Pyrolysis and Steam Gasification of Waste Paper

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Abstract

Main characteristics of gaseous yield from steam gasification have been investigated experimentally. Results of steam gasification have been compared to that of pyrolysis. The temperature range investigated were 600 to 1000°C in steps of 100°C. Results have also been obtained under pyrolysis conditions at same temperatures. For steam gasification experiments, steam flow rate was kept constant at 8.0 gr./min. Evolution of syngas flow rate with time, hydrogen flow rate, energy yield and apparent thermal efficiency have been investigated. Residuals from both processes were quantified and compared as well. Material destruction, hydrogen yield and energy yield is better with gasification as compared to pyrolysis under identical thermal conditions. This advantage of the gasification process is attributed mainly to char gasification process. Char gasification is found to be more sensitive to the reactor temperature than pyrolysis. Pyrolysis can start at low temperatures of 400°C; however char gasification starts at about 700°C. A partial overlap between gasification and pyrolysis exists and is also examined here. This partial overlap increases with increase in temperature. As an example, at reactor temperature of 800°C this overlap represents around 27% of the char gasification process and almost 95% at reactor temperature of 1000°C.

1. Introduction

Gasification is heating-up of solid or liquid carbonaceous material with some gasifying agent to produce gaseous fuel. The heating value of the gases produced is generally of low to medium calorific value. This definition excludes combustion, because the product flue gas has no residual heating value from complete combustion of the fuel. It does include partial oxidation of fuel or fuel-rich combustion, and hydrogenation. In partial oxidation process the oxidant (also called the gasifying agent) could be steam, carbon dioxide, air or oxygen, or some mixture of two or more gasifying agents. The gasifying agent is chosen according to the desired chemical composition of the syngas and efficiency.

Pyrolysis and gasification are important to reform solid and liquid hydrocarbons to clean gaseous fuel which can be further processed to obtain clean and pure gaseous fuel or liquid fuel. Pyrolysis is a thermal degradation process of organic compounds in the absence of oxygen or air to produce various gaseous component yield as well as yield of tar and char residues. The heating rate of the sample, pyrolysis temperature, and particle size and distribution has an important effect on the products evolved and their distribution during pyrolysis[1].

Gasification of solid wastes includes a devolatilization process at beginning of the process. At high heating rates, the sample undergoes pyrolysis and gasification in parallel; however, at low heating rates the sample undergoes first pyrolysis and then gasification in series in the order of pyrolysis then char gasification (see Figure 1). Percentage overlap between gasification and pyrolysis can be observed by plotting the evolution of syngas flow rate for both gasification and pyrolysis in the same figure. Our present results have shown an overlap between syngas flow from char gasification and gaseous yield from pyrolysis of 27% at low reactor temperature of 800°C to ~95% overlap at high (1000°C) temperature.

The focus of this paper is to examine main differences between the gasification process and the pyrolysis process. We use gasification by heating-up of solid or liquid carbonaceous material with some gasifying agent to produce gaseous fuels (often called syngas fuel). Pyrolysis is a thermal degradation process of organic compounds in the absence of oxygen or air to produce various gaseous components as well as tar and char residuals. The main differences between the gasification and pyrolysis processes are examined here with special focus on the evolution of syngas flow rate, hydrogen flow rate and overall hydrogen yield, energy yield, apparent thermal efficiency, evolution of H_2 and CO mole fractions and the residue remaining from the process at process temperatures of 600, 700, 800, 900 and 1000°C. The main difference between gasification and pyrolysis is absence of a gasifying agent in case of pyrolysis. Consequently, char inherently produced in the pyrolysis process remains in the product stream while steam-char reactions diminish the fixed carbon in sample with steam gasification. Difference in characteristics between gasification and pyrolysis has been investigated from the point of view of results obtained on energy yield as well as hydrogen yield. Char gasification reactions has relatively high activation energy as compared to pyrolysis reactions. This difference in activation energies reveals higher sensitivity of gasification on the reactor temperature than that of pyrolysis[1]. Higher values of activation energy in case of gasification result in longer gasification time. Consequently, char gasification is considered to be the rate limiting step in the overall gasification process.

The syngas produced from gasification is evolved from pyrolysis and char gasification of the material. Contribution of pyrolysis and char gasification to the overall syngas flow rate or hydrogen flow rate was clearly identified by plotting the syngas flow rate from pyrolysis, char gasification and overall syngas flow rate on the same plot.

