Noncatalytic Reformation of Sucrose in Supercritical Water

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Abstract

The effect of space time and temperature on the non-catalytic reformation of sucrose in supercritical water was studied in a specially designed 0.4-L Haynes Alloy 230 tubular reactor. Experiments were performed non-catalytically in a continuous mode of operation at a constant pressure of 24.05±0.04 MPa and at temperatures varying from 600°C to 760°C and space times between 55 to 245 seconds. Sucrose is a renewable, biological energy resource; the reformation of which would enable on-site and on-demand hydrogen production. Increasing space time and temperature increases the gasification percentage of sucrose along with the production of hydrogen gas, with temperature having a larger effect than space time. Gasification percentages of 99% were achieved using two different combinations of temperature and space time. A maximum of 7.9 moles of hydrogen gas was produced per mole of sucrose fed, which is 23% of the theoretical maximum possible, occurred at the highest temperature studied.

Introduction

Sucrose, $C_{12}H_{22}O_{11}$, commonly known as table sugar, is a naturally occurring disaccharide of glucose and fructose. It is produced in plants, and is commercially harvested from sugar cane and sugar beets due to its high concentration in these plants.[1] In the current energy market, sucrose is used to produce ethanol through fermentation. This ethanol must be further processed to remove the water and other contaminants in order to make a renewable liquid fuel. While the supercritical water reformation of other sugars such as glucose has been studied since the late 1970's, there is a dearth of literature on the non-catalytic supercritical water reformation of sucrose.[2-5] The purpose of these experiments are to investigate sucrose reformation to produce hydrogen, an emerging alternative fuel.

Apparatus & Chemicals

The water used in the reformer was deionized water, and the sucrose used was commercially available table sugar. The water and sucrose was mixed together to a predetermined ratio; for these experiments a ratio of 18.5 grams of water to one gram of sucrose was used throughout. This corresponds to a molarity of 0.16 mole of sucrose per liter of water, or a ratio of about 170 moles of water for every mole of sucrose.

The supercritical water system consists of a liquid feed system, preheat, reactor, reactor heaters, sample collection system, and data acquisition and control system, of which a schematic process flow diagram is illustrated in Figure 1 The supercritical water reactor has a volume of 383 mL, and is constructed of Haynes Alloy 230, which is an alloy of mostly nickel, chromium, tungsten, and molybdenum, among with other elements.[6] This allows the reactor to operate at temperatures up to 800 °C at a pressure of 36.2 MPa. Analysis of the gaseous effluent was performed using a HP 5890 Series A gas chromatograph with a thermal conductivity detector. The gas chromatograph is calibrated to detect hydrogen, nitrogen, carbon monoxide, methane, carbon dioxide, acetylene, ethylene and ethane. The total carbon content of the liquid effluent was analyzed with a Dohrmann DC-190 total organic carbon analyzer.

