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'THE EFFECTS OF RESIDENCE TIME, TEMPERATURE AND PRESSURE ON THE STEAM GASIFICATION OF BIOMASS'

by

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INTRODUCTION

The underlying science of thermochemical conversion of biomass materials to useful gaseous fuels is poorly understood. Recent experimental research in the U.S.A. (1) and Sweden(2) has offered new and important insights into the gasification process. The two research teams independently concluded that biomass gasification occurs in three steps: (1) pyrolysis, producing volatile matter and char; (2) secondary reactions of the evolved volatile matter in the gas phase; and (3) char gasification via the water gas reaction. Detailed understanding of the rates and products of these three steps offers important guidance for the improved design of biomass gasifiers.

Pyrolysis of biomass materials occurs under normal conditions at relatively low temperatures (300° to 500°C), producing volatile matter and char. Very rapid heating causes pyrolytic weight loss to occur at somewhat higher temperatures. In general, the volatile matter content of cellulosic materials approximates 90% of the dry weight of the initial feedstock. Woody materials contain between 70% and 80% volatile matter, and manures contain 60% volatile matter. However, it is

known(3) that cellulosic materials can be completely volatilized when subject to very rapid heating (>10,000°C/sec).

Volatile matter produced by pyrolysis of the biomass begins to participate in secondary, gas phase reactions at temperatures exceeding 600°C. These reactions occur very rapidly and yield a hydrocarbon rich syngas product. As recognized by Diebold(4), these reactions resemble the hydrocarbon cracking reactions employed in the manufacture of ethylene and propylene by the petrochemical industry(5,6). The secondary, gas phase reactions dominate the gasification chemistry of biomass.

At still higher temperatures (>700°C) pyrolytic char reacts with steam to produce hydrogen, carbon monoxide and carbon dioxide. Rates of gasification of biomass derived chars are known to be higher than coal derived chars (2); however much higher temperatures are required to achieve char gasification than were initially required for the pyrolysis reactions. Catalysis of char gasification has been reported(7,8), with limited success.

Research described in this paper focuses on the second step of the gasification process, and details the effects of temperature and residence time on product gas formation. Cellulose is used as a feedstock for pyrolytic volatile formation. Earlier papers(9,10) have discussed the effects of steam on cellulose pyrolysis kinetics. Two recent papers(11,12) presented early results on pelletized red alder wood pyrolysis/gasification in steam. Future papers will discuss results using other woody materials, crop residues and manures. Research to date indicates that all biomass materials produce qualitatively similar results in the gasification reactor described in the following section of this paper. Effects of pressure on the heat of pyrolysis of cellulose are also discussed as a prelude to future papers detailing the more general effects of pressure on reaction rates and product slates.

EFFECTS OF TEMPERATURE AND RESIDENCE TIME ON THE SECONDARY, GAS PHASE REACTIONS

Experimental Procedure

For the experiments described below dry, Whatman #1 filter paper stored in a dissicant bottle was used as feedstock material. The use of an oven to obtain "bone dry" material was found to be futile due to the hygroscopic nature of the cellulose. The cellulose was assumed to have the chemical composition 0.444 C, 0.062 H, 0.494 O on a mass fraction basis, and the char composition was determined to be 0.7835 C, 0.04 H, and 0.1765 O by an independent laboratory.

A specially designed quartz, tubular plug flow reactor was fabricated at Princeton to study the gas phase reactions. Rates of gas formation by species can be measured using the reactor either in a differential or an integral mode. Results described here emphasize the integral aspects of the tubular reactor since they are the easiest to interpret.

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

1) With all three furnaces cold, a small (0.1 to 0.5g) 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 peristaltic 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 is collected in a Teflon bag for later analysis.

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. Measured temperature variations along the length of the gas phase reactor have been described in an earlier publication(1).

The evolved gas composition was observed to undergo considerable variation during the course of the experiment; consequently ten gas standards were acquired to calibrate the HPGC for quantitative analysis of the following gases: Ar, N_2, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_4H_8, C_4H_{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 spectrometer. The HPGC uses a Poropak QS in series with a Porosil column operating between -50°C (cryogenic) and 200°C for gas analysis with a thermal conductivity detector (TCD). The carrier gas is a $8^1/_2$% H_2, $91^1/_2$% He mixture. A typical gas analysis takes 14 minutes.

