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Product Gas Distribution and Composition from Catalyzed Gasification of Mimosa

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Abstract- The aim of this study is to analyze the potential of giant sensitive plant or Mimosa for gaseous fuel production by means of gasification process. An experimental study was carried out in a bench scale, fixed bed gasifier with air at atmospheric pressure. Parametric investigation was performed to determine the effect of temperature (600-900°C), collection time (10-110 min) and catalyst to biomass ratio (0.5-2) on product gas yields and composition. Experimental results showed that high temperature favors hydrogen, carbon monoxide and carbon dioxide yield (11, 18 and 24 mol %), while methane was found to follow opposite trend. Production rates of hydrogen and carbon monoxide appeared to increase during volatile releasing step, but decrease during carbonization. With catalyst to biomass ratio of 1, high hydrogen and carbon monoxide concentrations in the product gas (27 and 29 mol%, respectively) were achieved.

Keywords- Biomass; Dolomite; Fixed Bed; Giant Sensitive Plant; Thermo-chemical Conversion; Renewable Energy.

1. Introduction

Biomass plays an important role in the world's energy resources, now representing around 10-14% share after coal and crude oil [1]. It is a renewable source, which can be diversified and has continuous supply of energy, compared to fossil fuels. It is also carbon neutral in its life cycle. Biomass resources include agricultural and forestry products and their derivatives, woods, woody plants and weeds, municipal solid wastes, animal wastes, wastes from food processing, and aquatic plants and algae. Biomass can be converted into useful forms of energy by means of a number of different processes to meet a variety of energy needs, including heat, electricity, transportation fuels and chemicals. Thermochemical conversion is well known process for biomass conversion from which includes direct combustion, pyrolysis, liquefaction, and gasification.

Gasification is a process used to convert biomass into a combustible gas. Gasification of biomass with air, oxygen, steam or a mixture of these gasification medium is a well established technology. The process produces a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, methane, and light hydrocarbons with organic and inorganic compounds from following reactions [2, 3].

It is well documented that important parameters affecting gas yields, gas compositions and tar content include biomass composition, temperature, heating rate, residence time, equivalence ratio (ER) and type of medium. Typically, increases in temperature, heating rate and residence time lead to increased gas product yields from gasification [4]. With increasing ER, the gas yields such as hydrogen and carbon dioxide were increased, while carbon monoxide, tar and low heating value of gas product was decreased [5, 6]. Low temperatures have some disadvantages such as low heating value of product gas and high tar content [7]. In order to obtain high gas yields, high temperatures were employed or catalytic substances were used to obtain high yields of fuel gas and reduce its tar content. Some attentions were paid in using dolomite as a catalyst in biomass gasification because it is inexpensive and abundant. But dolomite is known to be significantly active only above 800°C such that tar can be reduced by over 90% [8]. Dolomite was also reported to be effective as an in-bed additive for upgrading the product gas from air gasification process [5, 9].

One type of biomass sources that is often overlooked is weeds. Mimosa, known in Thai as a giant sensitive plant (*Mimosa pigra L.*) is one of the worst weeds because of its invasiveness, potential for spread, and economic and environmental impacts [10]. Mimosa forms dense stands that replace all native plant. It invasion threatens crop production. The inedible and thorny mimosa smothers and replaces grasslands, blocks access to stock watering points and hinders mustering, reduces the biodiversity of plant and animal life on the floodplains by outcompeting native plants and reducing available habitat for animals. The habitats of Mimosa are wet land places in the humid and sub-humid tropics. It grows along roadsides, watercourses and seasonally inundated wetlands. It is found on a wide variety of soils and is tolerant of flooding. Mimosa is native to tropical America but is now a serious weed in Africa, Australia [10], India, South-East Asia, Taiwan [11] , Northern part of Thailand and some Pacific islands [12]. It was purposely introduced to Thailand as a green manure and cover crop in tobacco plantation. It has been utilized for its ornamental value, medicinal use, and erosion control. Mimosa has also been used for animal feed, timber, temporary fences, and firewood. However, the use is still limited in small scale applications. Utilization as energy source may be useful options and a good mean for the weed management.