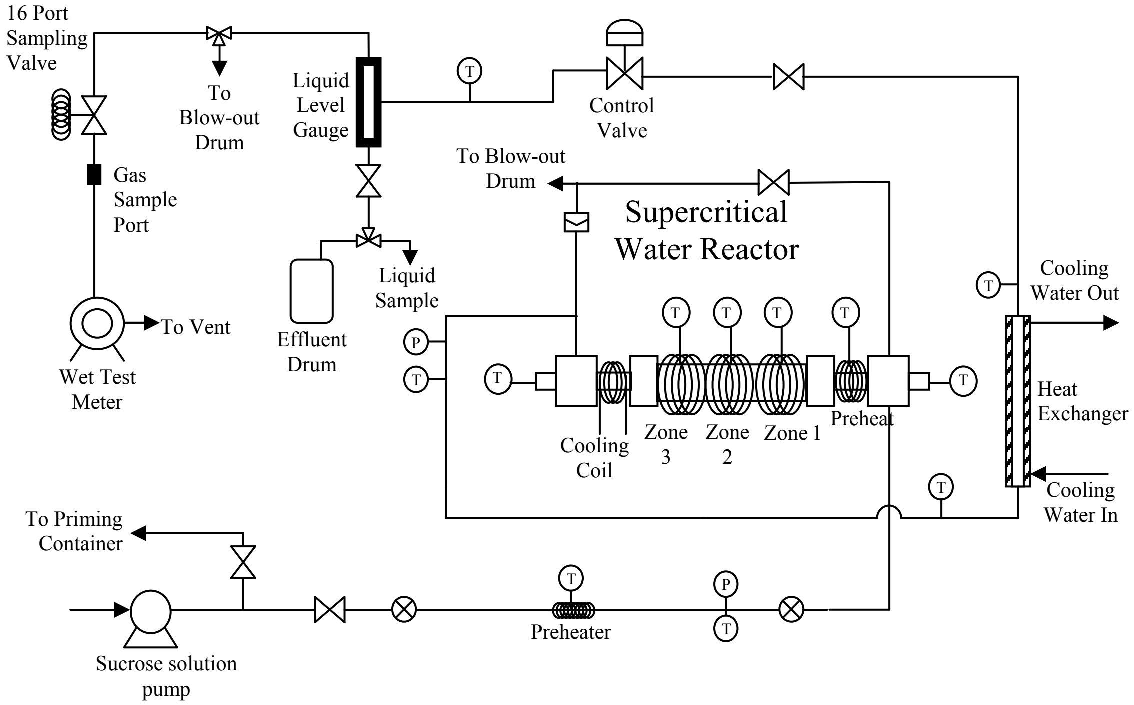

Figure 1. A schematic of the supercritical water reaction system at Missouri University of Science and Technology.

Chemical Reactions

When sucrose-water mixtures are heated, a variety of chemical reactions can take place. At temperatures near the atmospheric melting point of sucrose (185°C), sucrose splits into glucose and fructose, the two monosaccharides of this disaccharide sugar.[7] Also around this temperature, pyrolysis begins to occurs, whereby these sugars are further split into a variety of smaller fractions, creating gaseous hydrocarbons. It will be assumed throughout this paper that any gaseous hydrocarbons are the result of the endothermic pyrolysis reaction, although there may be other contributing reactions, which will be discussed later in this section. At higher temperatures, polymeric substances are formed via radical polymerization.[8] Repeated pyrolysis leads to hydrogen deficient fragments that, together with polymerization, function as coke precursors.[9]

Reformation, an endothermic reaction in which a hydrocarbon or sugar reacts with water to produce hydrogen gas and carbon monoxide, is an important industrial reaction and a promising avenue for hydrogen production. Currently, the widest use of reformation is in the reformation of natural gas to produce hydrogen for the chemical industry.[10] For present industrial applications, the reforming reaction is a catalytic reactions which is carried out at temperatures of 700 to 1100°C and pressures from 345 to 2400 kPa using a nickel catalyst.[11] The natural gas must be cleaned of sulfur and chlorine before being reformed to avoid catalyst poisoning.[12] The experiments conducted for this paper were all carried out non-catalytically, in that no catalyst was placed inside the reactor. It has been demonstrated that metallic reactor walls can potentially function as a catalyst in the reformation of various hydrocarbons in supercritical water, but these effects will have to be analyzed in future work.[3,13-15] In this paper, the production of carbon monoxide and hydrogen is indicative of the reformation reaction.

In addition to these reactions, the forward water gas shift (WGS) reaction can also occur. The water gas shift reaction is the reaction of carbon monoxide and water to form carbon dioxide and hydrogen gas. This would be a highly desirable reaction, since additional hydrogen is produced. The forward reaction is thermodynamically favored at temperatures of 815°C or below.[16] Most carbon dioxide present in the effluent gas is assumed to be the result of the water gas shift reaction. Total reformation, combined with all carbon monoxide going through the water gas shift reaction, could produce 35 moles of hydrogen gas per mole of sucrose fed, which is shown below.

$$C_{12}H_{22}O_{11} + 24\ H_2O \rightarrow 35\ H_2 + 12\ CO_2 + 5\tfrac{1}{2}O_2 \tag{1}$$

