HYDROGEN AND SYNGAS PRODUCTION VIA PYROLYSIS AND STEAM GASIFICATION OF BAGASSE IN A DUAL BED REACTOR

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Abstract

Steam gasification of bagasse followed by thermal cracking of tar was carried out at atmospheric pressure using a dual bed reactor. The first bed was used for the steam gasification and the second bed was used for thermal cracking of tar. Iron fillings were used as the packed bed material in the second bed. The effects of reaction temperature (600 to 900°C), packed bed height (40-100 mm) and steam/bagasse ratio on the product (char, tar and gas) yield and gas (H_2, CO, CO_2, CH_4, C_nH_m) composition were studied. Over the ranges of the experimental conditions used, the operating conditions were optimized for gasification temperature around 850°C, a steam/bagasse ratio of 0.6 and packed bed height of 100 mm, because a gas richer in hydrogen and carbon monoxide and poorer in carbon dioxide and hydrocarbons. It was observed that the steam gasification of bagasse in a dual bed process increased the gas yield from 0.622 to 0.762 (m^3/kg) and decreased the tar yield from 0.53 to 0.39 (g/g) compared to single bed process while the heating value of the product gas remained almost constant (10-11MJ/m^3). H_2 and CO yields increased to 18.02 and 49.3 vol.%, respectively and CO_2 yields shifted down to 27.06 vol.%. Methane and heavier hydrocarbon gases yields decreased to 5.34 and 0.262 vol.%. These variations are attributed to reforming of tar compounds with steam and/or CO_2 and water gas shift reactions.

Keywords: *Steam gasification; Bagasse; Dual bed reactor; Syngas production; Hydrogen production.*

1. Introduction

Recently, the global warming undesirable outcomes and energy supply issues have been drawn more and more attentions around the world. The anomaly climate is related to greenhouse gas concentration increasing so that how to reduce the greenhouse gas emissions became the major issue. Many scientists indicated that the development of renewable energy can effectively alleviate the current problems. Thus renewable energy should be widely explored to renovate the energy sources structure and keep sustainable development safe with increasing populations and economic development [1]. Biomass, in contrast to hydro, wind and sun, is the only renewable energy source that does not depend on the weather and guarantees a continuous energy generation.

Annually, more than six hundred thousand tons of bagasse is burned in Haft Tappe Industries Company in Iran, which creates serious environmental problems and wastes huge amounts of energy. There are several methods of utilizing this valuable biomass to generate energy and fuels, however, gasification processes, technologically offer more attractive option for large scale applications and is a more friendly way for using bagasse for energy purposes, given that due to the presence of non-oxidation conditions, the pollutant emissions are greatly low [2-9]. Gasification of biomass char using steam agent had notable advantages for the wide application. On the one hand, the gasification reaction was much more rapid using H_2O rather than CO_2 as an oxidant [10]. Theoretical calculations show that about 100 grams of hydrogen can be produced by one kilogram of bagasse. The hydrogen-rich gas produced from bagasse gasification, not only can be considered as an alternative energy source but also, hydrogen and synthesis gas produced in this process can be used in Oil, Gas and Petrochemical industries.

Substantial research on biomass gasification has been carried out during the past two decades, employing different gasifier configurations, oxidants, and modes of heating [1-18]. However, most of the biomass gasification studies conducted to date have been focused on the production

of direct-combustion gases, not on the production of hydrogen and synthesis gas (H_2 and CO) for subsequent use as an attractive feedstock for super-clean liquid fuels and chemical synthesis. It has been shown that, the steam gasification of biomass favors hydrogen and syngas yields [3-4, 8-10]. The optimum conditions obtained by different researchers are quiet different and strongly are dependent to the type of biomass. In our previous work [13], we studied the production hydrogen and synthesis gas via bagasse pyrolysis in a dual bed reactor. In this study, we planned to increase the hydrogen and synthesis gas yields by introducing the steam as a gasifying agent to the dual bed reactor system and enhance the gasification efficiency. Particular emphasis is given to measure the total gas, hydrogen and carbon monoxide yields and the low heating value (LHV) of the dry product gas.

2. Experimental

2.1. Materials

The biomass particles used for the experiments were obtained as shavings, from Haft-Tappe Industries located at Haft-Tappe, Khuzestan province, Iran. The biomass was dried in atmospheric conditions for two days, and ground to a particle size ≤ 1 mm diameter. The elemental composition of the whole biomass sample was analyzed using a CHNS analyzer (model NA 1500 from Carlo Erba Instruments).

