

HYDROGEN RICH GAS PRODUCTION VIA NONCATALYTIC GASIFICATION OF SUGAR CANE BAGASSE IN SUPERCRITICAL WATER MEDIA

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Abstract

Biomass gasification in supercritical water is a promising process for the production of hydrogen. In this research, a micro-reactor was used to study the supercritical water noncatalytic gasification of sugar cane bagasse. The reaction temperature was varied in the range of 400-520°C. Also the residence time and bagasse content were varied in the ranges of 5-30 min and 0.05-0.25 gram, respectively. Within the tested operation conditions, the reactor temperature of 520°C, residence time of 20 min, bagasse content of 0.05, and water density of 0.27 were the optimum conditions to maximize H₂ yield. At optimum conditions, 5.53 mmol of H₂/g of bagasse, 1.2 mmol of CO/g of bagasse and 1.9 mmol of light gaseous hydrocarbons/g of bagasse were obtained. The hydrogen gasification ratio of 0.287 was gained at the optimum conditions.

Keywords: *Hydrogen production; gasification; Sugar cane bagasse; supercritical water; yield.*

1. Introduction

Due to the increasing price and undesirable environmental effects of fossil fuels, production of energy from renewable resources has gained much attention in recent years. Biomass is considered to be one of the most promising resources for the production of future fuels. In many cases, because of large water content and high drying cost, biomass is not a suitable feedstock for conventional thermo-chemical gasification technologies. Supercritical and hydrothermal gasification processes offer attractive alternatives for the conversion of wet biomass to useful products. During these processes, biomass is hydrolyzed by water into smaller molecules. Therefore, contrary to conventional thermo-chemical processes, drying of biomass is not necessary. Consequently, hydrothermal gasification of a feedstock with as much as 90% water could become an economically favorable process. Furthermore, with the aid of this technology, hydrogen or methane can be generated at an elevated pressure, hence diminishing the need for pressurizing the final gas product [1].

Most commonly used biomass is of plant origin. Real plant biomass is a complex material that typically consists of cellulose, hemicelluloses and lignin. Therefore, various researchers have utilized model compounds; such as cellulose, glucose, xylan, glycerol, p-cresol, and phenol to study the supercritical and hydrothermal gasification processes and a large number of experimental investigations on these model compounds gasification in SCW were conducted [2-7]. They concluded that carbohydrates (i.e. cellulose and hemicelluloses) gasifies much easier than xylene and lignin, and lignin is the most difficult to gasify. Also, it was realized that lignin can interact with cellulose and change both the gas yield and product gas composition [8]. Other researchers expressed that, in SCW gasification of real biomass feedstock, char/coke may originate from not decomposed biomass by a solid-solid conversion and coke formation in biomass gasification process due to the presence of lignin, not only depends on the lignin amount but also strongly depends on the structure of lignin and interactions between other components in the real biomass [9].

These findings clearly reveal that, due to complexity of biomass (real plant biomass typically consists of 25% lignin and 75% cellulose and hemicelluloses), these model compounds are not able to accurately simulate the behavior of real biomass.

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 amount 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 biomass for energy purposes, given that due to the presence of non-oxidation conditions, the pollutant emissions are greatly low [10-23]. Theoretical calculations show that about 60-100 grams of hydrogen can be produced from one kilogram of bagasse. The hydrogen-rich gas produced from bagasse gasification in addition to being an alternative energy source, can be used in Oil, Gas and Petrochemical industries.

The objective of the present work is to explore the effects of important SCWG process parameters (reaction time, temperature and biomass concentration) to maximize the hydrogen yield in gasification of a real biomass (bagasse) in a batch micro reactor system to enhance the gasification efficiency. The reaction time effects, reactor temperature, and bagasse concentration on product yield and gas composition (H_2 , CO, CO_2 , CH_4 and other hydrocarbons) will be studied.

