raw	HTC (N_2)	HTC (CO_2)
M_{as} (%)	18.5 ± 0.2	-	-
V_{db} (%)	76.3 ± 0.2	74.4 ± 0.2	73.9 ± 0.2
A_{db} (%)	3.8 ± 0.1	1.9 ± 0.1	1.5 ± 0.1
FC_{db} (%)	19.9 ± 0.3	23.7 ± 0.3	24.6 ± 0.3
HHV(MJ/kg)	15.9 ± 0.3	17.2 ± 0.3	17.9 ± 0.3
C_{daf} (%)	44.2±0.2	48.6±0.2	50.5±0.2
H_{daf} (%)	6.6±0.2	6.0±0.2	6.3±0.2
N_{daf} (%)	0.1±0.1	0.1±0.1	0.1±0.1
O_{daf} (%)	49.1±0.5	45.3±0.5	43.1±0.5

M: Moisture, V: Volatile, A: Ash, FC : Fixed-carbon, HHV : Higher heating value, as: as-received, db: dry basis, daf: dry-ash-free basis

When comparing HTC in 100% N_2 and 100% CO_2 environments, it can be observed that HTC in CO_2 has the ability to slightly increase crystallinity compared to HTC in N_2. This result is consistent with findings from previous research [7]. Such improvements could optimize the utilization of bagasse feedstock, resulting in higher energy yields. Additionally, the minimal nitrogen content in bagasse implies that its use for gasification would yield a clean and environmentally friendly syngas product.

These enhancements could optimize the use of bioenergy feedstock, leading to higher energy yields and reduced transportation costs. The negligible nitrogen content in bagasse suggests that using it for gasification would result in a clean and environmentally friendly syngas product.

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Gasification rate of raw and HTC-treated bagasse

Figure 3 illustrates the average conversion rates of the raw and HTC-treated chars throughout the gasification process at 900 °C under 100% steam atmosphere. The measurements were repeated three times with a deviation below 5%, indicating the reliability of the results.

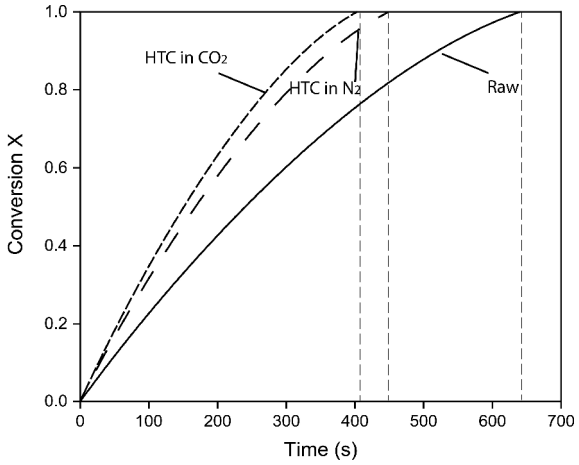

Fig. 3: Gasification rate of raw and HTC-treated bagasse

The conversion of raw bagasse char was completed after 650 s. In contrast, the conversion rate of HTC-treated samples were notably faster than its raw counterpart, taking only 410-450 s. During the HTC process, some of these complex compounds were eliminated, leading to a hydrochar with reduced ash content. This decrease significantly increased the gasification conversion rate, accelerating the char conversion process [5]. The enhanced char conversion rate of HTC-treated samples suggests a potential method for decreasing residence time while maintaining process efficiency.

When comparing HTC in N_2 and HTC in CO_2, it can be observed that the product from HTC in CO_2 yields hydrochar with slightly lower ash content, higher HHV, and higher crystallinity (as indicated by higher FC content). This confirms the impact of the CO_2 environment in hydrothermal processes.

Syngas composition

Table 2 reports the distribution of compositional gases in the syngas from raw bagasse and its hydrochar with supercritical steam gasification at 900 °C. The average syngas composition from 3 tests was employed for comparison to enhance result accuracy, considering the slight fluctuations observed in syngas composition during the gasification process. When comparing the gasification of raw bagasse, a syngas with lower H_2 content (14.5%) and CO content (37.2%) was observed. Additionally, the CO_2 content in the syngas was relatively high, averaging around 44.9%. Conversely, for HTC-treated bagasse samples, there was a slight improvement in the concentrations of H_2 and CO in the syngas, by approximately 3-5% for both compositions. Moreover, there was a reduction in the CO_2 level in the syngas. These results are consistent with prior research that utilized HTC under similar conditions to enhance the quality of biomass syngas [6,7].

Table 2. Syngas composition from gasification of raw bagasse and its hydrochar (wt%)

	Composition	1	2	3	Average
Raw	H_2	13.1	15.8	14.5	**14.5**
	CO	33.8	38.2	39.5	**37.2**
	CH_4	4.1	3.1	3.2	**3.5**
	CO_2	49	42.9	42.8	**44.9**
HTC in N2	H_2	16.9	18.1	17.8	**17.6**
	CO	39.9	40.5	40.8	**40.4**
	CH_4	3.1	4.1	3.3	**3.5**
	CO_2	40.1	37.3	38.1	**38.5**
HTC in CO2	H_2	18.6	19.3	19.1	**19.0**
	CO	39.9	42.9	42.8	**41.9**
	CH_4	3.7	4.7	3.3	**3.9**
	CO_2	37.8	33.1	34.8	**35.2**

This improvement can be attributed to the enhanced carbonaceous structure of the hydrochar obtained from HTC and the optimization of the reaction atmosphere by steam. When comparing HTC-treated bagasse in N_2 with that in CO_2, the syngas produced from HTC-treated bagasse in CO_2 had higher levels of CO and H_2. Additionally, it was observed that the content of these gases remained more stable during the operation. This could be attributed to the higher homogeneity of the CO_2 HTC-treated bagasse sample compared to that of the N_2 HTC-treated bagasse. This outcome suggests significant potential for the practical application of integrating HTC in CO_2 as a pretreatment method in the steam gasification process of bagasse, considering the increased amounts of H_2 and CO produced.

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Conclusion

The results showed that implementing HTC, had a significant impact on various attributes of bagasse. Furthermore, HTC in a CO_2 environment demonstrated superior performance compared to HTC in a N_2 atmosphere. This included an elevation in fixed carbon content (approx. 5 wt%) and HHV (approx. 2 MJ/kg), alongside a decrease in ash content (approx. 2 wt%). The gasification rate of hydrochar (410s) was notably swifter than that of raw bagasse (650s) in the same conditions. Furthermore, combining HTC in a CO_2 environment with steam gasification led to a substantial increase in H_2 and CO (about 5%). Together, these findings offer valuable insights for developing an efficient integrated process involving HTC and supercritical steam gasification using bagasse as a feedstock.

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