2.2. System description

Experiments were performed in a dual-bed reactor system at atmospheric pressure. The scheme of the reactor is shown in figure 1. Reactor was made up of quartz tubing with 10 mm internal diameter and 700 mm length, and placed inside a tubular furnace with 20 mm internal diameter and 200 mm outside diameter with total heating length of 700 mm and two temperature controlling zones. Two separate K-type thermocouples were placed inside the reactor via two thermo-wells to maintain and monitor the temperatures of two reactor zones via two separate PID temperature controllers (Model: Autonics-TZN4S, 0-1000°C). Nitrogen was used as an inert carrier gas and supplied at the desired flow rate from a cylinder through a mass flow controller (Brooks's 5850 model). Water was injected into the reactor by a syringe pump (HX-901A Guangzhou Huaxi Medical Science Technology Co,Ltd.) at the desired flow rate. One glass condenser in series below the reactor was applied to condense the tar and cool down the product gases. The product gases were collected in the saturated brine solution column (length: 1 meter , diameter: 10 cm, saturated solution of NaCl in water) to prevent CO_2 dissolution. The brine solution column was further connected to the overhead surge tank to receive the displaced brine solution.
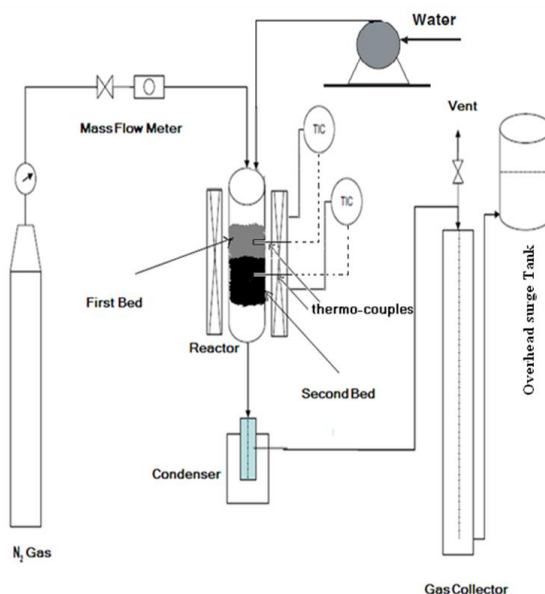

Figure 1 The scheme of the experimental setup

2.3. Experimental Procedure

Pyrolysis and steam gasification was carried out in the first bed while the second bed was used for further cracking of tar. Iron fillings (Shape: Spherical, Particle size: 200–1300μm, Surface area: 38 m^2/g, Density: 4.81 g/cm^3) were used as the packed bed material in the second bed. It was placed on the plug of quartz wool supported on the supporting mesh. The packed bed containing section of the reactor (second bed) was positioned in the second zone of the furnace. Bagasse was loaded to the first bed. Amount of bagasse loading was 1 g for all experiments, while the packed-bed height of filings varied from zero (single bed) to 100 mm. The N$_2$ flow rate was maintained at 40 ml/min. Water injection was started when the first-bed temperature reached to 100^{0}C. It took approximately 20–30 min to reach the final reaction temperature of 600–900^{0}C in the case of single bed experiments. In the case of dual bed experiments, the second zone of reactor was heated to the desired temperature (600–900^{0}C) with a nitrogen flow rate of 40 ml/min before the first zoon heating initiation. The reaction was allowed to be continued for the next 30 min after attaining the final desired temperature. In our previous work we found that the reaction time of 30 min is the best for this process [13]. Subsequently, the heating was stopped and the reactor was allowed to cool down. The experiments were performed 3 times under the same experimental conditions and the data reported here are averages of repetitive runs. Table 1 shows the design of expe-rimental (DOE) runs and the testing conditions. The reactor and glass condensers were cleaned using acetone and then dried with compressed air before next run.

Table1 Design of experimental runs

Run	Reaction Time (min)	First bed temperature (^{0}C)	Packed-bed height (mm)	Steam/Bagasse	Second bed temperature (^{0}C)
1	30	600	0	0.6	850
2	30	650	0	0.6	850
3	30	700	0	0.6	850
4	30	800	0	0.6	850
5	30	850	0	0.6	850
6	30	900	0	0.6	850
7	30	850	40	0.6	850
8	30	850	60	0.6	850
9	30	850	80	0.6	850
10	30	850	100	0.6	850
11	30	850	100	0.4	850
12	30	850	100	0.6	850
13	30	850	100	0.8	850
14	30	850	100	1	850

2.4. Product gas analysis

The volume of the collected product gas was measured on the basis of the displacement of the saturated brine solution. The product gas composition was measured using two gas chromatographs: Varian 3400 with a thermal conductivity detector (TCD) and Teyfgostar Compact with a flame ionization detector (FID). The volume percentage of each constituent compound in the gas product was calculated on the basis of the total volume of the N$_2$-free gas collected at the end of each run. The amount of condensed liquid (tar + water) in the glass condensers and the char left inside the reactor were measured by a weight difference before and after the reaction.

