

The effect of thermal pre-treatment on cassava rhizome properties for utilizing as green fuel in gasification

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Abstract. Cassava rhizome (CR) was torrefied to provide superior solid fuel quality for further gasification process. The torrefaction was carried out in the absence of oxygen at 220, 240, 260, and 280°C with a fixed residence time. Solid fuel after torrefaction has a higher calorific value from that of reduced volatile matters. The optimum energy yield of torrefied CR is 88.16% at 260°C. The heating value of 20.86 MJ/kg for a torrefied product can be achieved compared to 15.37 MJ/kg for untreated CR. The subsequent gasification of torrefied CR at temperature of 800°C yielded the highest gas product of 65 wt.%. The carbon and hydrogen conversions into CO and H₂ were 14.28% and 29.95%, respectively. Synthesis gas (syngas) from the conversion maintained the H₂/CO ratio of around 2–2.50, which is suitable for the Fischer–Tropsch process or can be used as the feedstock for petrochemical industry.

1 Introduction

The torrefaction treatment or mild pyrolysis is conducted at a temperature of 200–300°C in an inert atmosphere, i.e., in the absence of oxygen. During torrefaction, parts of the original component in the biomass, such as volatile compounds, lignocellulosic materials (hemicellulose, cellulose and lignin), are decomposed at different temperatures. Hemicellulose decomposes within a temperature range of 225–325°C, cellulose within 270–350°C, and lignin gradually over a range of 250–500°C [1]. Therefore, torrefaction may render the biomass into an attractive solid fuel with properties for further thermal conversion processes along with the ease of long-distance transportation, long term storage, and palletization [2, 3]. Cassava rhizome (CR) is the woody part between the stalk and the tapioca tuberous root. The carbon content and heating value of the cassava rhizome are suitable as renewable energy sources. Sirijanusorn et al. (2013) pyrolyzed CR in a counter-rotating twin screw reactor to obtain maximum bio-oil yield of 43.05 wt.% and a minimum char yield of approximately 5 wt.%. However, the acidity of the bio-oil obtained from the twin-screw reactor is pH 2.9, which was more than the free-fall reactor type (pH 3.50). Homchat et al. (2012) conducted a slow pyrolysis of fresh and dried CR with a large-scale metal kiln which resulted in less charcoal in the case of fresh CR (10–13 wt.%) due to the moisture content. However, this bio-oil product also contained high oxygenated compounds as acids with low pH value. Further improvement of fuel product properties from CR thermal conversion can be accomplished by upgrading the input raw materials via torrefaction. In this work, the

effect of different temperatures of cassava rhizome torrefaction was studied using a batch reactor to produce quality solid raw materials which were, subsequently, subjected to gasification to obtain quality fuel gas product.

2 Experimental

2.1 Biomass sample

The cassava rhizome (CR) used is agricultural waste from the tapioca field from the Nakon-sawan province in Thailand. The picture of the CR samples is shown in Fig. 1. The CR was air-dried for 24 h to reduce the moisture and then grinded and sieved to 0.850 mm – 2 mm. The analysis of moisture content, volatile matter, and ash was performed by ASTM E-871, ASTM E-872, ASTM E-1755-01, respectively. The elemental analysis was performed using the CHNO micro analyzer following the ASTM F-3174 method.

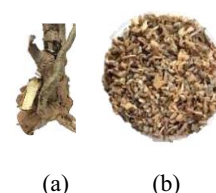


Fig. 1. Raw materials: (a) As received CR and (b) Ground and sieved CR 0.85 – 2 mm.

2.1 Torrefaction system

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The reactor vessel was a vertical stainless-steel tube with an internal diameter of 50 mm and a height of 500 mm. The temperature control was achieved by means of proportional–integral–derivative (PID) controller in which the reactor temperature was measured by the K-type thermocouples placed at the top, middle, and bottom sections of the reactor. During each run, the CR was fed into the reactor in 90 g. N₂ flow of 1 l/min was used to purge the reactor for 15 min before beginning the experiment and continuously applied to ensure ideal pyrolysis atmosphere in the reactor throughout the trial. The furnace was then activated and controlled to reach the final torrefaction temperature of 220, 240, 260, and 280°C and then held for 30 min. After the completion of the torrefaction process, the furnace was turned off and left to cool to ambient the temperature. Then, the torrefied CR was collected. The samples were weighed and stored in an airtight container to avoid reabsorption of moisture. The liquid product, condensed in two conical flasks, was collected for further analysis.