The complete recovery of moisture and tars from the reactor sometimes poses difficulties. The moisture 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 ranges between 0.7 and 1.0 for the results reported here. Our inability to close the carbon balance in part reflects the formation of water soluble carbonaceous compounds which are not subject to analysis by our existing instrumentation. Their presence is manifested by the color and smell of the collected water, which ranges from clear with an odor resembling automobile exhaust, to deep amber with a stronger, more noxious odor.

As designed the reactor bears some resemblence 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 gas in the gas phase reactor using the lowest steam flow and a 0.1 g sample is nominally 68% steam, 28% volatiles, and 4% argon carrier (on a volume percent basis). Somewhat larger samples, leading to an increase in volatile concentrations, do not markedly affect the results reported here.

Rates of gas production can be measured using the reactor in either a differential or an integral mode. The differential mode employs the Valco valve system to obtain fifteen 0.6 ml samples of gas evolved during the course of the experiment. With Ar tracer gas injected at a measured rate, the dilution of the tracer gas sample can be directly related to the "instantaneous" rate of volatile gas production in the reactor. For example, with a tracer gas flow of 5 ml per min., a dilution of 50% in the gas sample would correspond to an "instantaneous" volatile gas production rate of 5 ml per min. Unfortunately, departures from true plug flow of gas flow within the reactor (primarily due to the effect of the condenser on gas flow) make the differential mode experimental data more difficult to interpret than indicated above. Research reported here emphasizes the integral aspects of the reactor design.

When used in the integral mode total gas production by species is measured using teflon bags to collect all the reactor effluent. The dependence of total gas production on gas phase residence time in the gas phase zone of the reactor is determined using the combined data of many experiments. This data can be used to infer rates of gas production within the gas phase reactor. Kinetic models of gaseous species formation can be obtained through a study of the effects of both temperature and residence time on species production. Work in this exciting area is only now beginning at Princeton.

Results and Discussion

Figures 2, 3 and 4 display the dependence of gas production (g gas per g cellulose) by species on gas phase residence time for various gas phase reactor temperatures. For these experiments the steam superheater was maintained at 350°C, and the pyrolysis furnace at 500°C. This latter setting gave rise to a measured sample heating rate of 100°C/min. Residence time was varied by varying the peristaltic pump's water flow rate between 0.06 and 0.34 g/min., and by inserting a closed quartz cylinder into the gas phase reactor to reduce its apparent volume.

Data points reported in Figures 2-5 were accumulated over a period of six months using experimental techniques which evolved and improved during that time period. Data points with residence times of six seconds or less represent our "best" results. These data were obtained using a water flow rate of 0.34 g/min. for a 0.25 g sample to obtain residence times of 2 to 3 sec. Shorter residence times were obtained using a quartz insert to reduce the gas phase reactor's apparent volume. Longer residence times were obtained by reducing the water flow rate and cellulose sample size proportionately. Thus, data with residence times of six seconds or less represents the same steam flow/cellulose weight ratio.

Since cellulose pyrolysis occurs in about one minute with a heating rate of 100°C/min., the "best" data corresponds to a steam dilution ratio of about 1.4 g steam per 1 g cellulose feed. Available evidence suggests that higher steam dilution ratios have little effect on the gasification results. Efforts are presently being made to more fully elucidate the effects of dilution ratio on steam gasification products.

Of the various gases represented in Figures 2-4 the behavior of carbon dioxide is simplest to interpret, since it shows the least dependence on gas phase residence time or temperature. Apparently the primary mechanism for CO_2 formation rests in the initial pyrolysis process. Secondary, gas phase reactions at temperatures above 500°C contribute less to CO_2 formation. In order to increase gasification efficiency by reducing CO_2 formation (each molecule of CO_2 formed represents a net loss of carbon from the combustible products of the process), the conditions affecting the pyrolysis step of gasification must be carefully examined. For example, the use of high solids heating rate may reduce CO_2 formation.