3. Results and discussion

The biomass CHNS analysis is given in Table 2. As indicated, the C and H content in the sample is 64.55%. The balance is mostly oxygen.

Table 2 CHNS analysis of biomass species

	(wt.%)
N	0.69
C	58.1
H	6.45
S	0.19
O	34.57

3.1. Effect of first bed temperature

Numerous studies have been carried out on steam gasification of biomass at the temperature range of 600–1000^{0}C [14–17]. Considering the literature range and limitations of the operation, the temperature range of the first bed for the present study was chosen to be 600–900 ^{0}C with steps of 50 ^{0}C while maintaining a steam/bagasse (wt./wt.) ratio of 0.6, N_2 flow rate of 40 ml/min and packed bed height of zero. The final temperature effects on the products (char, liquid and gas) yield and gas composition have been presented in Figures 2 and 3, respectively. As expected, with increasing temperature from 600 to 900 ^{0}C, the char and liquid (tar + water) yields decreased from 6.4 to 3.8 wt% and from 75 to 55 wt%, respectively, whereas gas yield increased from 0.222 to 0.571 m^3/kg. This could be explained by higher char conversion with steam and the thermal cracking/steam reforming of tar at higher temperatures.
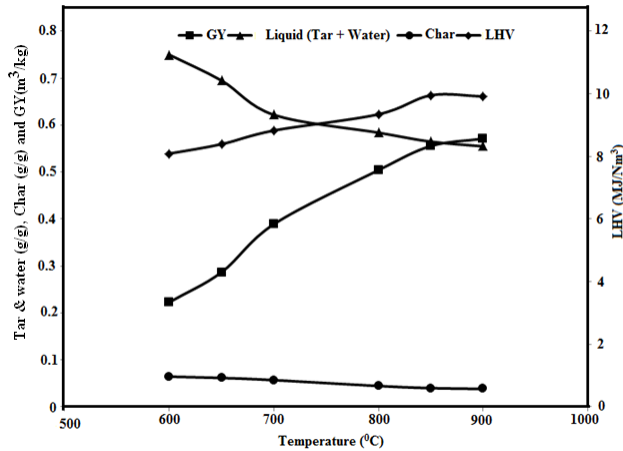

Fig. 2 Effect of final temperature of first bed on products yield (g/g of bagasse) at steam/bagasse ratio (wt./wt.) of 0.6
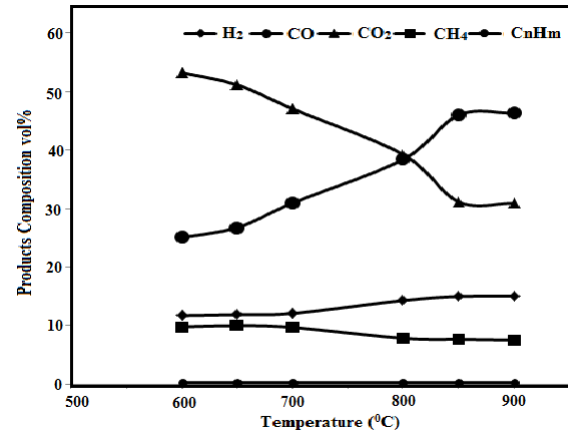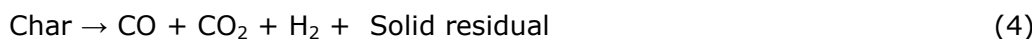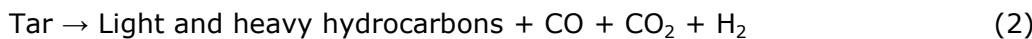
Fig.3 Effect of final temperature of first bed on gas composition (vol.%) at steam/bagasse (wt./wt.) of 0.6