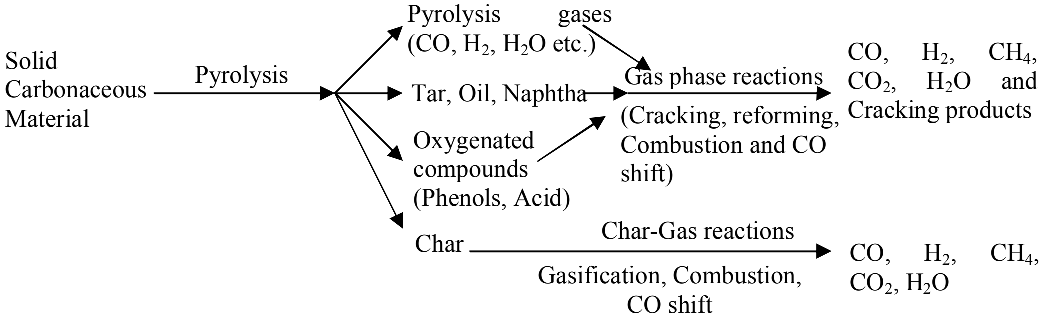


Figure 1. Reaction sequence for gasification.

2. Background

Roberts et al.[2] investigated the effect of pressure on apparent and intrinsic reaction kinetics. The apparent reaction rate at 10% conversion for the char-CO_2 reaction is a function of pressure. The results showed that pressure increases the apparent reaction rate of the char-CO_2. However, this increase is not constant over the pressure range 1-30 atm. As the pressure is increased to above 10 atm., effect of pressure is less and apparent reaction order is almost zero at pressures of 20-30 atm. However, the intrinsic reaction rate was not found to be affected much by the pressure. This supports that the shift in apparent reaction order at high pressures is not due to fundamental change in the reaction mechanism. They attributed this decrease in reaction order due to the following: at atmospheric pressure the surface of the sample is not saturated and the reaction rate is proportional to the number of surface complexes. As the pressure increases, more surface complexes are formed to result in an increase in reaction rate. At high enough pressures the surface will be saturated with complexes, such that increases in pressure will not lead to the formation of further surface complexes and the reaction rate will not increase. The apparent reaction order was reported to be zero[2].

Kaijitani et al.[3] investigated the gasification rate of coal using a pressurized drop tube furnace to simulate a two stage entrained flow gasifier. Specific surface areas of the investigated coal char increased rapidly with the progress of reaction and peaked at a conversion of 0.4.

Carbon dioxide adsorption was used to precisely evaluate the micro pores surface area as compared to calculating the surface area using the isotherm nitrogen adsorption analysis of at 77K by the BET method. They concluded that the examined char is considered to be dominated by micro pores because its specific surface area is nearly 10 times the size of the specific surface area resulting from nitrogen adsorption. They concluded that it is essential to measure the specific surface area of the char at the early stages of gasification with the use of isotherm carbon dioxide adsorption at 273K. They also noticed the widening of pores from micro-scale to meso-scale with the progress of reaction.

Authors made a comparison between the grain model and a random pore model. The equation to calculate the specific surface area in the grain model is $S = S_o(1-x)^{2/3}$. The specific surface area in the random pore model is $S = S_o(1-x)(1-\Psi ln(1-x))^{1/2}$, where, $\boldsymbol{x}$ is the conversion and Ψ is a dimensionless parameter that describes the initial pore structure as function of initial surface area, initial pore length and initial sample porosity.

Based on their experiments they concluded that the random pore model was better for describing the evolution of char specific surface area. Consequently, the reaction rate was described as[3]:

$$dx/dt = Ao.(P_A)^n{}_.\, e^{-E/RT}.(1-x).(1-\Psi ln(1-x))^{1/2}$$

Marquez et al.[4] investigated the kinetics of CO_2 and steam gasification of a grapefruit skin char. They found that this agriculture waste show a comparatively high reactivity and they attributed this to the catalytic effect of inorganic matter present in the sample. The reactivity (and also reactivity per unit area) of both steam and CO_2 gasification is found to increase with the increase in conversion, which supports their conclusion about the catalytic effect. However, lowering the catalytic effect by washing the sample with an acid leads to a decrease in reactivity thus confirming the catalytic activity of inorganic matter. Ash content in the tested char was 14.6% with potassium being the major metallic constituent. As gasification proceeds, potassium to carbon ratio increases and this consequently increases the catalytic effect of potassium. They also concluded that the reactivity versus conversion curve did not show a saturation of the catalytic effect even at a high conversion value of 0.9.