Methane formation is also relatively easy to interpret. Increasing temperatures and increasing residence times result in increased methane formation. The slope of the dashed lines in Figure 3 gives the apparent rate of methane production at the various temperatures studied. The dependence of this production rate on temperature can be used to estimate the activation energy for methane formation. Efforts to elucidate the mechanism of methane formation (most probably the pyrolysis/hydrogenation of higher hydrocarbons) and derive kinetic parameters are presently underway.

Carbon monoxide and hydrogen production data behave similarly, and reach a maximum at about 5 seconds residence time and 700° to 750°C. Future experiments are anticipated to show some increase in production of these gases with longer residence times due to improved experimental procedures.

Data for C_2H_6 production shows some similarity to that of CH_4; however C_2H_6 production reaches a maximum at temperatures of 650° to 700°C and residence times of about 2 seconds. Competitive rates of formation by pyrolysis and consumption by pyrolysis or dehydrogenation reactions probably explain this observed behavior.

Ethylene production is maximized by temperatures of 700° to 750°C and residence times of about 4 seconds; whereas propylene formation is favored by lower temperatures (650°C) and shorter residence times (2 seconds).

In general, these results indicate that the gas phase reaction temperature most significantly affects gasification results. The role of primary pyrolysis conditions and gas phase residence times are much less significant. Moreover, for temperatures above 650°C the initial rates of species formation are very high, so that much of the gas formation is complete in less than 0.5 sec. These very high rates of gas formation due to secondary reactions are of great significance for reactor design.

The preceding conclusions are substantiated by Figure 5, which shows the effect of gas phase temperature and residence time on the carbon, hydrogen and oxygen gasification efficiencies (carbon efficiency = carbon in gas ÷ feedstock carbon). Again, the gas phase reactor temperature most significantly affects the carbon and hydrogen efficiencies of the system.

Under the best conditions examined to date, 83% of the feedstock's energy was carried by the gaseous products of the process, and tar production was reduced to 2% of the feedstock weight. The gas had a heating value of 490 Btu/scf. Other pertinent statistics are given in Table 1.

Initial experiments in flowing argon with no steam present yield essentially the same results as the comparable steam runs. From this it appears that the gasification process is dominated by cracking reactions and not steam reforming reactions. Variations in heating rate of the cellulose from 50°C/min. to 200°C/min. do not markedly affect results.

EFFECTS OF PRESSURE ON THE PYROLYSIS HEAT OF REACTION

A comprehensive experimental research program to investigate the effects of pressure on the products of steam gasification of biomass is currently underway at Princeton. A stainless steel, tubular micro reactor designed to pattern the quartz reactor described earlier has been fabricated and is now being used in shakedown experiments. The pyrolysis furnace used with the quartz reactor system has been replaced in the pressurized steam system by a Setaram Differential Scanning Calorimeter (DSC). The DSC provides for quantitative determination of the effects of pressure on pyrolysis kinetics and heats of reaction. A more complete description of this instrumentation and experimental results will be given in future publications.

Figure 6 presents the results of three measurements of the heat of pyrolysis of cellulose at different pressures. At elevated pressures the pyrolysis reaction becomes exothermic, and char production increases from about 12% by weight of the cellulose feedstock at 1 bar to 16% at 6 bars pressure. Future research is expected to considerably refine this initial data and extend it over a broader range of pressures.

CONCLUSIONS

Gas phase, steam cracking reactions dominate the chemistry of biomass gasification. At temperatures above 650°C these reactions proceed very rapidly and generate a hydrocarbon rich syngas containing commercially interesting amounts of ethylene, propylene and methane. Increased pressure appears to inhibit the gasification process.

These results indicate that biomass gasifiers should be designed to provide for high heating rates and short residence times with gas phase temperatures exceeding 650°C. Transport reactors, characterized by large throughputs, high heating rates, modest pressures and short residence times appear to be ideally suited for this purpose. Future biomass gasifiers should rely on steam cracking to produce fuels and chemicals; thereby resembling the technologies presently employed for ethylene production.