It is generally referred by different authors that the process of biomass gasification occurs in three steps. First, a large amount of gas is produced in the initial pyrolysis at high bed temperatures. Second, the high temperature favors the tar cracking reactions, producing more light hydrocarbons and other gas phase products (CO, CO_2 and H_2). Third, char gasification is enhanced by the Boudouard reaction. The gasification mechanism of bagasse particles in the first bed may be described by the following reactions:

Bagasse → Gas + Tar+ Char   (1)

Tar → Light and heavy hydrocarbons + CO + CO_2 + H_2 (2)

Heavy hydrocarbons → Light hydrocarbons + H_2 (3)

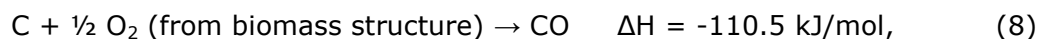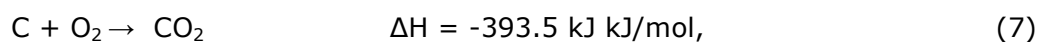Char → CO + CO_2 + H_2 + Solid residual   (4)

The final product gas composition of the biomass gasification process in the first bed of the reactor system is the result of combination of the above mentioned series of complex and competing reactions. The formation of H_2, CO and CO_2 through the final step of the gasification (Equation 4) can be studied by the reactions that govern biomass steam gasification, are the steam reforming reaction

C + H_2O → CO + H_2 ΔH = +131.3 kJ/mol,   (5)
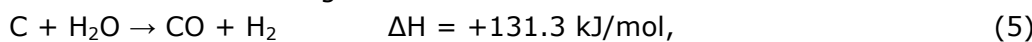
and the Boudouard reaction

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +172.5 \text{ kJ/mol}, \qquad (6)$$
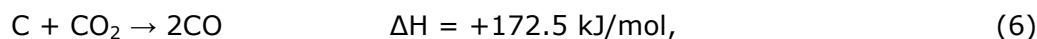
In addition to the pyrolytic cleavage and condensation reactions that break down the biomass lattice structure, the decomposition reactions of the oxygenated minerals releasing O_2, the oxidation of the char

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.5 \text{ kJ kJ/mol}, \qquad (7)$$

$$C + \frac{1}{2} O_2 \text{ (from biomass structure)} \rightarrow CO \qquad \Delta H = -110.5 \text{ kJ/mol}, \qquad (8)$$

and the water gas shift (WGS) and reverse water gas shift reactions (RWGS)

$$H_2 + CO_2 \leftrightarrow CO + H_2O \qquad \Delta H = \pm41.2 \text{ kJ/mol}, \qquad (9)$$
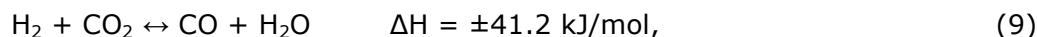
to release CO and CO_2 as the char degrades from a hydrocarbon skeleton to a mineral ash residue. Similar trends were obtained by other researchers [12,14,18]. The product gas was mainly composed of H_2, CO, CO_2, CH_4, and other heavier hydrocarbon gases. The H_2 and CO yields increased from 11.69 to 15.1 and 25.04 to 46.03 vol% (N_2 free basis), respectively, while that of CO_2 decreased sharply from 53.23 to 31.91 vol% with an increase in temperature from 600 to 900^{0}C. Increased carbon conversion as well as the Boudard reaction (equation 6) is partially responsible for the observed increase in CO and the corresponding decrease in CO_2 content at higher temperatures. Also, by increasing the temperature, methane and other heavier hydrocarbons volume percentages showed a marginal decrease from 9.76 to 6.41 and from 2.7 to 2.3, respectively. This could be explained by the likelihood of some secondary reactions of CO_2 as well as the steam-reforming reaction of hydrocarbons that produce CO and H_2. The low heating value of produced gases [13] showed a slight increase from 8.09-9.91 MJ/m^3. The gas compositions showed significant variation over the temperature range from 600 to 850°C. However, by increasing the temperature from 850 to 900°C, the variation of the gas compositions was not significant. The results obtained so far seem to suggest that the optimized steam gasification temperature for bagasse could be 850°C or above, because the gas obtained has greater content of hydrogen, fewer hydrocarbons and more importantly greater CO/CO_2 ratios. This temperature would also favor energy and carbon conversions, as well as gas yield.