2. Materials and Methods

2.1. Feed materials

The biomass particles used for the experiments was obtained as shavings, from Haft-Tappe Industries located at Haft-Tappe, Khuzestan, Iran. They were dried under atmospheric conditions for 48 hours, and ground to a particle size <150 micro meter in diameter. The elemental composition of the whole biomass sample was analyzed in a CHNS analyzer.

2.2. Reaction setup and experimental outline

A batch reactor made of 316 stainless steel tube with total volume of 21 ml has been used in this study (Figure 1a). Bagasse was mixed with a certain amount of deionized water and injected into the reactor using a syringe in each experimental run. The reactor was plunged in a molten salt bath that contains a mixture of potassium nitrate, sodium nitrate and sodium nitrite. The molten salt bath temperature was controlled using an electrical heater and a PID temperature controller. Temperature and pressure were measured using a K-type thermocouple and a pressure gauge. Figure 1b show typical changes in reactor pressure. After a given reaction time, the reactor was taken out of the molten salt bath and plunged in a water bath for rapid cooling to room temperature. All experiments were performed 3 times under the same experimental conditions and the data reported here are the averages of repetitive runs.

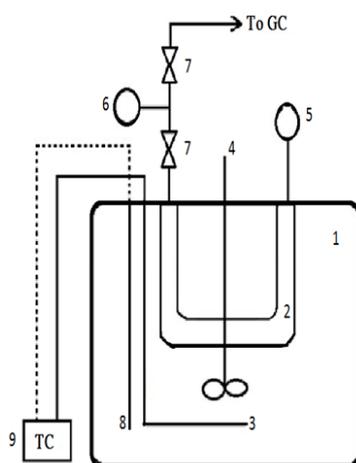


Figure 1a Scheme of the home made tube batch microreactor: 1) molten salt bath, 2) batch tube reactor, 3) electrical heater, 4) mixer, 5) high pressure gauge, 6) low-pressure gauge, 7) high-pressure valve, 8) k-type thermocouple, 9) PID temperature controller

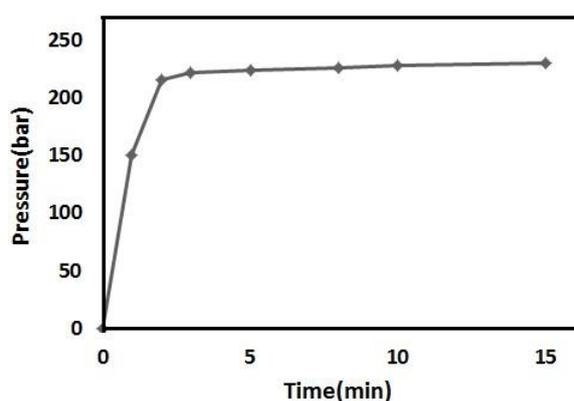


Figure 1b A typical variation of reactor pressure with time (T:440°C, bagasse loading: 0.15 g, water loading: 6.5 g)

In this study, influences of reaction time, bagasse concentration, water densities, and reaction temperature on the gasification of bagasse were investigated. In order to determine the effect of each parameter on the percentage conversion of the feed, only one parameter was changed for each experiment. At the end of each experiment, reactor free volume, final pressure and temperature were used to calculate the gas yield. The amounts of each product gases were measured and analyzed using gas chromatographs (Varian 3400 and Teyfgostar-Compact). For each experiment, the carbon gasification ratio (CGR) which is

the ratio of the amount of carbon in the gaseous products to the amount of carbon in the bagasse and hydrogen gasification ratio (HGR) which is the ratio of the amount of hydrogen in the gas phase to the amount of hydrogen in the bagasse were measured after each experiment. Mathematically, CGR and HGR are defined as:

$$\text{CGR} = \{Y_{\text{CO}} + Y_{\text{CH}_4} + Y_{\text{CO}_2} + 2Y_{\text{C}_2\text{H}_4} + 2Y_{\text{C}_2\text{H}_6}\} / \{\text{mmol Carbon / g bagasse}\}$$

$$\text{HGR} = \{Y_{\text{H}_2} + 2Y_{\text{CH}_4} + 2Y_{\text{C}_2\text{H}_4} + 3Y_{\text{C}_2\text{H}_6}\} / \{\text{mmol H}_2 / \text{g bagasse}\}$$

3. Results and discussion

The CHNS analyses of the biomasses are given in Table 1. As indicated, the C and H content in the sample is 64.55%. The balance is mostly oxygen.

