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'SECONDARY REACTION KINETICS OF PYROLYTIC VOLATILES FROM PELLETIZED WOOD WASTES WITH STEAM'

by

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INTRODUCTION

As discussed in the preceding, companion paper, red alder is known for its rapid growth; consequently red alder is believed to be well suited for use in an energy plantation.[1] Densified red alder is particularly interesting as a fuel because the pellets are much more economical to transport than chips, sawdust, or other wood forms. Although it is customary to release the pellets' energy by combustion processes, we thought it interesting to investigate the suitability of pellets for medium Btu gas production by pyrolysis/steam reforming. In future years densified wood residues could compete with coal and peat as feedstocks for synthetic gaseous and liquid fuel production.

Previous research at Princeton has shown pyrolysis/steam reforming of biomass materials to be a two step process.[2] At relatively low temperatures (300° to 500°C)

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biomass pyrolyzes, producing a char and volatiles. At somewhat higher temperatures (550° to 700°C) the volatiles react with steam to produce a hydrocarbon rich synthesis gas. Oil and tar production is greatly reduced by the steam reforming step; however some water soluble compounds (methanol, acealdehyde, etc.) remain. At significantly higher temperatures the water gas reaction can be used to gasify the char residue, but the demanding conditions required make char gasification of lesser interest in the design of an economical gasifier.

In this paper we examine the influence of temperature and residence time on the secondary, gas phase reactions of pyrolysis volatiles from red alder pellets with steam. The data presented is sufficient to define measured rates of gaseous species production for CO, CO_2, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8. Somewhat more data is needed to identify reaction mechanisms, activation energies, orders, and other reaction parameters.

EXPERIMENTAL PROCEDURE

A specially designed quartz tubular plug flow reactor has been fabricated at Princeton to study the gaseous phase steam reforming reactions. Kinetic rates of gas formation by species can be measured using the reactor either in a differential or an integral mode. Results described in this paper emphasize the integral aspects of the tubular reactor since they are the easiest to interpret.

A schematic of the experimental layout is given in Fig. 1. A typical experiment using the reactor follows the procedure outlined below:

1) With all three furnaces cold, a small (0.1 to 0.5 g) sample of the material to be pyrolyzed is placed in the center of the pyrolysis reactor.

2) An inert gas is bled through ports D and E to cool the sample and purge the reactor, while furnaces 1 and 3 bring the steam superheater

and the gas phase reactor to the desired temperature.

3) The parastaltic pump is actuated and begins to pump water into the steam generator at a measured rate. Concurrently, a small amount of inert tracer gas (argon) is continuously injected through port A into the rear of the reactor.

4) When condensed water first begins to appear in the pyrolysis reactor, Furnace 2 (which was preheated to the desired pyrolysis temperature) is moved into place around the pyrolysis zone of the reactor.

5) When pyrolysis temperatures are reached the six port Valco valve is switched and the 34 port Valco valve automatically takes 15 samples of the gas stream for later analysis in the Hewlett Packard 5834a Gas Chromatograph (HPGC). Unsampled gas may be collected in a Teflon bag for later analysis, or vented to the atmosphere.

6) When all 15 samples have been taken, the six port valve is switched again and the samples are automatically analyzed by the HPGC. Gases collected in the Teflon bag are sampled using a gas tight syringe and analyzed by the HPGC.

7) The char and tars produced during the experiment are collected and weighed. Water collected in the condenser is also weighed.

Temperatures within the reactor are controlled by various temperature controllers and monitored by type K thermocouples with continuous recording on chart recorders.

The evolved gas composition was observed to undergo considerable variation during the course of the experiment; consequently gas standards were acquired to calibrate the HPGC for quantitative analysis of the following gases: Ar, N_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, C_5H_{10}, C_5H_{12}, and C_6H_{14}. Identification of the higher hydrocarbons ($>C_3$) is obscured by the fact that some other pyrolysis products have similar retention times. Analyses given in this paper for light hydrocarbons ($\leq C_3$) have been checked using a mass spectroscope. The HPGC uses Poropak QS columns operating between -50°C (cryogenic) and 200°C, and a carbosieve column at room temperature for gas analysis with a thermal conductivity detector (TCD). The carrier gas is a 8½% H_2, 91½% He mixture.

The complete recovery of moisture and tars from the reactor sometimes poses difficulties. The mositure is absorbed on dry paper towels and weighed; whereas the tars condense on a rolled piece of aluminum foil inserted in the condenser. Mass balances are always better than 0.8, but can be misleading because much more water is used during the course of an experiment than solid reactant. The carbon balance is a better measure of the experiment's quality, and customarily has the value 0.8 for the results reported here. The remaining carbon is believed to be present in the condensed water as water soluble compounds (methanol, acealdehyde, etc.). Semi-quantitative measurements made to date indicate that there are sufficient amounts of these (unidentified) compounds to nominally account for the missing carbon.