Table 3 compares the steam gasification results with those of bagasse pyrolysis (without steam) in our last work [13] at 850°C, reaction time of 30 min and bed height of zero. This table shows that using steam as second gasifying agent increases the amount of produced gas by a factor of 1.4. Also the contents of H_2 and CO are significantly higher than that using pyrolysis process in the absence of steam. In addition the amount of CO_2 is significantly lower in the case of steam gasification. Higher rates of carbon conversion and Boudourd reaction are responsible for the observed increases in total gas, H_2, CO and the corresponding decrease in CO_2 content at steam gasification in comparison to pyrolysis in the absence of steam.

Table 3 Comparing the results of the steam gasification process and pyrolysis process [13] (T=850^{0}C, Reaction time=30min and Steam ratio=0.6)

Parameter	Steam gasification process	Pyrolysis process
GY (m^3/kg)	0.555	0.396
(Tar + Water) (g/g)	0.565	0.445
LHV (kJ/Nm^3)	9.955	11.06
CH_4(Vol%)	6.660	10.11
C_nH_m(Vol%)	0.240	0.45
H_2(Vol%)	14.96	13.70
CO(Vol%)	46.03	44.95
CO_2(Vol%)	32.11	30.65

3.2. Effect of packed-bed height

The packed-bed height of the second stage was varied from 40 to 100 mm with steps of 20 mm while keeping the final temperatures of the first and second bed at 850 ^{0}C, N_2 flow rate at 40 ml/min, and steam/bagasse (wt./wt.) at 0.6. Figures 4 and 5 shows the effect of the packed-bed height on the product yields and gas compositions. By increasing in the packed-

bed height, the liquid yield decreased from 53 to 39 wt%, while the gas yield increased from 0.622 to 0.762 m³/kg. H_2 yield increased from 15.13 to 18.02 vol.% and CO and CO_2 yields shifted up and down in the range of 46.76–49.3 and 31.71–27.06 vol.%, respectively. Methane yield showed a slight decrease from 6.12 to 5.34 vol.%. A while no significant variation was observed for other hydrocarbon yields (Their yields were constant in the range of 0.271–0.262 vol%). These variations can be attributed to the thermal cracking of tar over iron fillings and reforming of CH_4 and tar compounds (Equation 3) with steam and/or CO_2 and water gas shift reactions (equations 7 and 9).
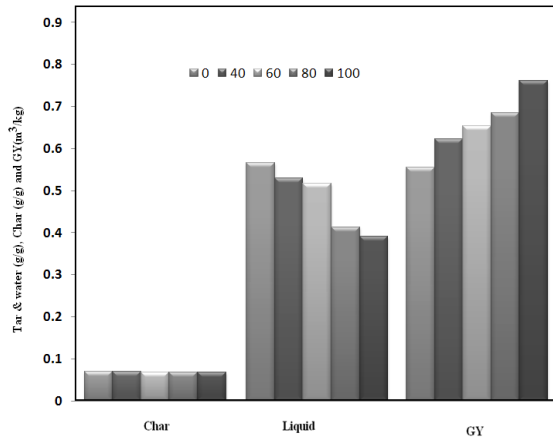

Fig. 4 Effect of packed-bed height on the product yield (g/g of bagasse) at steam/bagasse (wt./wt.) of 0.6, final temperature of first bed and second bed at 850⁰C
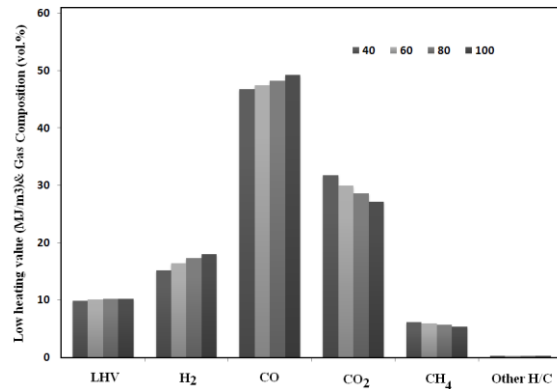

Fig. 5 Effect of packed-bed height on gas composition (vol.%) and Low heating value at steam/bagasse (wt./wt.) of 0.6, final temperature of first bed and second bed at 850⁰C