Table 1 CHNS analysis of biomass species

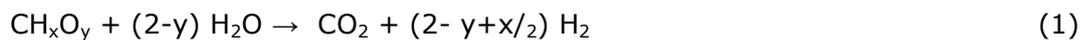
	% wt.
C	58.1
H	6.45
N	0.69
S	0.19
O	24.57

In order to determine the time required for gasification of bagasse, the effects of reaction time on conversion and product gas composition have been studied at 440°C, 0.15 gram biomass, and 6.5 cm³ water loadings. Afterwards, the effects of reaction temperature, water loading and feed concentration on the gasification yield have been studied at the determined reaction time.

3.1. Reaction Time

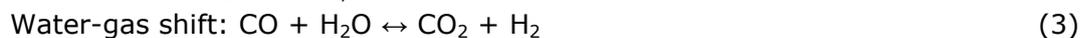
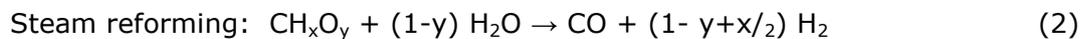
Reaction time is varied by increasing the duration of SCW gasification process from 5 to 30 min after the temperature of the reactor reaches its maximum. Table 2 presents the gasification yields (mmol of gas/g of bagasse) for the whole gaseous products and H₂, CO, CO₂ and CH₄ at reaction time of 20 min for bagasse loading of 0.15 g and water loading of 6.5 g.

It is referred by different authors that, the biomass gasification in SCW is a complex process, but the overall chemical conversion can be represented by the simplified net reaction:



where x and y are the elemental molar ratios of H/C and O/C in biomass, respectively.

The reaction product is syngas whose quality depends on x and y. The reaction (1) is an endothermic reaction. It is known from the reaction (1) that water is not only the solvent but also a reactant and the hydrogen in the water is released by the gasification reaction. Equation (1) summarizes the overall reaction, but a group of competing intermediate reactions, which are essential for the successful gasification, need to be considered as follows:



The results on table 2 shows that, the final product gas composition of the bagasse SCW gasification process is the result of combination of the above mentioned series of complex and competing reactions.

Table 2 The gasification yields (mmol of gas /g of bagasse) for the whole gaseous products and H₂, CO, CO₂, CH₄ and heavier hydrocarbons (T=440°C, Reaction time= 20 min, bagasse loading: 0.15 g, water loading: 6.5 g).

	(mmol of gas /g of bagasse)
Total gas	25.6
H ₂	7
CO ₂	13.6
CO	2.2
CH ₄	2.8

Figure 2 and 3 depicts the effect of reaction time on the SCW gasification products. It is seen that, the amount of total generated gas increases as reaction time increases from 5 to 20 min but no significant change in the conversion occurred by extending the reaction time to 30 min. As shown in figure 3, the hydrogen yield increases by increasing the reaction time, reaches a maximum at reaction time of 20 min and then starts to decrease. Also, extending the reaction time increases the methane yield from 0.73 to 1.73 mmol/g of bagasse. As the reaction time increased from 5 to 20 min, the methane yield increased significantly, while the total gasification yield increased by a factor of 1.22. Although, beyond 20 min reaction time, the total yield of the product gas is not changed, the composition continued to change slightly. The decrease in H₂ yield and increase in the methane yield can be attributed to methanation process (equation 4). According to the reaction 4, consuming three mole H₂ generates one mole CH₄ and consumes one mole CO. Therefore downward trend of H₂ yield should be sharper than rising trend of CH₄ and CO yields. When the objective of biomass gasification in SCW is hydrogen production, the reaction (4) must be restrained and CO reacting with water to form CO₂ and H₂ (reaction 3) must be affectionate.