2.2 Gasification system

In this study, a free-fall gasifier was utilized. The main reactor setup was composed of a biomass feeder, carrier gas controller, electrical furnace, stainless-steel reactor, condenser, and gas collection system. Reaction temperature was 600 – 800°C. The ratio of N₂ and O₂ was adjusted to a target equivalence ratio (ER = 0.4). The CR was semi-continuously fed into the system at a rate of 1.0 g/min for a 20-min run. The liquid products, such as tar and other heavy hydrocarbons as well as condensate, were retained in condensers and gas washers. The gaseous product was analyzed with a portable gas analyzer (Gasboard-3100p) which is capable of continuous real-time qualification of CO₂, CO, H₂, CH₄ and C_mH_n. The solid product from the gasification process was settled at the bottom of the reactor and, later, collected for further analysis.

3 Results and discussion

3.1 The solid fuel properties of torrefied CR

The component, proximate, and ultimate analyses of CR when compared with other studies were as listed in Table 1. The CR sample used in this work showed proximate and ultimate analysis values comparable with previous works [3, 5]. The CR raw materials have less fixed carbon (10–20 wt%), more volatiles (65–81 wt%). Lower heating value (LHV) range in CR was 15–20 MJ/kg which similar to typical biomass. The yield of the liquid product was improved from 6.95 wt% to 11.72 wt% when the temperature increased from 220°C to 280°C. The yields of the gaseous product were relatively small for the torrefaction at this temperature range.

The proximate analysis of the torrefied CR at temperatures of 220, 240, 260, and 280°C are shown in Fig. 1. It was found that the removal of volatile matter and moisture content led to a decrease in the O/C ratio. Volatile matter refers to the part of the CR that was

released when the CR was heated at 220–280°C. The loss of volatile matter of CR was around 40 wt%, which resulted in higher fixed carbon content of 37–40 wt%. The ash content increased from 5.22–15.26 wt% after torrefaction at 220–280°C. The effect of the torrefaction temperature is more pronounced than other factors as the volatile matter content of the torrefied CR decreased significantly with an increase in the temperature.

Table 1. Characteristics of Cassava Rhizome.

Properties	This work	[3]	[5]
Proximate analysis (wt.%)			
Moisture	8.60	8.80	0.83
Ash	5.22	11.20	3.72
Volatile matter	74.70	65.00	76.21
Fixed carbon	12.02	15.00	20.08
Ultimate analysis (wt.%)			
C	37.60	49.50	52.33
H	5.41	6.50	5.95
N	0.37	1.10	1.03
S	0.15	–	0.08
O	37.50	42.90	40.62
Other*	18.97	–	–

The fixed carbon, ash and carbon content of the torrefied CR also increased with the temperature. Likewise, the previous studies with torrefied biomass, such as reed canary, wheat straw, eucalyptus wood and bark, resulted in a higher content of the ash remaining in the biomass samples [4-5]. However, the moisture content in the torrefied CR in the present study was less than 0.20 wt% with a torrefaction temperature of 280°C.

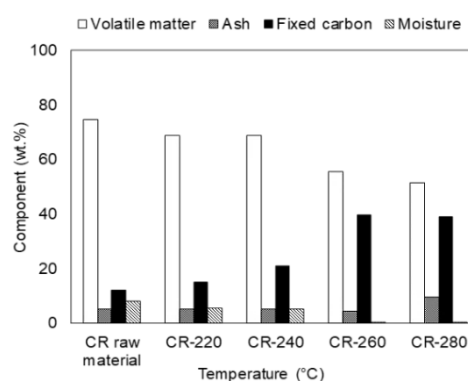


Fig. 1. Proximate analysis of CR and torrefied products.

The results of the mass yield, energy yield, and energy density (ratio) from the present study are presented in Table 2. During torrefaction, only volatile matter with low calorific value are removed as most of the CR mass loss, though this does not result in any significant energy reduction. Here, 31.97 wt% of the weight loss occurs during the torrefaction at high temperatures (280°C). Some authors have already reported greater weight loss when lignocellulosic samples were torrefied above 250°C. This can be because each pseudo component (hemicellulose, cellulose and lignin) is particularly affected at temperatures above 250°C.

The gas yield during torrefaction increased monotonously with an increase in the reaction temperature. The energy density ratio altered with the temperature in which the

optimal temperature of 260°C and 280°C gave the energy density ratios of 1.36 and 1.28, respectively. The LHV of the CR raw material was 15.37 MJ/kg. After torrefaction at temperatures of 220°C, 240°C, 260°C, and 280°C, LHVs of 16.45 MJ/kg, 15.64 MJ/kg, 20.86 MJ/kg, and 17.90 MJ/kg were obtained, respectively. The relationship between the LHV, the energy yield and the mass yield with the torrefaction temperature is shown in Table 2.