The general trend of increase in the steam to sample ratio is to increase the yield of total syngas, H_2, and CO_2, while the yield of CO and CH_4 decreases[5-10]. The increase in H_2 and CO_2 yield and the decrease in CO yield are attributed to the acceleration of the forward reaction rate of the water gas shift reaction ($CO + H_2O <=> CO_2 + H_2$)[5, 7-10]. On the other hand the increase in steam to sample ratio increases the methane reforming reaction to cause a reduction in the yield of methane[6]. Therefore, increase in steam to sample ratio results in a direct increase in the ratio of H_2/CO[6, 8].

3. Experimental Setup

Figure 2 shows a photograph of the laboratory scale experimental facility used for gasification and pyrolysis experiments. Steam is generated by well mixed stoichiometric combustion of hydrogen and oxygen. Steam generated is then introduced into a gasifying agent heater. The gasifying agent heater temperature is kept at same temperature as the main reactor in which sample material undergoes gasification. Steam is then introduced to the main reaction chamber containing the hydrocarbon sample. The syngas flowing out from the main reactor is sub-divided into two branches; one passes to the sampling line while the remaining syngas is vented to the exhaust system. The bypass line has a non return valve and a flow meter to insure the desired unidirectional flow out from the reactor. The syngas sample is then introduced to a condenser followed by a low pressure filter and a moister absorber (anhydrous calcium sulfate). Syngas flow is then introduced to a three way valve. This three way valve allows sampling by two means. First mean is by storing the syngas in sampling bottles that are at elevated pressures. Second way is to introduce syngas directly to the micro GC. Sampling bottles are used only when short sampling intervals are needed (0.5 to 1 min). However, direct sampling and analysis are carried out by the GC when longer sampling time intervals are desired. A constant flow rate of inert gas (nitrogen) is introduced with the oxygen flow. The nitrogen is detected by the GC and used to determine the flow rate of different syngas species produced during gasification.

The gasification conditions are given below:

- Steam flow rate: 8.0 g/min
- Nitrogen flow rate: 2.6 LPM
- Reactor temperature: 600, 700, 800, 900 and 1000°C
- Sample mass and material: 35 grams of paper

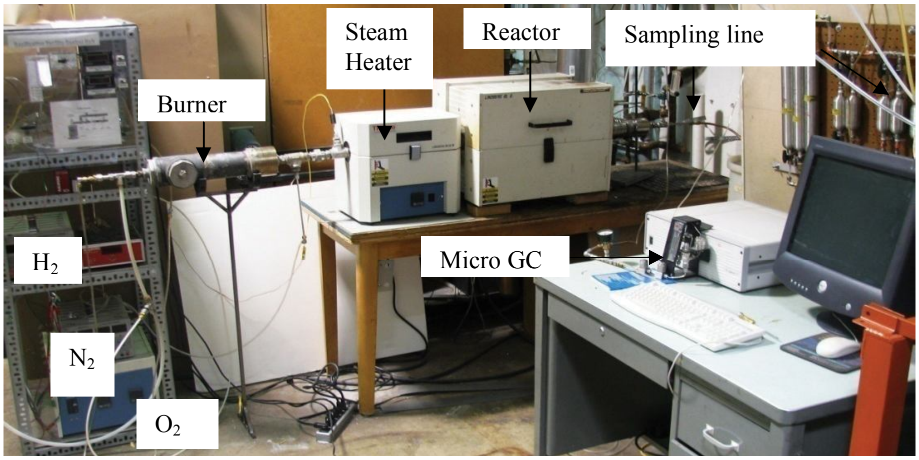


Figure 2. A photograph of the experimental setup.

4. Results and Discussion

The focus here is to elaborate the difference in syngas yield from gasification and pyrolysis. Investigated differences in syngas characteristics will include syngas chemical composition and total yields of major main gaseous species. The discussion will also include time dependent flow rate of syngas, chemical composition and hydrogen flow rate, and overall yield of hydrogen. Residuals from both gasification and pyrolysis processes were also compared at all the temperatures examined. In the following results are presented on the syngas flow rate, hydrogen yield, evolution of hydrogen, remaining residue and overall energy yield during the gasification and pyrolysis process.