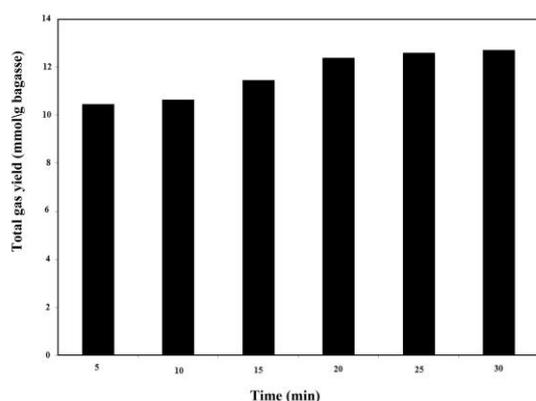


Figure 2 The total gasification products yield vs reaction time (T:440°C, bagasse loading: 0.15 g, water loading: 6.5 g).

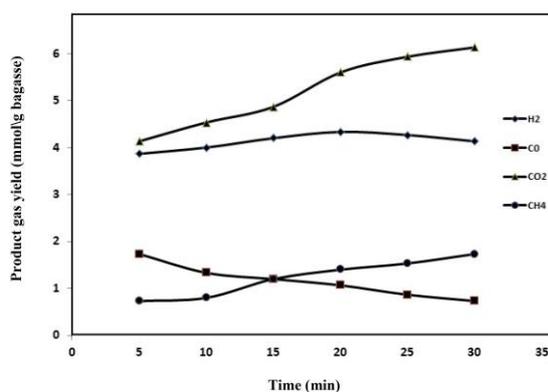


Figure 3 The bagasse product gasification yields vs reaction time (T:440°C, bagasse loading: 0.15 g, water loading: 6.5 g).

Figure 3 also shows that the yield of CO₂ increases as reaction time increases from 3 to 25 min but no significant change in the CO₂ yield occurred by extending the reaction time to 30 min. This figure also shows that the yield CO decreases with time slightly which is due to reaction of CO with water to form CO₂ and H₂ by increasing time.

Figure 4 show the CGR and HGR values calculated using the gasification results. As shown, the HGR increased by increasing the reaction time, reached a maximum of 0.221 at reaction time of 20 min and then did not show significant increase. Since the aim of this work is to maximize the hydrogen yield, reaction time of 20 min was selected as the optimum reaction time. While by increasing the reaction time from 5 to 30 min, the CGR increased by a factor of 1.30.

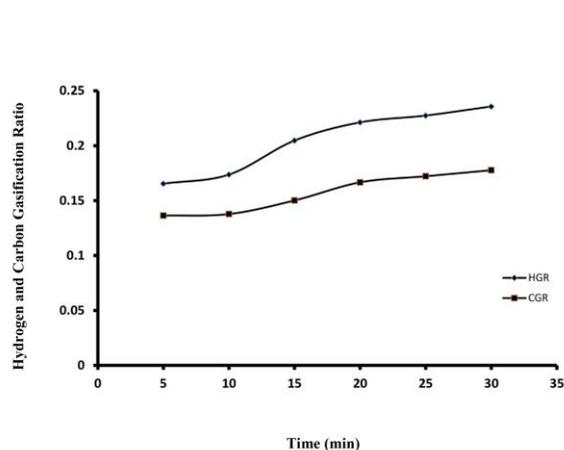


Figure 4 The CGR and HGR versus reaction time (T:440°C, bagasse loading: 0.15 g, water loading: 6.5 g).