From the existing literature, reports on utilization of the weed as bioenergy material were quite scarce. Studies on thermal decomposition of Mimosa in inert and air atmospheres were carried out [13, 14]. Preliminary investigation on gasification of Mimosa in a laboratory scale[15, 16] and a pilot plant [17] showed promising results. But work on the effects of temperature and catalyst to biomass ratio on gasification of Mimosa is non-existent. Attempt was therefore made to fill this gap. In this study, influences of reactor temperature and catalyst to biomass ratio were experimentally studied. Effects of difference air flow rates and collection times on product gas yields and composition were also investigated.

2. Materials and Methods

2.1. Raw Biomass Material

Mimosa was used as biomass material in this study. The stalk of Mimosa were cut, milled, sieve and classified to fraction of particle size of 0.1-0.7 mm. Proximate and ultimate analyses as well as analysis for the heating value and composition of Mimosa were carried out [15]. Results of this biomass samples are presented in Table 1. It was shown that Mimosa has high volatile content (71.1 %). Carbon and oxygen account for 43.9 and 48.7% w/w, respectively, with calorific value of 17.5 MJ/kg. These values are similar to those of hard woods. The weed appears to be a promising candidate for bioenergy material.

2.2. Experimental Setup and Procedure

The experimental setup employed in this work was similar to our previous study [16]. The laboratory scale, test rig used in this study is a fixed bed reactor, schematically shown in Fig 1. The cylindrical reactor has an inside diameter of 40 mm and is 0.5 m high. It was equipped with a 5 kW heating coil and surrounded by thick insulating wool. The heating coil and the reactor were electrically separated by small ceramic spacers. There was a fixed grate between the middle and the bottom. The outlet of the gasifier is connected to gas coolers and traps where tarry components are removed, and to a sampling bag. Air is supplied from a compressed tank, serving as a purge gas and protective gas to avoid coking occurred on the surface of the reactor before and after operation and is measured with a calibrated flow meter. Reaction temperature is measured by a thermocouple inserted thru its cover and can be automatically controlled by means of a data logger. Prior to the test, the empty reactor was heated externally by an electrical heater for about 30 min.

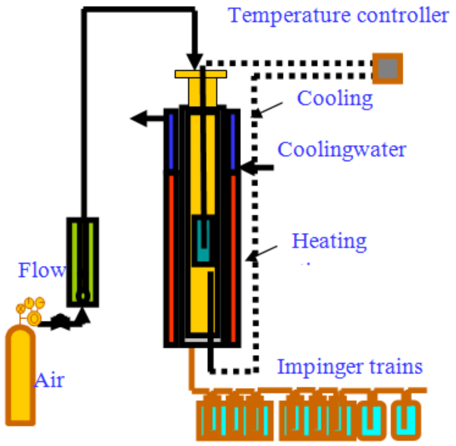

Fig. 1. A fixed bed reactor

Pre-weighed batches (10 g) of biomass materials were then introduced into the reactor. Air was supplied and regulated such that oxidation zone inside the gasifier can be established and gaseous products produced from the biomass is combustible.The reaction was initiated by moving the basket downward into a heating section where the reaction temperature was kept at the pre-determined values. After about 110 min, the biomass sample was taken out of the heatingsection immediately into a cooling section to terminate the reaction. In this study, reactor temperature was obtained from thermocouple readings inside the reactor and represented as gasification temperature. The gaseous products were collected at the exit of the dry filter in a 0.40 dm3 sampling bag. The volatiles were immediately sent for composition analysis. A Shimadzu Gas Chromatography model GC-8A was used to analyze CO, CO_2, H_2, CH_4, O_2 and N_2. The high purity standard gases were used to calibrate the instrument. The duration of operation for certain condition is determined by ensuring that no combustible gas is released and gas yield is dropped to more than 10% of its steady value. At the end of every experiment, the solid and liquid residues are weighed to determine mass balance. The gas yield is computed directly, based on its measured volume. Experiments were performed for air gasification at 100 $cm^3 min^{-1}$ with Eq.(1) varying temperatures between 600 - 900°C, Eq.(2) with varying gas collection times, and Eq.(3) catalytic gasification with natural dolomite at varying catalyst and biomass ratios at 900°C. It should be noted that the residence time of the volatile phase is varied during the experimental runs depending on the air flow rates. All experiments were carried out isothermally.