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TABLE 1

SELECTED GASIFICATION RESULTS FOR CELLULOSE

Steam Superheater Temperature	350°C
Pyrolysis Reactor Temperature	500°C
Gas Phase Reactor Temperature	700°C
Gas Phase Reactor Residence Time	3.5 sec
Sampe Weight	0.125 g
Char Residue Weight	0.012 g
Char Residue Weight Percent	10%
Tar Residue Weight	0.003
Tar Residue Weight Percent	2%
Gas Volume Produced	84 ml
Gas Heating Value	490 Btu/scf
Calorific Value of Gases	13.7 MM Btu/ton
Calorific Value of Char	2.8 MM Btu/ton
Calorific Value of Tars	0.5 MM Btu/ton
Mass Balance	0.84
Carbon Balance	0.96
Gas Analysis (Vol %)	
CO	52
H_2	18
CO_2	8
CH_4	14
C_2H_4	6
C_2H_6	1
C_3H_6	0.1
other	0.9

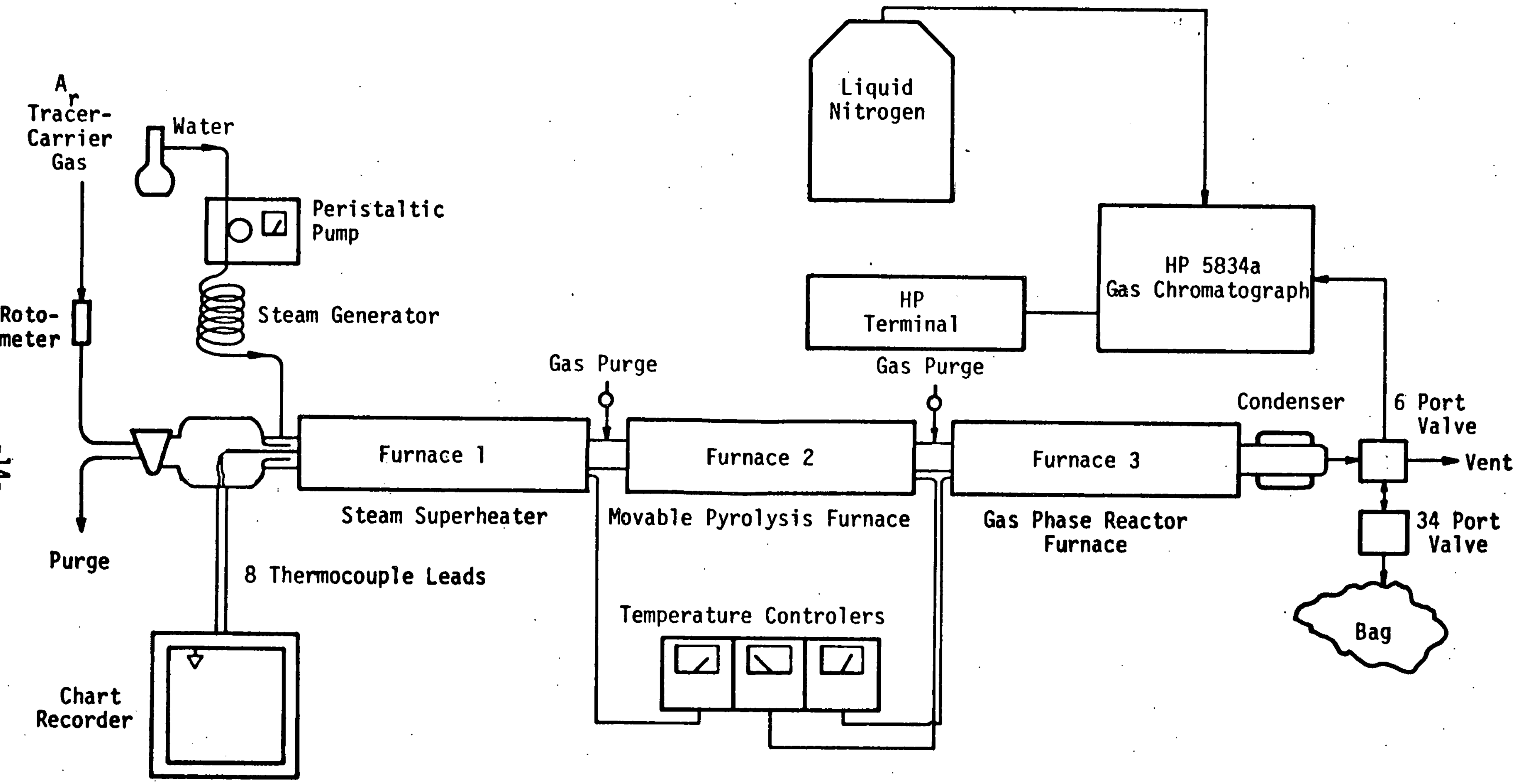

Figure 1

SCHEMATIC OF THE TUBULAR QUARTZ REACTOR EXPERIMENT

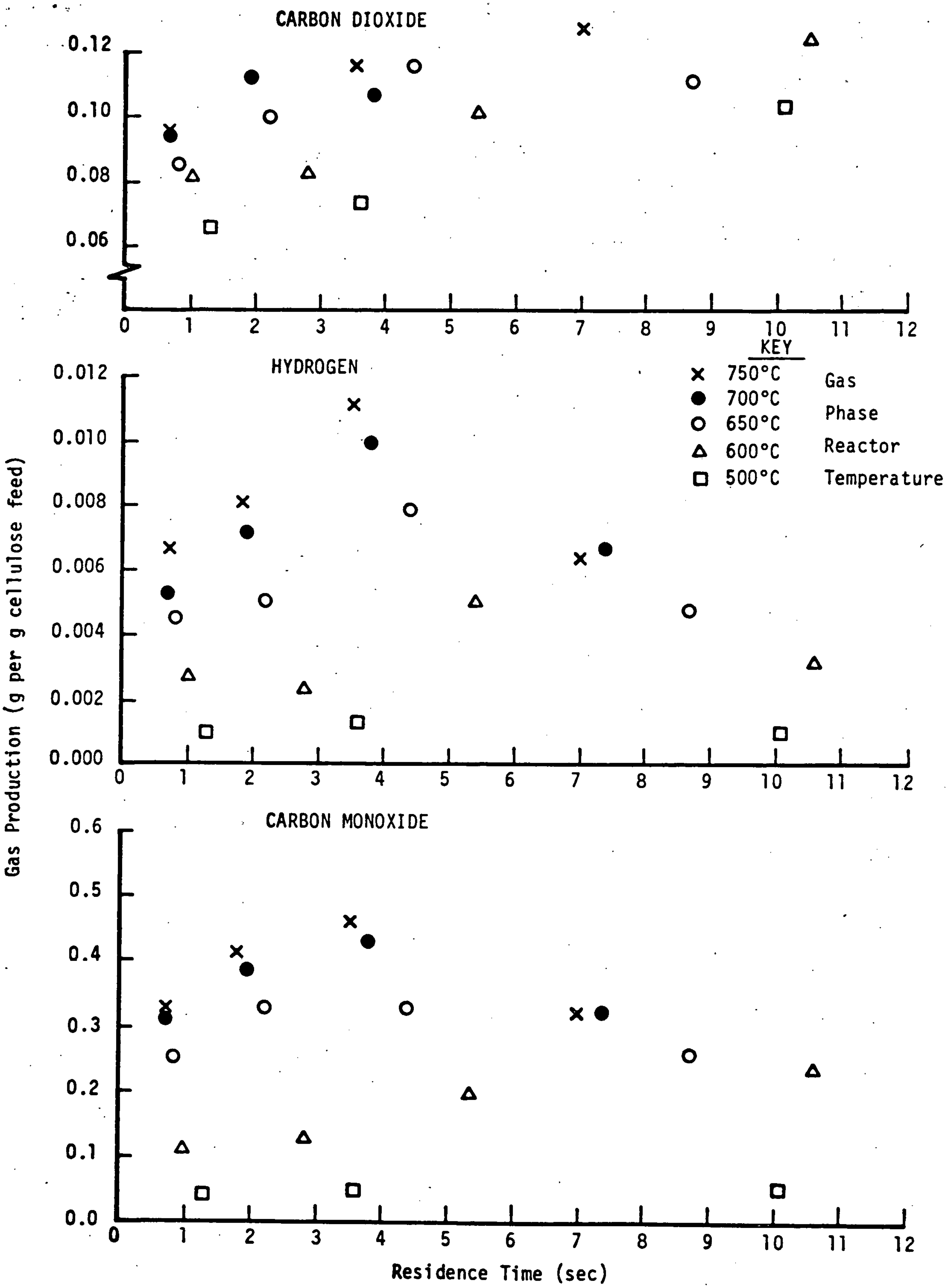

Figure 2 Non hydrocarbon gas production vs. residence time as a function of gas phase reactor temperature.