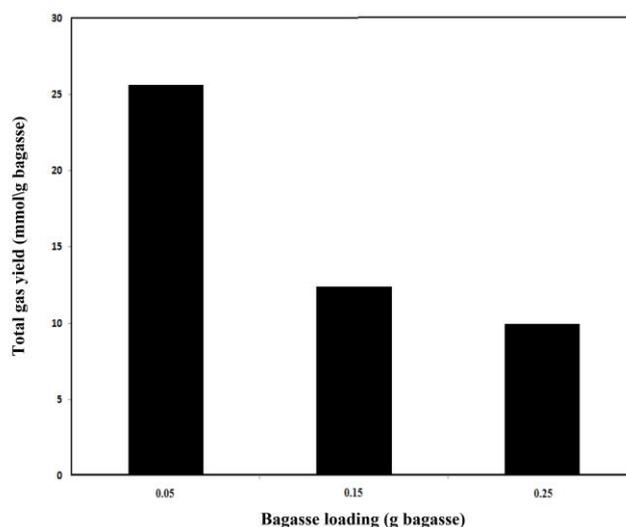


Figure 5 The total gasification products yield vs bagasse content (T:440°C, Reaction time: 20 min, water loading: 6.5 g).

3.2. Bagasse content effects

Figures 5 and 6 shows the total gas yield as a function of bagasse initial content. The bagasse content changed in the range of 0.05 to 0.25 grams while the amount of water fixed at 6.5 ml. As shown in figure 5 the total gas yield (mmol of gas/ g of bagasse) decreased dramatically by increasing the concentration of bagasse. Increasing bagasse concentration from 0.05 to 0.25 gram decreased the total gas yield from 26.62 to 9.96 mmol/g of bagasse. Also, the hydrogen and CO₂ yield decreased by a factor of 2.46 and 3.27, respectively. In addition, CO yield decreased by a factor of 1.32. Increasing the bagasse content, decreases the water concentration in the reactor which in turn, suppress the steam reforming reaction (reaction 2) and hence decreases the bagasse conversion and gas yield. However, there was a small decrease in methane yield which is due to decreasing the reaction of CO and H₂ to produce methane (reaction 4) at low water/carbon ratios. The CGR and HGR values were calculated from the gasification data and shown in figure 7. In accordance with the results shown in figures 5 and 6, the CGR and HGR are decreased with increasing the bagasse concentration. These results are in agreement with the results reported by other researchers. They were reported that, gasification of biomass feedstock with high biomass content is more difficult than that with low biomass content [24-25].

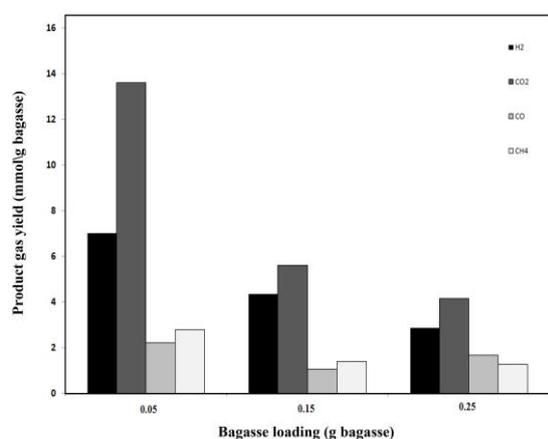


Figure 6 The CGR and HGR versus reaction time (T:440°C, bagasse loading: 0.15 g, water loading: 6.5 g)