3. Results and Discussion

3.1. Effect of Reaction Temperature

The effect of temperature on product distributions from gasification of Mimosa is shown in Fig. 2.A clear increase in gas yields with increasing reaction temperature was observed, similar to that reported in [4, 18]. At higher temperatures, higher gas production may be attributed to the pyrolysis step [19] with endothermic (reactions Eq.(1, 3-5, 8), cracking reactions of the tar (reaction Eq.(2)) and gasification reactions of the char (reactions Eq(3, 5, 7, 8). These reactions are favorable at elevated temperatures, from 600 to 900°C. It was found that when the temperature was increased from 600 to 900°C, the gas yields increased from 59.5% to 81.1%, while the tar and char decreased from 20.5% to 11.9% and 20.0% to 7.0%, respectively. Reduction of the char yields with increasing temperature was due to higher degree of carbonization reaction with air [7]. Fig. 3 shows the effect of temperature on the gas composition. It was found that concentrations of H_2, CO and CO_2 were increased and whereas CH4 were decreased at elevated temperatures, in similar trends with those reported in [4, 6, 19-22]. A product gas with H_2, CO, CO_2 and CH_4, concentrations of 10.8, 17.9, 24.5, 12.6 and 5.1 mol% was generated at 900°C.

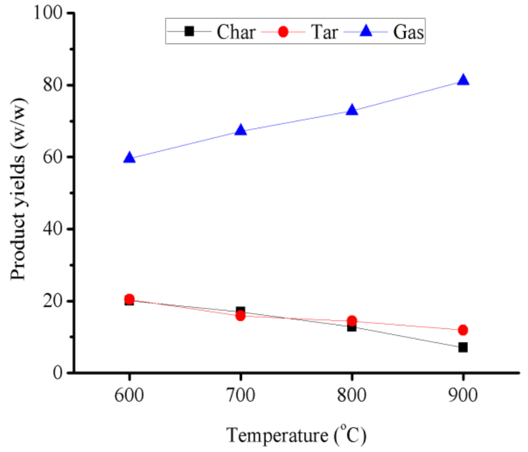

Fig. 2. Effect of temperature on product yields

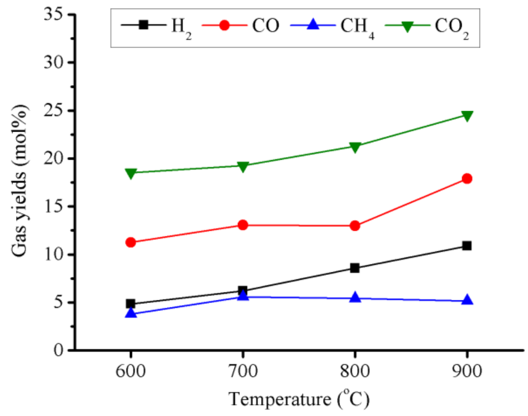

Fig. 3. Effect of temperature on product gas composition

From Fig. 4, increasing temperature resulted in an increase in the H_2/CO and CO/CO_2 at molar ratios from 0.4 to 0.6 and 0.6 to 0.7. Increase in temperature appeared to strengthen the endothermic reactions, such as reactions Eq.(3-5) and Eq.(8), leading to increased H_2 and CH_4 contents and decreased CO_2 contents.

