Conversion of cassava rhizome using an in-situ catalytic drop tube reactor for fuel gas generation

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ABSTRACT

The air-gasification of cassava rhizome mixed with $Ni/\alpha-Al_2O_3$ catalyst in a drop tube reactor for production of fuel gas was carried out in this work. The conversion was performed at different temperatures from 873 to 1073 K, equivalence ratio (ER) of 0.2—0.6, and semi-continuous feeding of raw material for 30 min. Gas yields, cold gas efficiency (CGE) and lower heating value of fuel gas (LHV) were compared with non-catalytic cases. Generally, higher temperature and ER significantly improved the performance of cassava rhizome gasification. Similar for both of non-catalytic and catalytic cases, at optimum temperature of 1073 K and ER of 0.6, the maximum gas yields were closed to 80% while yields of char and tar were kept minimal at 4% and 11%, respectively. Addition of prepared catalysts resulted in greater CGE and LHV of 92% and 8.6 MJ/N m^3, respectively, comparing to the non-catalytic case of 61% and 6.36 MJ/N m^3, respectively. Moreover, the measured gas distribution data were comparable with the result obtained from thermodynamics conversion model based on minimization of Gibbs free energy of product gases using elemental composition of cassava rhizome ($C_{3.13}H_{5.2}O_{3.52}N_{0.03}S_{0.04}$.) constrained by mass and energy balances for the system. As a result, the gas product distribution and characteristics obtained from this experimental implied its suitability for heat and power applications.

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1. Introduction

The depletion of fossil fuels and concern over global warming and climate changes has stimulated a search for alternative forms of energy that are renewable and environmentally friendly. Biomass is arguably one of the great potential renewable resources, due to its abundance and environmentally benign aspect. Biomass can be converted to energy via thermochemical conversion processes, such as direct combustion, pyrolysis and gasification. Thailand is an agricultural based country that has a variety of associated by products. The major ones are cassava, sugar cane, paddy and maize which yield cassava rhizome, bagasse, rice husk and corn stalk as corresponding residues, respectively. Large quantities of about 8—10 million tonnes of cassava rhizome are generated by cassava plants. Cassava rhizome could be used for energy production by combustion process or transformed into fuel gas by gasification technology. Several agricultural residues had been gasified or pyrolyzed in previous experimental works [1—4] but report on gasification of cassava rhizome is very limited.

The gasification process is one of the promising thermochemical conversion methods. Using biomass sources, such as forestry and agricultural wastes, is an ethical solution the food versus fuel debate, but they require a robust conversion technology for efficient and economical fuel production. The primary reaction of biomass gasification involves endothermic devolatilization step, which releases a large amount of undesired tar products. High tar emission is a major problem for using biomass as a feedstock in the gasification process. Tar is a complex mixture of condensable heavy hydrocarbons including both long chain and poly aromatic hydrocarbons with up to five individual rings [5,6]. These tar products have low reactivity and may cause damage in biomass gasification systems. Tar may be reduced by means of adjusting operating conditions, using mechanical separations (cyclones, filters, and scrubbers) and implementing catalytic gasification treatment. The use of catalytic processes can be separated into 2 methods: primary and secondary. In primary method, the catalyst is incorporated or mixed with the feed biomass to achieve the so-called *in-situ* catalytic gasification. The later method involves addition of catalysts in a secondary reactor to remove the tar outside the main gasifier

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Nomenclature

f	fugacity (atm)
G^t	total Gibbs free energy of system (kJ)
$\overline{G^0_{f,i}}$	standard Gibbs free energy of formation (kJ/kmol)
n	numbers of moles
P	pressure
R	universal gas constant (8.314 kJ/kmol K)
T	temperature (K)

Greek letters

y_i	mole fraction of gas species i $\left(i = \frac{n_i}{n_{tot}}\right)$
μ	chemical potential
$ø$	fugacity coefficient

Superscripts

o	standard reference state

Subscripts

i	ith gas species
tot	total

[7,8]. The basic type of catalysts is dolomite, a natural mineral, which has been widely tested in biomass gasification. The efficiency of calcined dolomite in reducing tar during gasification depends on the gasifying agent [4,9,10]. Besides minerals, combining metals such as nickel, platinum, palladium, rhodium, and ceria with several supporters was developed for catalytic tar destruction. Tomishige et al. [11] reported the Rh/CeO$_2$/SiO$_2$ addition during the gasification with air, pyro-gasification, and steam reforming of cedar wood. Asadullah et al. [12] who tested the Rh/CeO$_2$/SiO$_2$ with biomass in dual-bed gasifier reported high conversion to gas and good selectivity of syngas. Ni-based catalysts were studied for biomass gasification such as works by García et al. [13] and Pengmei et al. [14] who steam gasified pine sawdust. They found that Ni-based catalyst was active for tar cracking in the primary reactor with temperature ranging from 973 to 1073 K [15]. Ni catalyst is noted to be commercially available and very effective not only for tar reduction but also for decreasing the amount of nitrogenous compounds [16].