Table 2. Properties of CR torrefaction at different temperatures.

Properties	CR-220	CR-240	CR-260	CR-280
Mass yield (wt.%)	92.54	89.10	79.41	68.03
Energy yield (%)	99.07	96.98	88.16	77.81
Energy density ratio	1.07	1.12	1.36	1.28
LHV(MJ/kg)	16.45	17.30	20.86	19.70
C	45.45	45.39	51.25	49.39
H	4.22	4.22	3.42	3.55
N	<0.01	0.29	0.12	0.59
O	50.33	50.11	45.22	46.47

This ultimate analysis can also be used to classify the biomass using the Van Krevelen diagram (Fig. 2). The Van Krevelen diagram was established with the samples' O/C ratio as X-axis and H/C ratio in Y-axis. The O/C and H/C ratios decrease parallel to the torrefaction temperature 220–260°C. The effect of torrefaction on major chemical elements in the samples is significant. Before the torrefaction, the CR raw material has the highest O/C and H/C atomic ratio. CR has an O/C ratio of 1.12 and H/C ratio of 1.73. With torrefied CR at 220°C, these ratios are reduced to 0.63 and 1.11, respectively. The O/C ratio reaches a value of 0.66 and the H/C ratio a value of 0.79 for CR-260. This result is related to the decreasing of oxygen content in the torrefied CR, for O/C in CR raw material was 1.12 to 0.66 when torrefied at 260°C.

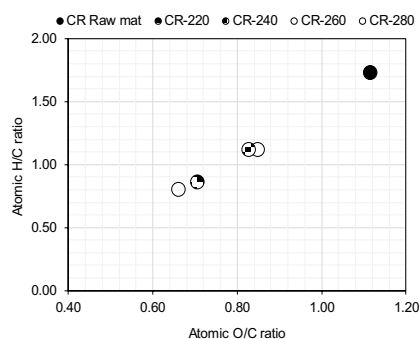


Fig. 2. Van Krevelen plot for CR and torrefied CR at 220–280°C.

The relation between the CR heating value and hydrogen-oxygen content can be confirmed with the heating value of torrefied CR, as shown in Table 2. The Nitrogen content in the CR raw material was reduced by more than 50%, from 0.37 to 0.12 at a temperature of 260°C and was not present when torrefied at 220°C. The NO_x formation during torrefaction and gasification is

negligible due to the low nitrogen element in CR. The results indicated that the heating value of torrefied CR increases by more than 35% when processed at 260°C for 30 min.

3.2 Gasification of torrefied CR

The major component of gases from gasification are CO, H₂ and CO₂. The product yields from gasification were as illustrated in Fig. 3. The gas quantity derived from utilizing CR-260 as raw material increased to 55.45, 60.21 and 67.00 wt.% for temperatures of 600, 700 and 800°C, respectively, which are 10–15% less than that of the CR raw material. It is important to note that the pyrolysis step that occurs during the process also contributes to the CO₂, CO, CH₄ and lower amounts of H₂ and other hydrocarbons. These result from the primary decomposition of the solid fuel and secondary reactions of the volatiles. This is mainly due to the loss of volatiles from the prior torrefaction process. Similarly, the gasification of CR-260 also resulted in a lesser amount of liquid yields (9.50–19.50 wt.%). It can be noted that increasing in gas yields with temperature is mainly from the greater decomposition of liquid products. These volatile hydrocarbons are converted to flue gas. The remaining non-volatile material, containing high carbon content, is referred to as solid or char. Here, the solid product was measured from 34.15%–25.50% as temperature the fell from 800°C to 600°C.

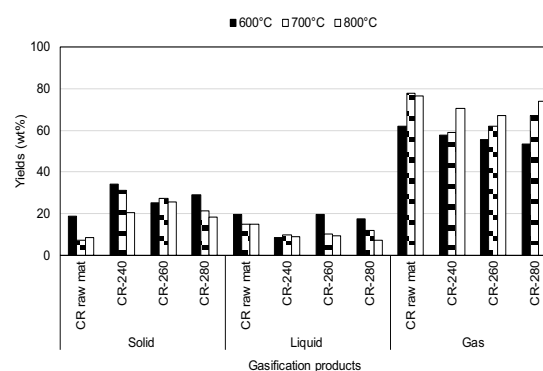


Fig. 3. Products from gasification of CR.