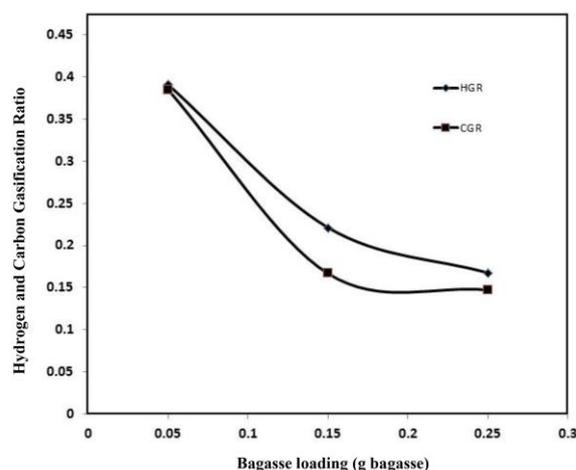


Figure 7 The total gasification products yield vs bagasse content (T:440°C, Reaction time: 20 min, water loading: 6.5 g).

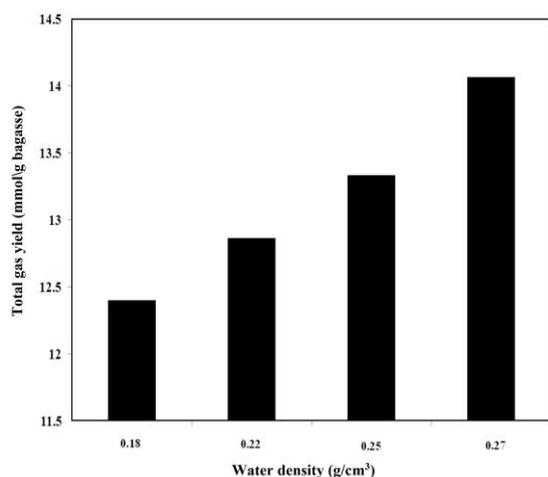


Figure 8 The total gasification products yield vs. water density (T:440°C, Reaction time:20 min, bagasse loading: 0.15 g).

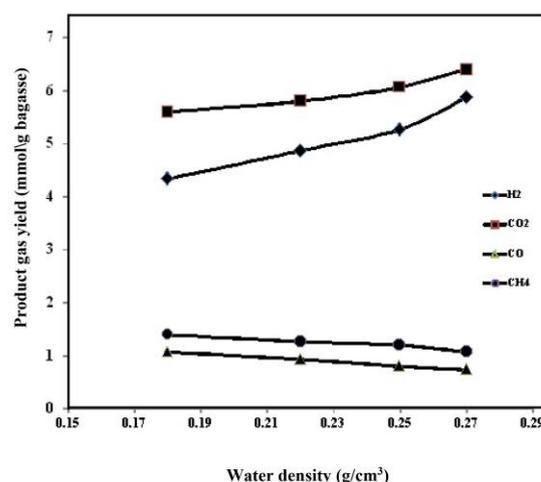


Figure 9 The bagasse product gasification yields vs. water density (T:440°C, Reaction time:20 min, bagasse loading: 0.15 g).

3.3. Water density effect

The effect of water density on bagasse SCWG was evaluated by changing water density from 0.18 to 0.27. Figures 8 and 9 shows the effects of water density on the gasification yields (mmol of gas/g of bagasse) for the whole gaseous products and H₂, CO, CO₂ and CH₄ for the gasification of 0.15g bagasse at reaction time of 20 min and reactor temperature of 440°C. As shown on these figures, total gas yield increased by a factor of 1.14. The H₂

yield increased with water density from 4.3 to 5.9 mmol of gas/g of bagasse. CO_2 increased from 5.6 to 6.4 while, CO showed a decrease from 1.06 to 0.73 mmol of gas/g of bagasse. Likewise, CH_4 decreased from 1.4 to 1.06 mmol of gas/g of bagasse. These data suggest that water gas-shift (reaction 2) might be strongly affected by water density. Higher water density means that more water molecules are available in a given volume. In terms of chemical kinetics, this higher concentration increases the average number of collisions and should favor the rate of reaction 2 in supercritical water.

The CGR and HGR values were calculated from the gasification data and shown in figure 10. The result showed that maximum hydrogen gasification ratio of 0.248 is achieved at water density of 0.27. Increase in water density did not change the CGR significantly.