4.1 Syngas Flow Rate

Figures 3, 4 and 5 show the syngas flow rate for both pyrolysis and gasification at different temperatures. Flow rates from pyrolysis and gasification show similar trend during the first few minutes. The values are almost the same in both cases. Pyrolysis shows a rapid increase in flow rate at the beginning of the process followed by a rapid decrease in flow rate until the flow rate reaches an asymptotic value of zero. In contrast, the results from gasification process show positive values of flow rate for a longer period of time, indicating the presence of char-steam reaction. The area confined between the pyrolysis curve and the gasification curve reveals the presence of char gasification. One can see this area is almost zero in the case of gasification at 600^{o}C. This indicates the absence of char gasification process at this temperature. This is further confirmed by the results on residuals remaining given in section 4.4. Increase in temperature decreased char gasification time. One can notice the partial overlap between gasification and pyrolysis at 700^{o}C. This partial overlap increases with the increase in temperature. For example, at reactor temperature of 800^{o}C, pyrolysis ends at about 15 minute while gasification prevails for a long time (~ 45 minutes). Overlap between gasification and pyrolysis is extended from the 4th minute until the 15th minute. This overlap at the 800^{o}C represents around 27% of the char gasification process. An examination of the data at 900^{o}C (Figure 4), shows that the overlap exists between the 3rd and the 10th minute, while char gasification ends at about 17th minute. These values reveal a 50% overlap between gasification and pyrolysis. The overlap at 1000^{o}C temperature is almost 95% of the char gasification time.

4.2 Hydrogen Yield

Figures 6 and 7 show the effect of reactor temperature on hydrogen flow rate for both gasification and pyrolysis processes. The common effect of increase in reactor temperature in both processes is that increase in reactor temperature increases hydrogen flow rate and decrease in time of hydrogen release. This is attributed to the endothermicity of hydrogen release for both processes and increase in reaction kinetics with the increase in reactor temperature. However, gasification shows higher hydrogen flow rates than pyrolysis at same process temperature. Additional hydrogen production is attributed to the gasification of char with steam and also from the partial contribution of water gas shift reaction. One more important result is that hydrogen evolution in case of gasification is relaxed over a longer period of time than hydrogen evolution from pyrolysis. This is due to the slower reaction kinetics of char gasification, which leads to the extension of the gasification process for a longer time duration. For example, at 800^{o}C the results for both pyrolysis and gasification shows that hydrogen release in the case of pyrolysis is almost zero at the 12th minute, while one can see considerable flow rate of hydrogen at 20th minute in case of gasification. For 600^{o}C case, both gasification and pyrolysis yielded same amount of hydrogen (see Figure 8). This is attributed to almost negligible gasification reactions at this temperature.

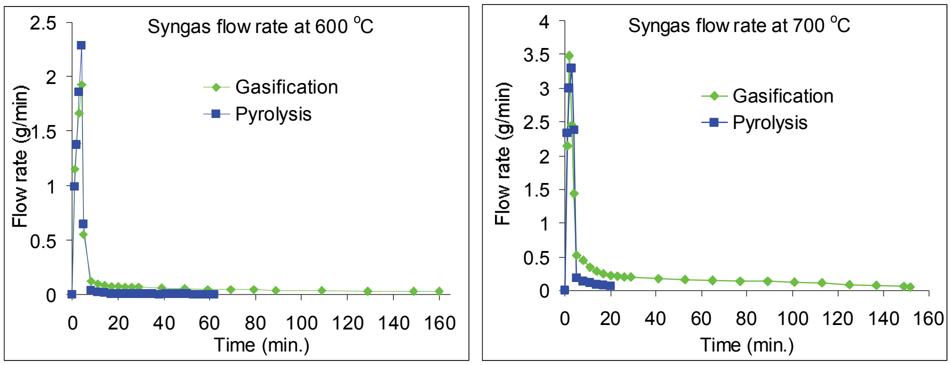
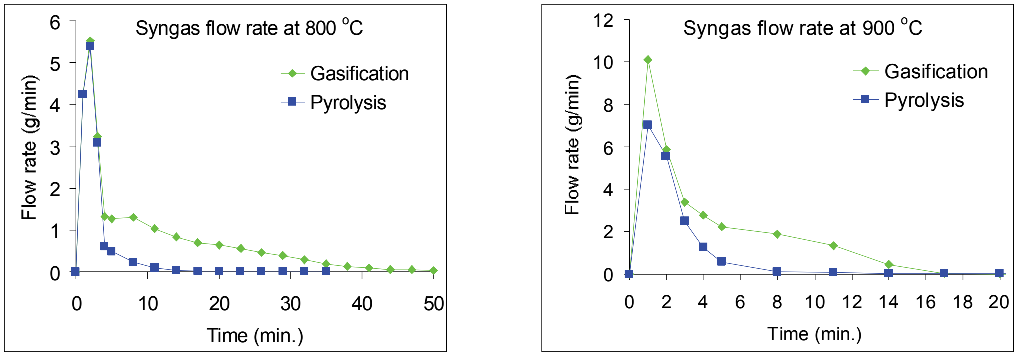