The theoretical maximum amount of hydrogen that could be produced is therefore 35 moles of hydrogen gas per mole of sucrose fed. The theoretical maximum also assumes that the oxygen contained in the sucrose would not react with either the carbon monoxide or hydrogen, which is very unlikely given the structure of disaccharide as well as the nature of supercritical water oxidation.[17,18] Various other reactions, like methanation or the Boudouard reaction, could also be possible. The methanation reaction involves one mole of carbon monoxide and three moles of hydrogen gas producing one mole of methane and water. This would be counterproductive since the goal is to produce hydrogen gas. Previous studies involving the supercritical water gas shift reaction saw no methanation at conditions similar to those encountered during in this paper.[19] The Boudouard reaction is a reversible reaction that involves two moles of carbon monoxide reacting to produce one each of carbon dioxide and elemental carbon. The high temperatures used in this paper should limit the Boudouard reaction; the equilibrium constant favors carbon monoxide production at temperatures above 680°C.[16,20-23] Another reaction conceivable is direct dehydration of disaccharide, thus generating carbon, or lighter hydrocarbons, and water. The large excess of water used in these experiments would favor reformation or water gas shift over other reactions. The discussion was limited to the aforementioned reactions for simplicity and because they effectively and accurately describe all of the products observed.[24]

Experimental

The temperature of the reactor as well as the space time of the solution in the reactor was varied to investigate the effects upon the effluent gas composition as well as sucrose gasification. Experiments were performed non-catalytically in a continuous mode of operation at a constant pressure of 24.05±0.04 MPa and at a constant water-to-sucrose ratio of 18.5 grams of water per gram of sucrose. The temperatures were varied from 600°C to 760°C at a constant space time of 95±6 seconds. The space time was varied from 55 to 245 seconds at a constant temperature of 683±2°C. The space time was varied by changing the inlet solution flow rate and calculated using the Peng-Robinson equation of state based upon the reactor temperature, pressure and the properties of pure water. Table 1 outlines the reactant solution flow rate, temperature, pressure, and space time. Run numbers 1, 2, 3 and 5 have a varying temperature with a constant space time, while the others have a constant temperature with a varying space time. Run numbers 3 and 5 are duplicates.

Table 1. Experimental matrix for sucrose reformation in supercritical water. Water-to-sucrose ratio is constant at 18.5-to-1 by mass and pressure at 24.05±0.04 MPa. The space time and temperature are varied.

Run #	Temp (°C)	Pressure (MPa)	Solution Flow (g/min)	Space Time (sec)
1	595	24.00	14.9	112
3	688	24.14	15.3	94
5	685	23.94	15.6	92
2	758	24.12	15.4	84
4	681	24.12	6.0	245
6	677	23.96	26.5	55

Results and Discussion

The results of the experiments outlined in Table 1 are shown in Table 2, which lists the liquid and gaseous components of the reactor effluent. More detailed analysis of the gas effluent is done later in this paper. If the carbon present in the inlet sucrose does not leave as gas it either comes out in the liquid effluent or stays behind as solid pyrolysis remnants, so any carbon not accounted for in the liquid or gas remains in the reactor as solid.

Table 2. Liquid and gas effluent compositions and the percent of carbon accounted for in liquid and gas for the experiments conducted.

Run #	Liquid total organic carbon (ppm)	% of inlet carbon in liquid	Gas flow rate (L/min)							% of carbon accounted for in liquid and gas
			H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	Total	
1	3804	11.1%	0.06	0.22	0.08	0.10	0.010	0.020	0.48	81.1%
3	949	2.8%	0.23	0.08	0.15	0.30	0.005	0.041	0.80	95.4%
5	709	2.1%	0.28	0.05	0.15	0.30	0.007	0.033	0.81	86.9%
2	46	0.1%	0.44	0.03	0.19	0.42	N.A.	0.017	1.10	99.9%
4	84	0.2%	0.13	0.01	0.07	0.15	N.A.	0.017	0.38	99.5%
6	1056	3.1%	0.40	0.17	0.24	0.46	0.012	0.055	1.34	90.1%

As seen in Table 2, temperature has an effect on the percentage of carbon that exits the reactor as liquid. As temperature increases, that percentage decreases, going from 11% at 595°C to 0.1% at 758°C. Space time also has an effect, but less so than temperature. The largest percentage of carbon in the liquid occurs at the shortest space time, run number 6, while the longest space time, run number 4, has very little carbon in the liquid. Any carbon not accounted for in the liquid or gas phase must remain in the reactor as solid. On occasion this solid was removed from the reactor, but at this time has not been analyzed.