As designed the reactor bears some resemblance to a dilute phase transport reactor in that the solids and volatile pyrolysis products are present only in low concentrations in the steam reactant. During pyrolysis the composition of the gas in the gas phase reactor using the lowest steam flow and a 0.1 g sample is nominally 96% steam, 3% volatiles, and 1% argon carrier (on a volume percent basis).

When the pyrolysis furnace is set at 500°C the sample undergoes heating at the measured rate of 100°C/min during pyrolysis. All the experiments presented here use this heating rate. Somewhat higher rates can be obtained by setting the pyrolysis furnace at a higher temperature; however preliminary work suggests that this parameter does not have a marked effect on results.

RESULTS AND DISCUSSION

A series of six experiments were performed using the apparatus described in the preceding section. These experiments examined the effects of temperature and residence time in the gas phase reactor on the gaseous pyrolysis products. The temperature of the steam superheater was held at 350°C and the pyrolysis furnace at 500°C for all the results reported here. Residence time was varied by increasing the steam flow rate through the reactor, and by using a quartz insert to reduce the apparent volume of the gas phase reactor.

Results from the six experiments are given in Figures 2 - 4. The higher temperature in the gas phase reactor strongly favors the production of gas and a nominal residence time of 6 to 9 seconds appears to be optimal. Although the gas phase reactor temperature has little effect on CO_2 formation, the production of CO, H_2, CH_4, and C_2H_4 is essentially doubled by an increase in its temperature from 600°C to 700°C. Only the formation of methane appears to be favored for residence times longer than 7 sec at 700°C. Experimental error may account for the small reduction in gaseous species production at a given temperature for residence times longer than 6 to 9 seconds. Another possible explanation for this reduction is the change in the concentration of steam in the gas phase reactor due to the increased flow rate used to reduce the residence time. However, the apparent concentration of steam only changed from 96% in the low flow case to 97.5% in the higher flow case, which would not seem significant in most situations. The shortest residence time was obtained using a quartz insert to reduce the gas phase reactor volume.

Table 1 gives results for gas production from red alder pellets under the most favorable conditions examined in this paper. The dry, product gas has a heating value of 1.87×10^{7} j/m³ (502 Btu/scf), and over 3.5×10^{6} j/kg (3 MM Btu/ton) of energy was converted to the gaseous fuel product. Char carries the bulk of the product energy: roughly 6.8×10^6 j/kg (5.9 MM Btu per ton of feedstock input). The carbon balance of 0.8 suggests that some carbon containing compounds were formed which dissolved in the water collected in the condenser and were not subjected to further analysis. Relatively crude, semi-quantitative evaporation experiments confirmed this theory.

Although sufficient data exists to determine the rates of production of the individual gaseous species, no attempt has been made in this paper to do so. This is because the interpretation of the rate data is obscured by the apparently complex set of chemical reactions occurring in the gas phase reactor. Further work is required to elucidate the mechanisms of steam pyrolysis/gasification.

CONCLUSIONS

The effects of gas phase temperature and residence time on the products of the pyrolysis/steam reforming of red alder pellets have been investigated. Of the conditions studied, residence times of 6 to 9 seconds at 700°C produces the largest quantity of medium Btu gas from the pellets.

The quantity of gas produced is less than one-half that obtained from cellulose under similar conditions.[2] This relative paucity of gas yield may be an artifact of the pelletizing process, or it may reflect an inherent difficulty in gasifying red alder wood. Of course, more extreme conditions than examined here could be used to obtain higher gas yields. However, the high cost of reactors utilizing extreme conditions militates against their use for biomass gasification. More research is needed to determine the desirability of pelletized fuels for gasification processes, and the optimal conditions for steam pyrolysis/gasification of biomass.