Figure 3. Syngas flow rate at 600^{o}C and 700^{o}C from pyrolysis and gasification.



a) 800°C b) 900°C

Figure 4. Syngas flow rate at 800°C and 900°C from pyrolysis and gasification.

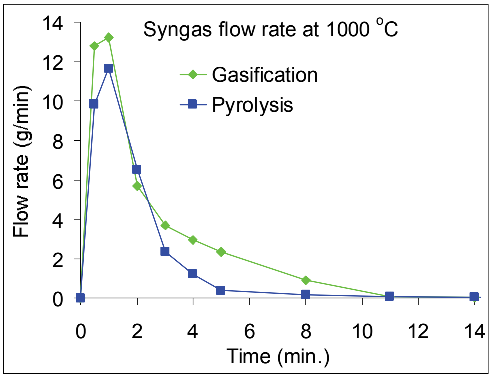


Figure 5. Syngas flow rate at 1000°C from pyrolysis and gasification.

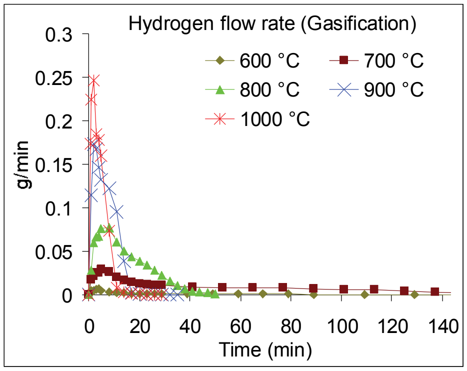


Figure 6. Hydrogen flow rate (gasification).

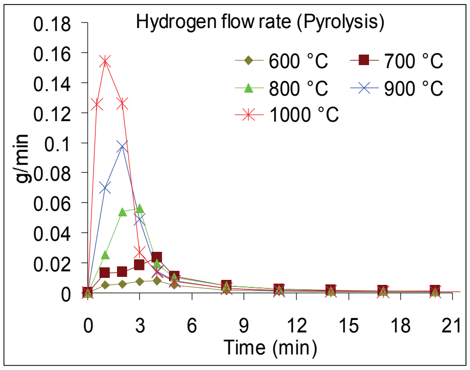


Figure 7. Hydrogen flow rate (pyrolysis).

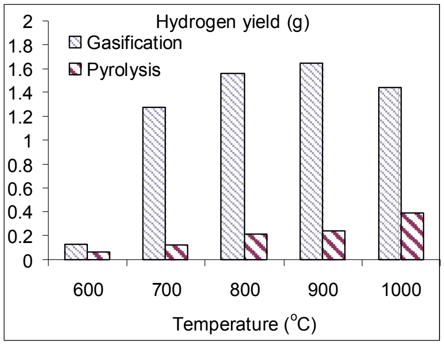


Figure 8. Hydrogen yield from pyrolysis and gasification.