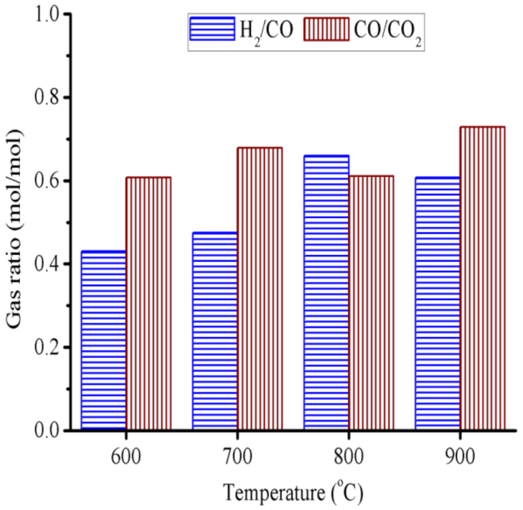

Fig. 4. Effect of temperature on product gas ratio

High concentrations of H_2 may come from thermal decomposition of heavy hydrocarbons and tars into lighter hydrocarbons (reaction Eq.(2)) [21, 24]. It was found to increase due to endothermic reactions Eq.(4-5) at low temperatures and exothermic reaction Eq.(6) at high temperatures. The increase in gas yields was also observed from 600 to 900°C. It might be attributed to the fact that reactions Eq.(3) and Eq. (5) were favored at high temperature [18], and reforming of tar and char were accelerated. From 600 to 900°C, the H_2 content was found to increase greatly. This observation could be a result of exothermic behaviors of reactions Eq.(8-10) [20, 21]. High CO_2 was produced from decomposition of carboxyl groups and from the exothermic reactions Eq(6-7). When temperature was increased, the CO_2 concentration was found to decline. The product gas from wood that has high content in lignin have high yields of CO_2 [22], similar to our observation here.

Gasification:
Biomass $\longrightarrow$ char + tar + gases (H_2, CO, CO_2, CH_4) (1)
Thermal decomposition:
tar $\longrightarrow$ gases (H_2, CO, CO_2, CH_4) (2)
Boudouard reaction:
$C + CO_2 \leftrightarrow 2CO$ - 162 kJ/mol (3)
Steamreforming reaction:
$CH_4 + H_2O(g) \leftrightarrow CO + 3H_2$ - 206 kJ/mol (4)
Water gas reaction:
$C + H_2O(g) \leftrightarrow CO + H_2$ - 131 kJ/mol (5)
Water–gas shift reaction:
$CO + H_2O \leftrightarrow CO_2 + H_2$ + 41 kJ/mol (6)
Oxidation:
$C + O_2 \leftrightarrow CO_2$ + 408 kJ/mol (7)
Hydrogasification:
$C + 2H_2 \leftrightarrow CH_4$ - 75 kJ/mol (8)
Methane steam reforming reaction: (9)
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ + 206 kJ/mol
$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ + 165 kJ/mol (10)

3.2. Effect of Collection Time

Fig. 5 shows the effect of collection time at 800°C on gas yield. It was found that H_2 and CO increased from 7% and 18% to 14% and 29% after 20 min, and subsequently decreased to 5% and 10% after 110 min. Meanwhile, CO_2 was found to increase with time from 5% to 33%. Changes in H_2 and CO were similar to those reported by Encinar et al. [23]. The first 10 min was volatile releasing process. High volatile matter content biomass material will have long devolatilization time which can delay the subsequent char gasification and carbonization processes [24]. An increase in residence time of the volatile phase resulted in increasing gas yield. There were many highly competitive reactions in these processes. Formation of H_2 and CO appeared to be more rapid than other gases. Within reaction time of 60 min, the yields of CO and CO_2 were parity, but after that, CO_2 was found to be more competitive [24]. High concentration of CO_2 seemed to suppress CO yield, in line with those reported by Mitsuoka et al. [25].

3.3. Effect of catalyst

In this work, dolomite was used as catalyst for gasification. The effect of catalyst was studied for the temperature at 900°C. Fig. 6 shows the gas, tar and char yields between the non-catalytic and catalytic processes. It can be seen that the gas yields were higher when catalyst was used, while tar and char yields were lower for the uncatalyzed process. This observation was in line with [22, 26].

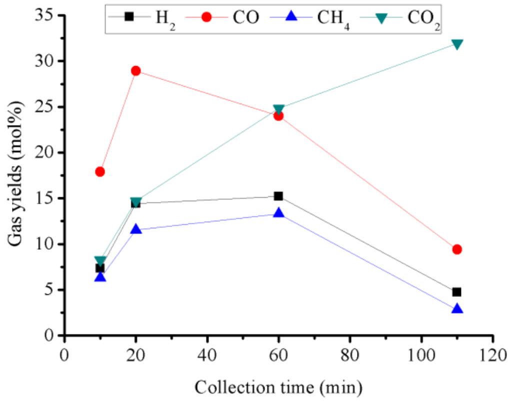

Fig. 5. Effect of collection time on product gas composition at 800 °C

Catalyst was found to have positive effect on tar elimination causing change in the gas composition and heating value [27].