The assessment of the gasification process by analyzing the energy and exergy efficiencies is a productive method to understand the progression of the interested chemical reaction process. There are a number of researches on analysis of biomass gasification in fixed bed reactor which based on a chemical equilibrium modeling or thermodynamic equilibrium analysis. These models are typically based on Gibbs free energy minimization [17,18]. Some works also applied the thermodynamic model to predict the equilibrium composition during supercritical water gasification (SCWG) of glucose, cellulose and biomass. They found that the model prediction measurement is acceptable within the degree of deviation [19].

Several software packages based on the Gibbs free energy minimization may be used for thermodynamic biomass gasification estimation which can then predict the concentrations of chemical species when specified elements or compounds reach a state of chemical equilibrium [20]. In addition to carbon, hydrogen, and oxygen, biomass also composes of many though much smaller amount of inorganic species and mineral content. During biomass gasification process, numerous gaseous, volatile alkaline and other harmful compounds in gas phase or in condensable forms. They can corrode or foul downstream process as well as deactivate most catalysts. Prediction of the occurrences of these species would enable engineers to design more robust biomass conversion systems. Therefore the fate of inorganics during biomass gasification was the main focus of some previous works such as Froment et al. [21] who clarified the behavior of some inorganics and major elements for wood gasification in several reactors (fluidized bed and entrained flow) under autothermal conditions. It can be noted that the elemental measurements agreed with the calculation for N, S, Cl, Al, Ca, Mg and Mn but could not predict for K and Na because these alkaline elements are in limited amount in the gas sampling.

The present work predicts the composition of the producer gas for CR gasification on the basis of stoichiometric thermodynamic equilibrium with the aim to compare the results with the measurement of fuel gas and other volatile produced from air-gasification at different operating conditions (ER and temperature) using a drop tube gasifier with primary catalytic method of nickel supported on α-Al$_2$O$_3$ catalyst. Thermodynamic equilibrium calculation was performed using Gibbs free energy minimization calculation.

2. Experimental

2.1. Raw material

The cassava rhizome (CR) sample used in this work was obtained from tapioca fields in an eastern province of Thailand. CR sample was first grinded to about 0.2–2.0 mm size. The dried biomass samples were characterized for bulk density, proximate analysis (moisture content, volatile content, ash content and fixed carbon content (by difference)), elemental analysis and heating values. Analysis results of the sample are listed in Table 1. The CR elemental compositions of carbon, hydrogen, oxygen, nitrogen, and sulphur were found to be 37.60, 5.41, 55.93, 0.37, and 0.69 wt.%, respectively, in which the corresponding empirical formula may be written as C$_{3.13}$H$_{5.2}$O$_{3.52}$N$_{0.03}$S$_{0.04}$. The CR has a typically compact lignocellulosic fibrous structure as noticed from its SEM analysis.

2.2. Catalyst preparation

In this experiment, α-Al$_2$O$_3$ supporter has surface area of 7.39 m^2/g and particle size of 7.55 μm. The 12Ni/α-Al$_2$O$_3$ catalyst was prepared by impregnation method. The catalyst was calcined in air at 1123 K for 3 h and reduced in H$_2$ at 973 K for 2 h and sieved to particle size of 15 μm. In any trials, catalyst was carefully mixed with the cassava rhizome at 20 wt.%.

2.3. Gasification system setup

In this study, a laboratory-scale drop tube reactor was implemented. It composted of a biomass feeder and an electrical furnace. Reaction temperature was regulated by a PID temperature controller from 873 to 1073 K. Gas pre-heater was used to warm up carrier gas (nitrogen) prior to enter the reaction zone. Alumina balls (diameter 1 mm) were placed as supporting material at the lower

Table 1
Characteristics of cassava rhizome.

Proximate analysis	wt.% (dry)	Ultimate analysis	wt.% (dry)
Moisture	8.60	C	37.60
Ash	0.74	H	5.41
Volatile matter	74.70	N	0.37
Fixed carbon	15.96	S	0.69
		O	56.20
Bulk density (g/ml)	0.12	LHV (MJ/kg)	15.37