4.3 Residual material after pyrolysis and gasification

Figure 9 shows residual material leftover after the pyrolysis and gasification process. Pyrolysis shows higher percentage of residual material as compared to that obtained from the gasification process. Residual materials from the pyrolysis process are mainly the char remaining from the devolatilization process. On the average the char percentages is about 20% of the initial sample mass from pyrolysis. This value represents the amount of fixed carbon in the sample as shown by the dark color material collected. In contrast, the residual materials collected in the case of gasification are white ash (no dark color material). Ash represents about 8~9% in the paper. The residuals percentage being of the order of 8% in case of gasification, confirms the gasification of all the char (fixed carbon) left over from the pyrolysis process. The gasification of all the carbon content in the sample is also confirmed by the presence of only white color ashes leftover from the gasification process as compared to black color char leftover from the pyrolysis process (see Figure 10). It is important to note the absence of steam-char reactions at low temperatures (less than 700°C). Residuals from the gasification process at 600°C showed considerably higher values than that at successively increased temperatures. Mass of residuals at 600°C (for gasification) was 23% of the initial sample which is comparable to the residuals mass from a pyrolysis process. This indicates that only pyrolysis took place at this 600°C temperature.

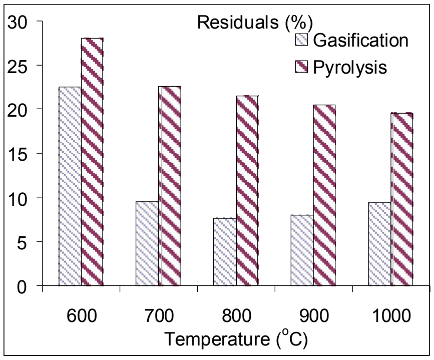


Figure 9. Char and ash residuals from pyrolysis and gasification.

a) b)

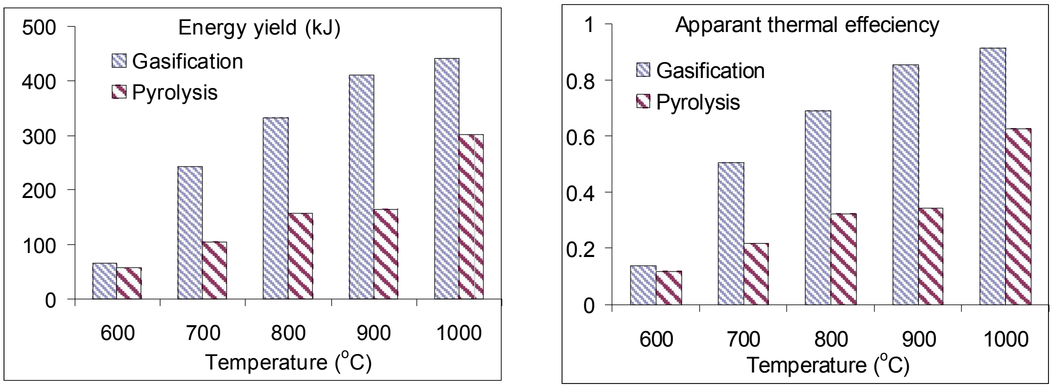
Figure 10. Char leftover from a) pyrolysis and b) ash leftover from gasification.

4.5 Energy Yield

Figure 11 shows the effect of reactor temperature on energy yield from the paper sample. Increase in reactor temperature increases the energy yield from the sample for both pyrolysis and gasification cases. As for the pyrolysis process, increase in temperature allow for better breakdown of long chains of hydrocarbons and consequently allow the release of more gaseous yield from the process. More specifically increase in the pyrolysis temperature increases the CO yield at the expense of CO_2 yield. This increase in CO yield at the expense of CO_2 yield raises the quality of syngas beside the initial increase in overall syngas yield. As for gasification, same trend is observed; increase in the reactor temperature increases energy yield from the sample. This is attributed to two reasons. First, the gasification process starts with rapid devolatilization of volatile component in the sample (pyrolysis) which is enhanced with the increase in reactor temperature. Second, it promotes in better steam-tar reforming process at elevated temperatures. In general, gasification shows higher energy yields than pyrolysis. However, the energy yields from gasification and pyrolysis at 600^{o}C are comparable. Gasification did not show higher energy yield than pyrolysis at this low temperature. The same would be expected if the experiments were carried out at even lower temperatures. This indicates the absence of char gasification reactions at this low temperature. This is confirmed by the residual material results shown in Figure 9. The material remaining from the gasification process at 600^{o}C is considerably higher than that obtained at successively increased temperatures.