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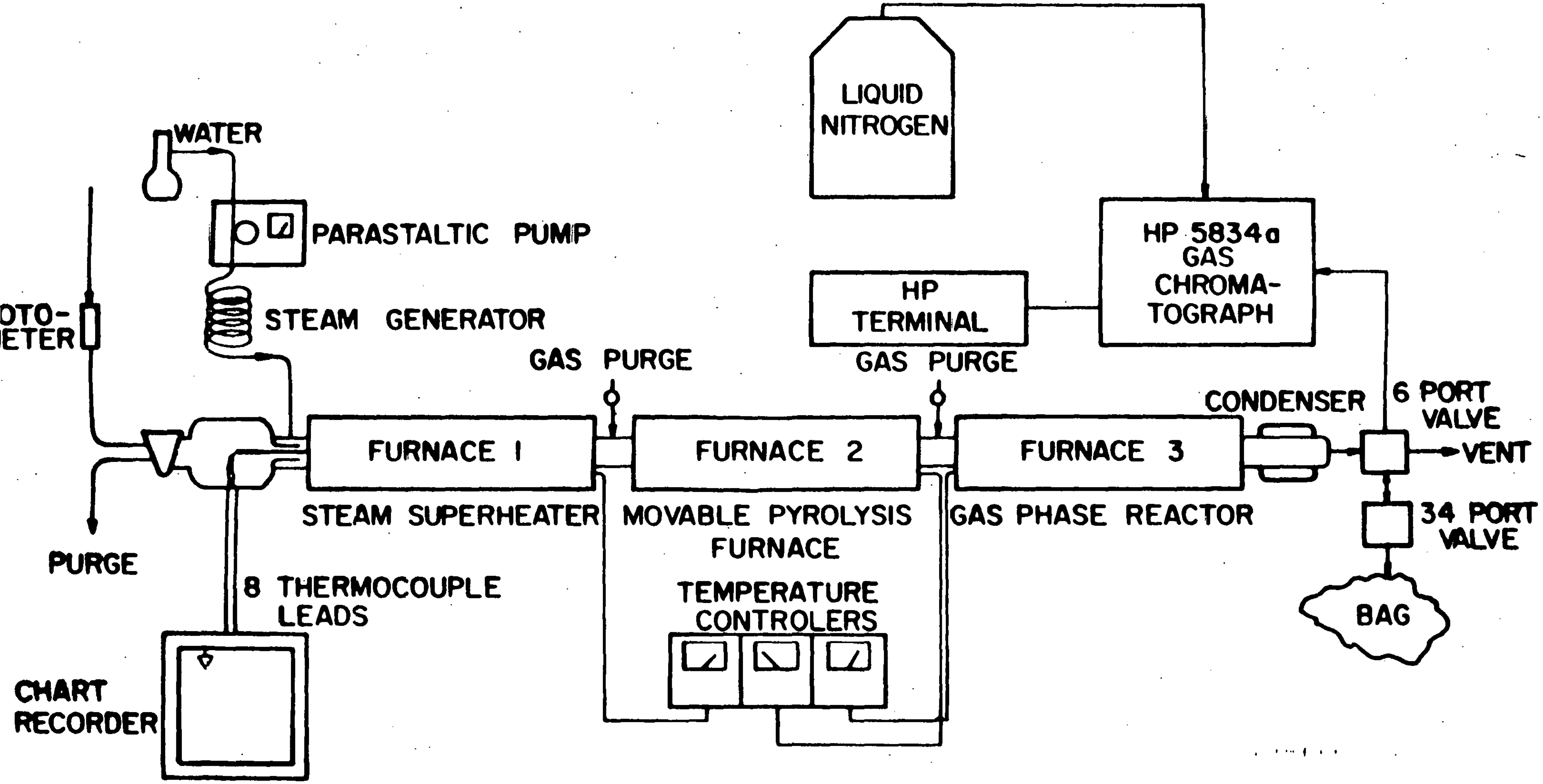
TABLE 1

EXPERIMENTAL RESULTS FOR THE OPTIMUM GASIFICATION CONDITIONS STUDIED IN THIS PAPER

Steam Superheater Temperature	350°C
Pyrolysis Reactor Temperature	500°C
Gas Phase Reactor Temperature	700°C
Gas Phase Reactor Residence Time	6.9 sec
Sample Weight	0.10 g
Char Residue Weight	0.032 g
Char Residue Weight Percent	32%
Tar Residue Weight	0.0089
Tar Residue Weight Percent	9%
Gas Volume Produced	18.7 cc
Gas Heating Value	502 Btu/scf
Calorific Value of Gases	3.1 MM Btu/ton
Calorific Value of Char	5.9 MM Btu/ton
Calorific Value of Tars	1.9 MM Btu/ton
Mass Balance	0.84
Carbon Balance	0.8
Oxygen Balance	0.84
Hydrogen Balance	0.84
Steam Consumption (g steam per g cellulose)	0.3
Gas Analysis (Vol %)	
CO	35
H_2	9
CO_2	29
CH_4	17
C_2H_4	7
C_3H_6	1
C_2H_6	1
other	1

FIGURE 1



EXPERIMENTAL LAYOUT