Effect of space time

Run numbers 3 through 6 investigate the effect that space time has on the supercritical water reformation of sucrose. The net effect of the variation in space time on the gas composition and sucrose gasification is illustrated in Figure 2. The sucrose gasification percentage, the left axis of Figure 2, is the molar flow rate of carbon that was present in all gases divided by the molar flow rate of carbon in the inlet sucrose. The species gas yield, the right axis of Figure 2, is shown in dimensionless numbers, and is calculated from the molar effluent flow rate of each gas species divided by the inlet molar flow rate of sucrose, to account for variations in inlet flow rate.

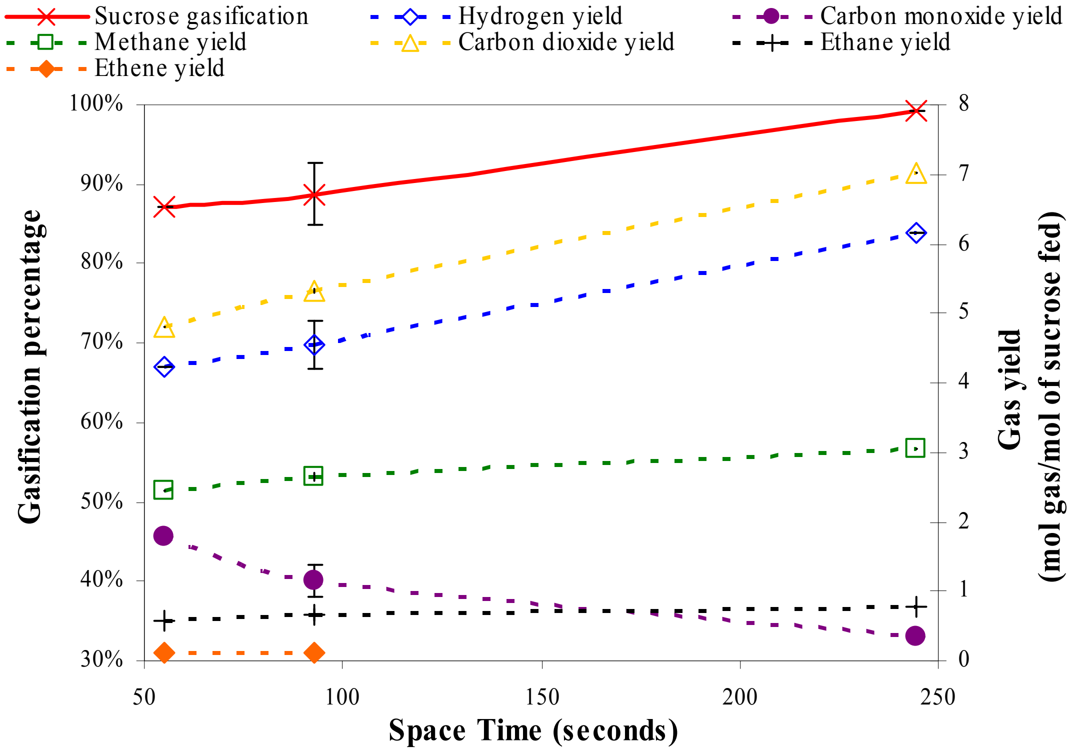

Figure 2. Dimensionless gas yield and sucrose gasification percentage as a function of space time. Temperature constant at 683±2°C, pressure 24.04±0.05 MPa, with an 18.5-to-1 water-to-sucrose ratio by mass.

Because there were duplicate runs performed at a space time of 93±1 seconds, the results were averaged and error bars are used for the standard error. The sucrose gasification percentage increases with increasing space time in the reactor, going from 87% at the shortest space time to 99% for the longest (245 seconds), an increase of 14%. Referring to Table 2, the percent of carbon accounted for in the liquid and gas for increasing space time increased, reaching 99.5% at a space time of 245 seconds, meaning less solid coke is produced with longer space times.

The hydrogen and carbon dioxide yield increases with space time, with hydrogen increasing 46% from the smallest to larges space time, while carbon dioxide also increases 46% over the same interval. The carbon monoxide yield decreases with increasing space time, which could be attributable to the progress of the water gas shift reaction. This reaction would also partially contribute to the increasing hydrogen and carbon dioxide flow rates. The methane yield did not change as much as the other yields for increasing space time, increasing 24% over the interval. Ethane also increased, 32%, with increasing space time. Ethene gas was only present in trace amounts for the two shortest space times, and was not detectable for the longest. It could be that the pyrolysis reaction occurs fast enough that the increase in space time has little effect. Because hydrogen gas yield is increasing, it is assumed that methanation plays a very small, if any role, in the methane gas yield. Longer space times seem to favor reformation and the water gas shift reaction, as seen by the increasing hydrogen, carbon dioxide and sucrose gasification percentage, and the decreasing carbon monoxide yield. Pyrolysis is effected less by time in the reactor, based on the smaller increase in the methane and ethane yield.