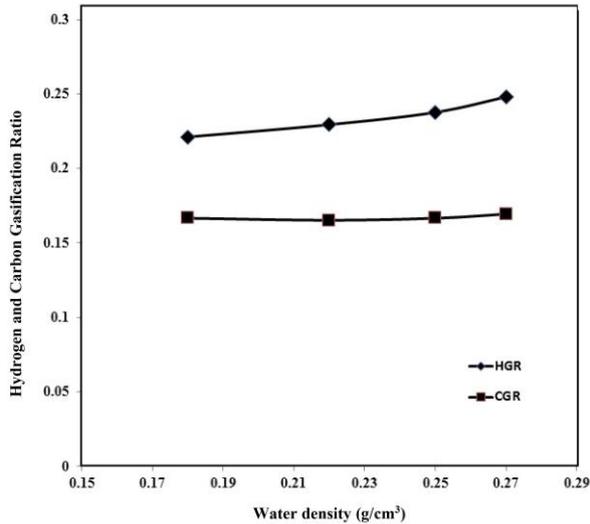


Figure 10 The CGR and HGR vs. water density (T:440°C, Reaction time:20 min, bagasse loading: 0.15 g).

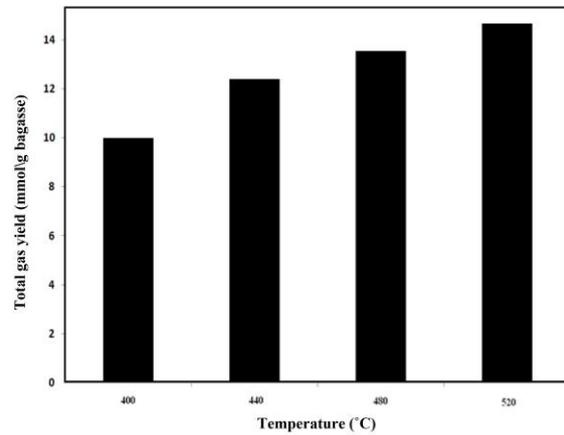


Figure 11 The total gasification products yield vs. temperature (Reaction time:20 min, bagasse loading: 0.15 g, water loading: 6.5 g).

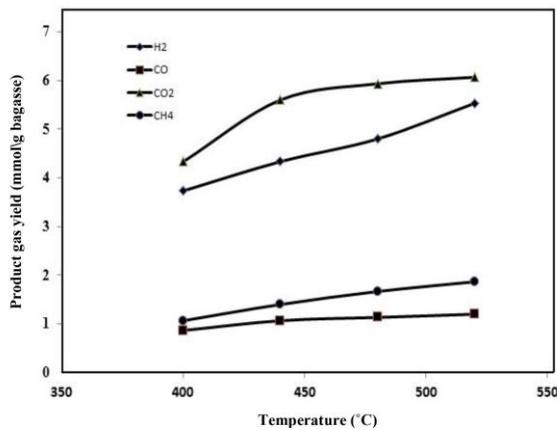


Figure 12 The bagasse product gasification yields vs. temperature (Reaction time:20 min, bagasse loading: 0.15 g, water loading: 6.5 g).

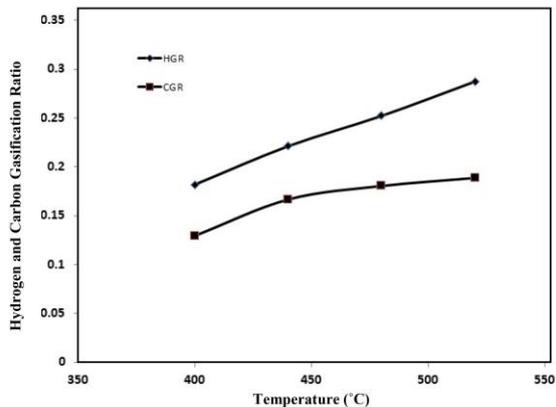


Figure 13 The CGR and HGR vs. gasification temperature (Reaction time:20 min, bagasse loading: 0.15 g, water loading: 6.5 g).