3.3. Effect of steam to bagasse ratio

The steam/bagasse ratio (wt./wt.) supplied in the reactor was varied from 0.4 to 1 while keeping the final temperature of the first and second bed at 850⁰C, N_2 flow rate at 40 ml/min, and packed-bed height at 100 mm. The effects of steam/bagasse on products yield and gas composition are presented in figures 6 and 7.
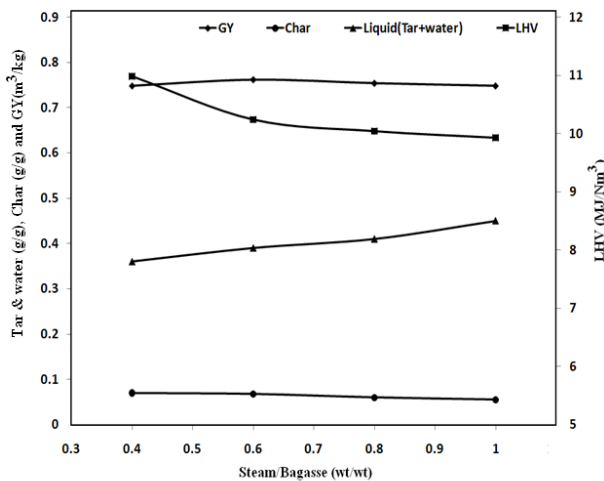

Fig 6 Effect of steam/bagasse (wt./wt.) on the product yield (g/g of bagasse) at final temperature of first bed and second bed 850⁰C, and packed-bed height of 100 mm
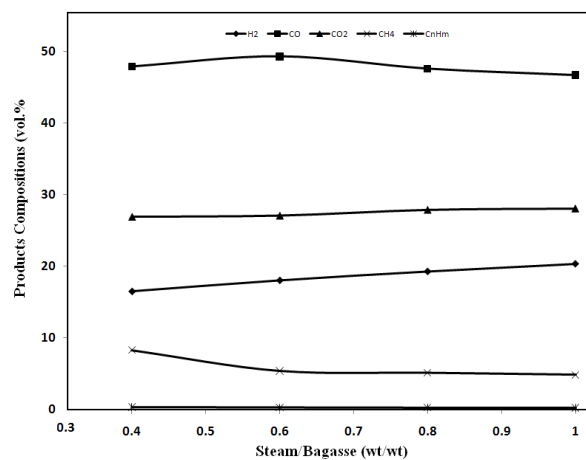

Fig 7 Effect of steam/bagasse (wt./wt.) on gas composition (vol.%) at final temperature of first bed and second bed 850⁰C and packed-bed height of 100 mm

As shown, by increasing in steam/bagasse weight ratio from 0.4 to 1, the char content decreased from 7 to 5.5 wt%, while liquid (tar + water) increased from 36 to 45 wt%. Also, by increasing in steam/bagasse weight ratio, the gas yield increased, reached the maximum of 0.762 m³/kg at steam/bagasse ratio of 0.6 and then decreased slightly to 0.748 m³/kg. It

seems that the shorter residence time of steam in higher input steam velocities caused the results observed. It can be concluded that, steam participating in gasification process is less and this nonreactive steam appears as water in liquid (Tar + water) output. Hydrogen increased from 16.5 to 20. 3 vol%, while CH_4 (8.29 to 4.82 vol%) and other hydrocarbons (0.306 to 0.197 vol%) decreased gradually with increasing the steam/bagasse ratio. By increasing the steam/bagasse ratio from 0.4 to 0.6, the CO increased to 49.3 vol% and then dropped slightly to 46.7 vol% with further increase in steam/bagasse. At the same time, CO_2 increased slightly from 26.9 to 28.05 vol% by increasing in steam/bagasse ratio from 0.4 to 1. The char gasification and reforming reactions are enhanced with an increase in steam/bagasse ratio, which can be witnessed from the decrease in char, CH_4, and other heavier hydrocarbons. It can be concluded that, the optimal steam/bagasse ratio for gas yield is 0.6. However, steam/bagasse ratio of 1, was considered to be suitable for H_2 production.

4. Conclusions

Steam was found to be an effective gasifying agent in comparison to pyrolysis process to increase the hydrogen and syngas yields in the product gases. The dual bed process was found to be effective to reduce the liquid yield and increase gas yield. Temperature of 850^0C was found to be favorable for higher gas yield and hydrogen production within the temperature range studied. It was observed that an increase in the steam/bagasse (wt./wt.) ratio caused significant increase in hydrogen (20.3 vol.%) and total gas (0.762 m^3/kg of bagasse). Total gas, hydrogen and syngas yields increased with increase in the packed-bed height from 40 to 100 mm. For bagasse the operating conditions were optimized for a gasification temperature around 850^0C, a height packed-bed of 100mm and a steam to bagasse ratio of 0.6, in order to produce of a gas richer in hydrogen and carbon monoxide and poorer in carbon dioxide and hydrocarbons.

5. ACKNOWLEDGEMENT

6. References

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