4.6 Syngas and Hydrogen Flow Rates

The syngas flow rate curve from the overall process of gasification is a sum of two curves. First curve is the syngas flow rate due to pyrolysis the second is the flow rate due to char gasification. Figure 12 shows the role of pyrolysis and char gasification in the overall process. One can see the domination of pyrolysis at the initial minutes and the relaxed behavior of char gasification in later minutes. The hydrogen flow rate during gasification incorporating pyrolysis and char gasification is shown in Figure 13 and reveals the important role of stream as a gasifying agent in hydrogen production.



a) b)

Figure 11. Energy yield and apparent thermal efficiency for pyrolysis and gasification.

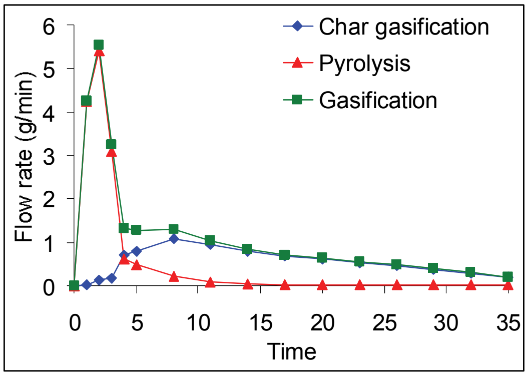


Figure 12. Syngas flow rate at 800^{o}C.

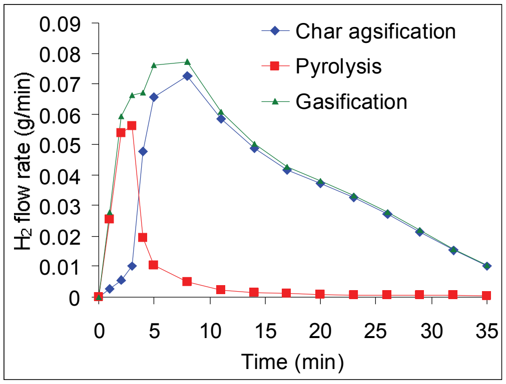


Figure 13. Hydrogen flow rate at 800^{o}C.

5. Conclusions

Experiments on paper gasification and pyrolysis have been carried out at several different process temperatures. The results showed the effect of char gasification on syngas flow rate, processes residuals, energy yield, hydrogen yield and variation in syngas chemical composition. Gasification is found to give better results in terms of increased material destruction, and increased yields of hydrogen and chemical energy. This advantage of the gasification process is attributed mainly to the char gasification process. The char gasification is found to be more sensitive to the reactor temperature than pyrolysis. The pyrolysis process can start at very low temperatures of 400^{o}C; however char gasification starts at 700^{o}C. Char gasification reactions were observed to be slower than that of pyrolysis. On the energy side, gasification of 35 grams of white paper yielded ~ 250 to 440 kJ as compared to 50 to 300 kJ in case of pyrolysis, for reactor temperature ranging from 700 to 1000^{o}C. For reactor temperature of 600^{o}C pyrolysis and gasification yielded almost the same amount of fuel chemical energy and hydrogen yield. This was significantly different at higher temperatures. This result confirms the absence of gasification reactions at reactor temperature lower than about 700^{o}C. The effect of reactor temperature on evolution of syngas flow rate with time showed that increase in reactor temperature increases syngas flow rate and lasts for shorter periods of time. An overlap between char gasification and pyrolysis was observed from the syngas flow rate plots at reactor temperatures higher than 800^{o}C. An overlap of 27% was noticed at 800^{o}C, 50% at 900^{o}C and almost 95% at 1000^{o}C. The extent of pyrolysis and char gasification to the syngas flow rate has been unraveled which showed the domination of pyrolysis in the first few minuets and the extension of char gasification for longer time.

Acknowledgments

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Dr. Ashwani Gupta is Distinguished University Professor at the University of Maryland, College Park. He received his Ph.D. and higher doctorate, D.Sc, from The University of Sheffield, U.K. He has co-authored three books, over eight chapters in different books and over 450 technical papers. He is a Fellow of AIAA, ASME, SAE and the U.K. Institute of Energy. He is co-editor of the Environmental and Energy Engineering book series published by CRC press. He is an associate editor for AIAA J. Propulsion and Power, J. Applied Science, Intl. J. of Reacting Systems, and Intl. J. Spray and Combustion Dynamics. He has received several national awards and best paper awards from AIAA and ASME. At the University of Maryland, he has received the College of Engineering Research award and President Kirwan Research award and prize.