In the CR-260 gasification, hydrogen conversion efficiency to H₂ increased with an increase in temperature, as understood from Fig. 4 (a) and (b). Among the CR raw material, CR-260 and CR-280 indicated significant differences in terms of hydrogen conversion to H₂: For CR-260, as gasification temperature increased from 600°C to 800°C, hydrogen conversion changed from 14.11% to 29.95% while minimal increase was obtained from the CR raw material. From 600 to 800°C, the H₂ content was increased greatly. The phenomenon of higher H₂ gas occurs because of a rapid pyrolysis step when CR is dropped into the reactor. During this step, any available oxygen from H₂O, CO₂, or CO evolving from the CR structure itself is adsorbed by the porous CR particle. The trapped oxygen can react with the char and CO then convert to CO₂ at all gasification condition (600–800°C). Hence, CO₂ contributes to the increases in its concentration. In this work, the higher temperature was

not favourable for CO production. Hence, the content of CO decreased with an increase in temperature. This results in a rather steady amount of CO in the gasification product. CO obtained from the CR gasification is less than the previous works as described in the next section. This is because of the difference in the gasifier set-up and biomass. The CO concentration in the gas composition of Sadhwani et al.'s (2016) study increased continuously throughout the temperature range. The CO value changes from 5.8% up to 11.3% at a temperature range of 700°C to 934°C. This can be concluded as a result of a difference in the biomass type, gasification, carbon dioxide as an oxidizing medium, and the bubbling fluidized bed gasifier. Additionally, the types of the thermal conversion reactor and the operating conditions, such as the temperature, oxidizing agent, biomass particle size and type of bed/catalyst materials, influence the gas products and yields [6-9].

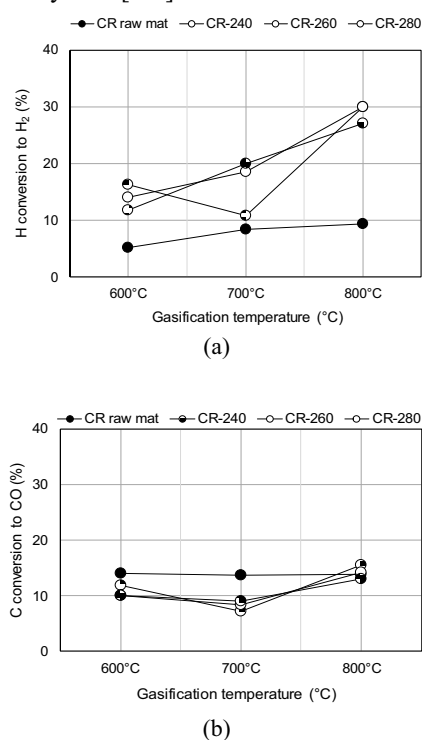


Fig. 4. Gas product from gasification: (a) Hydrogen conversion to H₂ and (b) Carbon conversion to CO.

From the gasification of the CR raw material, H₂/CO was lower than that of the torrefied CR at any condition. The H₂/CO ratio obtained from the CR gasification showed a maximum value of 0.61 at 700°C, while using CR-260 as a raw material yields a much higher ratio of 2.25 at similar gasification conditions. However, the H₂/CO molar ratio was decreased with an increase in reaction temperature, due to the increase in the concentration of CO. This is because the water–gas shift reaction favors the generation of CO at a higher temperature. Likewise, Yan et al.'s (2010) work on steam gasification of Pinus char in a fixed-bed reactor reported H₂/CO ratios of 4.15 and 3.74 at 800 and 850°C, respectively. It can be noted that the effect of the steam medium in the gasification process improved the carbon conversion efficiency. The

fractions of the CO, CO₂, and H₂ were influenced by the equilibrium of the water–gas shift reaction. Furthermore, the syngas from the air gasification with H₂/CO ratio > 2–2.5 would be suitable for the Fischer–Tropsch process (gasoline and light olefins synthesis) just as for the case of CR-260 at 700°C. While the ratio of 1.41 from gasified CR-260 at 600°C can be applied in the production of acetic acid, aldehydes, isobutane, isobutanol, and higher alcohols (C1-C6).

4 Conclusion

Biomass torrefaction has a positive effect on the product from the subsequent gasification process. The O/C and H/C from cassava rhizome torrefaction are 0.66 and 0.79 respectively. A lower O/C ratio indicates the increased content of C and a calorific value which implies higher gasification efficiency. The properties of torrefied cassava rhizome is comparable to that of peat, as the heating value of cassava rhizome increased from 15.37 MJ/kg to 20.86 MJ/kg. CR torrefaction enhances the gasification, in which hydrogen conversion to H₂ increased significantly, which led to improved H₂/CO when compared with non-torrefied biomass. Further research should focus on the possibility of utilizing the by-products from this process (liquid and gas) to alter the torrefaction atmosphere which may, consequently, improve the efficiency of the overall process as well as the quality of the torrefied solid.

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