As stated in the chemical reactions section, the theoretical maximum production of hydrogen gas would be 35 moles per mole of sucrose fed. As seen in Figure 2, the most that was produced was 6.1 moles of hydrogen per mole of sucrose, which represents 18% of the theoretical maximum. Much of the missing hydrogen is in the form of the gaseous hydrocarbons, methane, ethane and ethene. Also, any carbon monoxide in the effluent gas, being capable of producing hydrogen through the WGS reaction, should be considered. If these gaseous products were to be totally reformed to hydrogen, including the water gas shift reaction, the dimensionless hydrogen yield would increase to 29.3 moles of hydrogen gas per mole of sucrose, which accounts for 84% of the theoretical maximum. The remaining hydrogen is either in the liquid effluent or is oxidized by the oxygen contained in the sucrose to form water. A small amount may remain in the reactor as a component of the coke formed during pyrolysis.

Effect of temperature

Temperature is the other variable of interest. Run numbers 1, 2, 3 and 5 investigate the effect of increasing temperature while the pressure was held constant at 24.05±0.05 MPa and at a space time of 95±6 seconds, the results of which are presented in Figure 3.

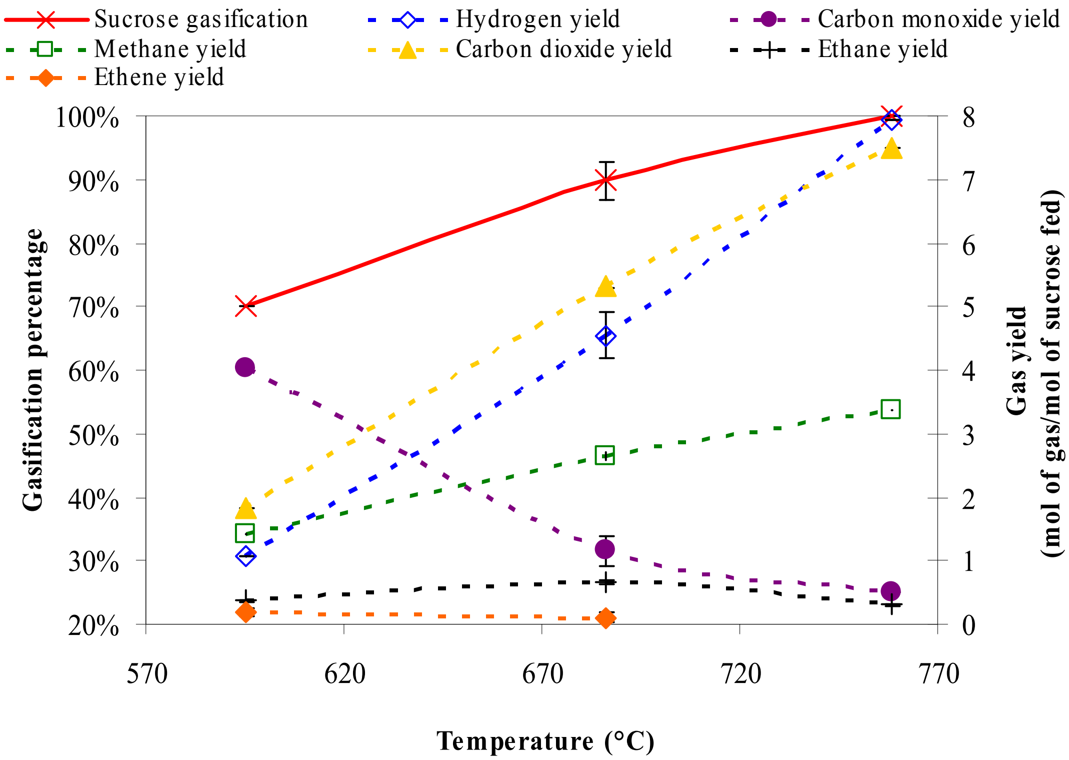

Figure 3. Dimensionless gas yield and sucrose gasification percentage as a function of temperature. Space time constant at 95±6 seconds, pressure 24.05±0.05 MPa, with an 18.5-to-1 water-to- sucrose ratio by mass.