3.4. Temperature effect

Temperature shows a significant effect on biomass gasification in SCW. Figure 11 illustrates the total gas yield for the gasification of 0.15g bagasse at reaction time of 20 min and temperature of 400-520°C. As expected, reaction temperature had a positive effect on the total gas yield and therefore on gasification efficiency. As shown, by increasing the reaction temperature from 400 to 520°C, the total gas yield increased by a factor of 1.47. Increasing the reaction temperature increases the rate of the endothermic steam reforming reaction (reaction 2) and as a result increases the gas yield. Also, it has been suggested that, at low temperature conditions the liquid volume fraction in the reactor is higher than that in high temperature conditions. There is little head-space for gasification in high liquid volume fractions and consequently a larger portion of the gaseous products can dissolve in the liquid and react with other substances such as intermediate products and tar, which

causes the overall reduction in the gasification yield. So the higher liquid volume fractions that occur in low temperature conditions cause lower gasification yields.

Analyses of product gas are shown on figure 12. It is seen that, the increase in gasification yield was primarily due to the larger production of hydrogen and carbon dioxide. Increase in reaction temperature increased the hydrogen yield from 3.73 to 5.53 mmol/g of bagasse. It has been suggested that free-radical mechanism dominates the conversion of biomass at high temperatures, which is composed of two phases: an induction period (the generation of a radical pool) and a fast free-radical reaction period. The both steps play an important role in reaction kinetics. The induction time and free-radical concentration depend on temperature and reactants [26]. In general, temperature has a great influence on the induction period. Al-Duri *et al.* [27] reported the induction times of 3.6 s and 1.5 s at 400°C and 450°C for high temperature degradation of nitrogen compounds, respectively. So, high temperature drives the gasification reaction via a free-radical mechanism that is necessary for H₂ and CH₄ formation. Also, higher temperatures drive the methane steam-reforming reaction that causes increase in hydrogen yield. In addition, the intermediate products such as acids, aldehydes, phenols and short chain alcohols bear the hydrolysis at higher temperatures, and produce H₂. At the same time the carbon dioxide yield increased from 4.33 to 6.07 mmol/g of bagasse. Considering bagasse formula as CH_{1.33}O_{0.397}, when the biomass gasification goes to completion, according to the equation (1) the H₂ to CO₂ molar ratio should be equal to $(2 - y + x/2) = 2.2$. Although, the data in figure 9 show that increasing the reaction temperature from 400 to 520°C increased the equilibrium H₂ to CO₂ molar ratio from 0.86 to 0.92, these data show that the reaction is significantly far from the equilibrium.

Figure 12 also shows that, increasing the reaction temperature from 400 to 520°C, increases the yield of methane significantly. These findings suggest that, higher reaction temperatures favor light gaseous hydrocarbons production.

The CGR and HGR values were calculated from the gasification data and shown in figure 13. The result showed that maximum hydrogen gasification ratio of 0.287 is achieved at 520°C. So, the reaction temperature of 520°C is selected as the optimum reactor temperature for bagasse SCW gasification. Increase in reaction temperature increased the CGR by a factor of 1.46.

4. Conclusion

The supercritical water gasification of bagasse was studied using a batch micro reactor. It was observed that the gas yield increased with the reaction time up to 25 min, beyond which significant change was observed neither in the gas yield nor in the product composition. Maximum hydrogen yield was observed in the reaction time of 20 min. It was observed that the gas yield decreased with increasing the initial bagasse concentration. The maximum hydrogen yield of 5.53 mmol of H₂/g of bagasse and the maximum carbon oxide yield of 6.07 mmol of CO/g of bagasse were achieved at the maximum reactor temperature of 520°C.

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