The evolution of the concentrations of the gas produced (%mol) as a function of catalyst to biomass ratio at 900°C was shown in Fig. 7. It can be seen that the presence of dolomite clearly encouraged the production of H_2. At the catalyst to biomass ratio equal to 1, H_2 content was amounted to 27.6 mol% and CO was about 29 mol%. The quantity of CO_2 was found to be higher than that obtained from the uncatalyzed case [22, 28]. As far as the product gas ratio was concerned (Fig. 8), H_2/CO was found to increase with increasing catalyst to biomass ratio while The light hydrocarbon appeared to decrease. H_2/CO and CO/CO_2 exhibited similar trend that they reached maximum at the catalyst to biomass ratio of 1. At 900°C, the presence of catalyst did not appear to improve H_2 production.

In comparison with temperature, the presence of the catalyst was found to affect the product gas compositions more. For non-catalyzed experiments, water-gas reaction seemed to be promoted at high temperatures. This was consistent with the tendencies found from 600 to 900°C where CO and CO_2 were decreased. The catalyst used appeared to cause higher CO_2 content in the product gas [7, 29].

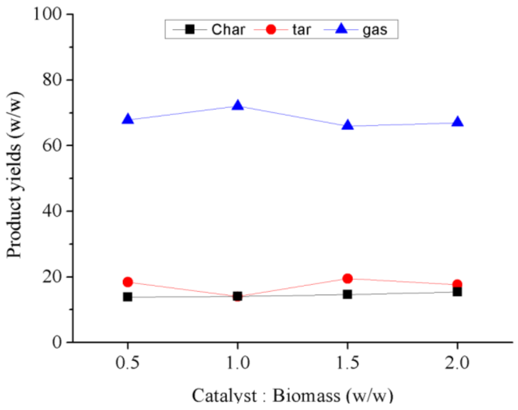

Fig. 6. Effect of catalyst biomass ratio on the product yields

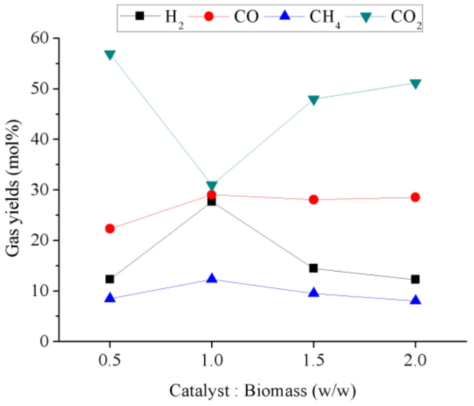

Fig. 7. Effect of catalyst to biomass ratio on product gas composition

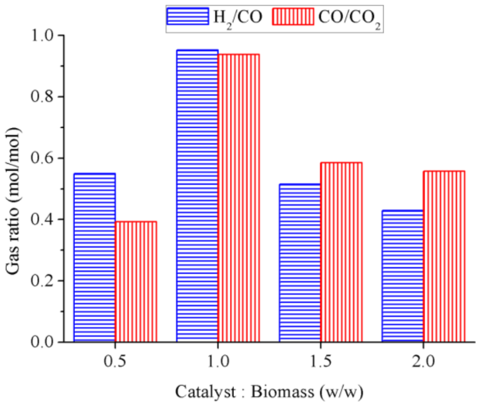

Fig. 8. Effect of catalyst to biomass ratio on gas ratio

4. Conclusion

Study on air gasification of Mimosa has been presented. Effect of reaction temperature and catalyst to biomass ratio on the product distribution has been experimentally investigated. The results showed that increasing temperature have positive effect on the production of H_2, CO and CO_2 and reduction of CH_4 content in the product gas. Maximum H_2 concentration of 11 mol% was achieved at 900^oC.

The collection time appeared to have positive effect on H_2 and CO yields during devolatilization and char oxidation process. The presence of catalyst in gasification process was generally believed to improve the product distribution. However, within the range considered in this work, yields of H_2 appeared to peak at the catalyst to biomass ratio of 1. Increasing the amount of catalyst did not offer higher H_2 content.

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