Again, because run numbers 3 and 5 are duplicates, the results are averaged and error bars for the 686±1°C point representing the standard error are used. The sucrose gasification percentage increases with increasing temperature, going from 70% at 595°C to 99% at 758°C, a 43% increase. As stated above, the percent of carbon accounted for in the liquid and gas effluent increases as temperature increases, meaning less solid formation inside the reactor. Dimensionless hydrogen gas yield increased from 1.1 to 7.9, a 646% increase with increasing temperature. Carbon dioxide saw a 307% increase, while methane increased 136% with increasing temperature over the range studied. Carbon monoxide decreased 87% with increasing temperature, having a dimensionless yield that decreased from 4.0 to 0.51 with increasing temperature, perhaps due to greater activity of the water gas shift reaction. Other gaseous species did not exhibit a straight line increase like the previous examples. Ethane increases 82% before decreasing 54% for the three increasing temperatures. There is no ethene detectable at 758°C, and it decreases 50% from 595°C to 686°C.

The amount of hydrogen gas produced at the highest temperature, 7.9 moles per mole of sucrose fed, is again far below the theoretical maximum. This is 23% of the theoretical maximum hydrogen production. The increase in sucrose gasification, along with hydrogen and carbon dioxide yield and the decrease in carbon monoxide, indicates that both reformation and the water gas shift reaction are temperature dependant, increasing with increasing temperature. Pyrolysis also increases with increasing temperature, but less than the reformation products, as indicated by the smaller increases in methane and ethane yields compared to hydrogen or carbon dioxide. Pyrolysis does not seem to be as strongly temperature dependant as the reformation or water gas shift reaction. This finding is also in agreement with that with supercritical water reformation of jet fuel.[9,24]

Over the range of temperatures and space times that were analyzed in these experiments, temperature had a significantly larger effect on the sucrose gasification percentage, hydrogen, carbon monoxide and carbon dioxide flow rates than space time. During the space time increase from 55 to 255 seconds, gasification increased 14% while hydrogen and carbon dioxide yields increased 46%. When the temperature was increased from 600 to 760°C, gasification increased 43%, hydrogen yield 646% and carbon dioxide 307%.

Conclusion

The non-catalytic reformation of sucrose in supercritical water was studied in a 0.4-L Haynes Alloy 230 tubular flow reactor. Three space times, 55, 92 and 255 seconds, were evaluated at 683±2°C, a pressure of 24.05±0.04 MPa, with an 18.5-to-1 water-to-sucrose ratio by mass. In general, as the space time increased the sucrose gasification percentage increased, as did the effluent hydrogen and carbon dioxide yield. Carbon monoxide yield decreases with increasing space time, while methane and ethane increased, but increased less than the hydrogen or carbon dioxide yield. Longer space times seem to favor reformation and water gas shift more than pyrolysis. A maximum of 6.1 moles of hydrogen gas per mole of sucrose fed (18% of the theoretical value), along with a gasification percentage of 99%, was achieved at a space time of 255 seconds. Experiments were performed at temperatures of 595, 686, and 758°C at the same pressure and water-to-sucrose ratio as the previous experiments. The sucrose gasification percentage, as well as the hydrogen and carbon dioxide yield, all increase with increasing temperature, which may be due to the reformation reaction becoming more active at higher temperatures. The increases in hydrogen and carbon dioxide yields, along with the modest increase in methane and ethane yields, indicates that the reformation reaction is more dependant on temperature than the pyrolysis reaction. A maximum of 7.9 moles of hydrogen gas per mole of sucrose fed (23% of the theoretical maximum), along with a gasification percentage of 99%, was achieved at 758°C. Increasing temperature and space time increased the percentage of carbon accounted for in the liquid and gas, meaning less solid was produced and remained in the reactor at these conditions. Increasing temperature, over the range studied, had more effect than increasing space time on the gasification percentage and the hydrogen, carbon monoxide and carbon dioxide yields.

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