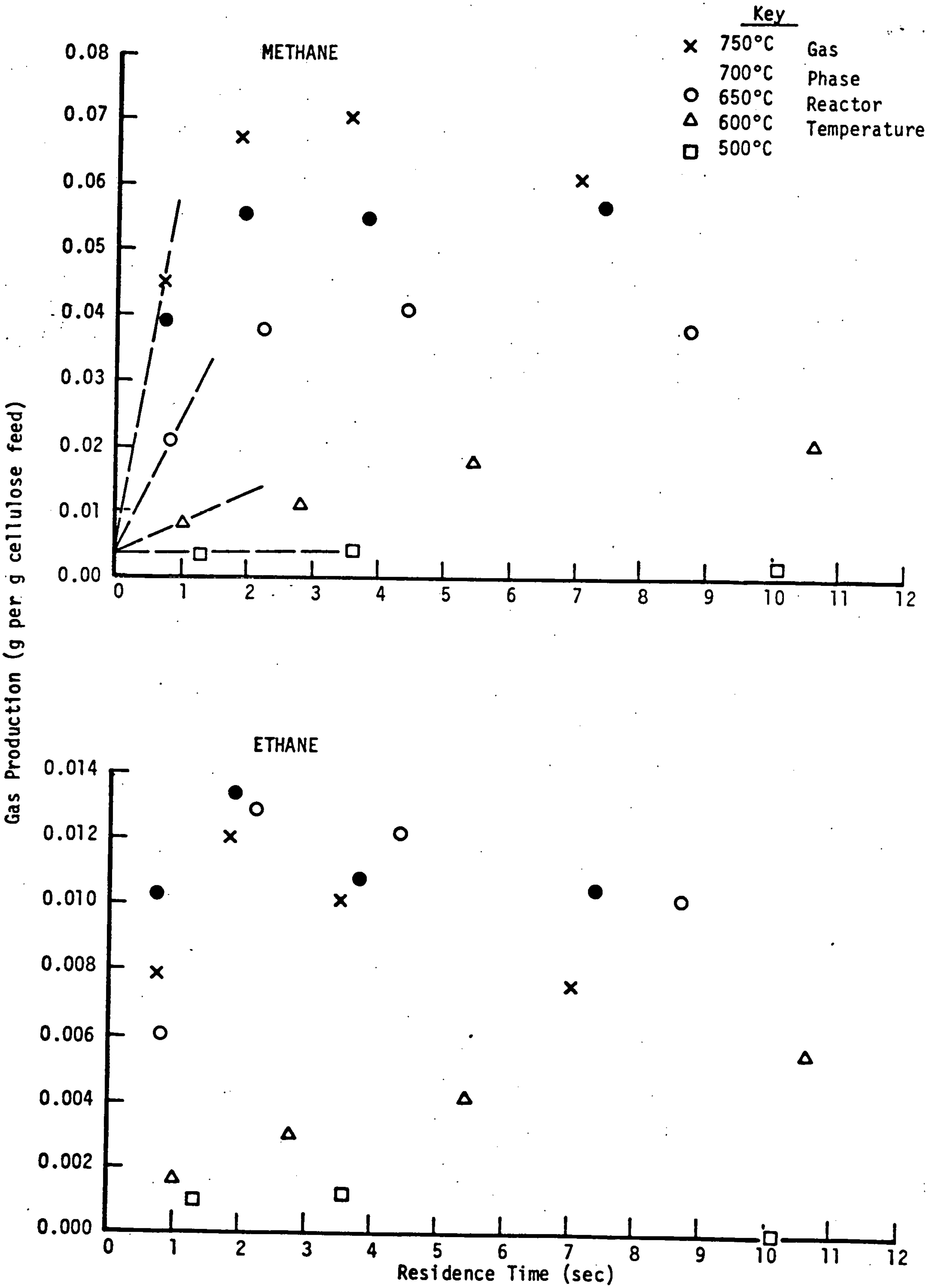

Figure 3 Paraffin production vs. residence time as a function of gas phase reactor temperature.

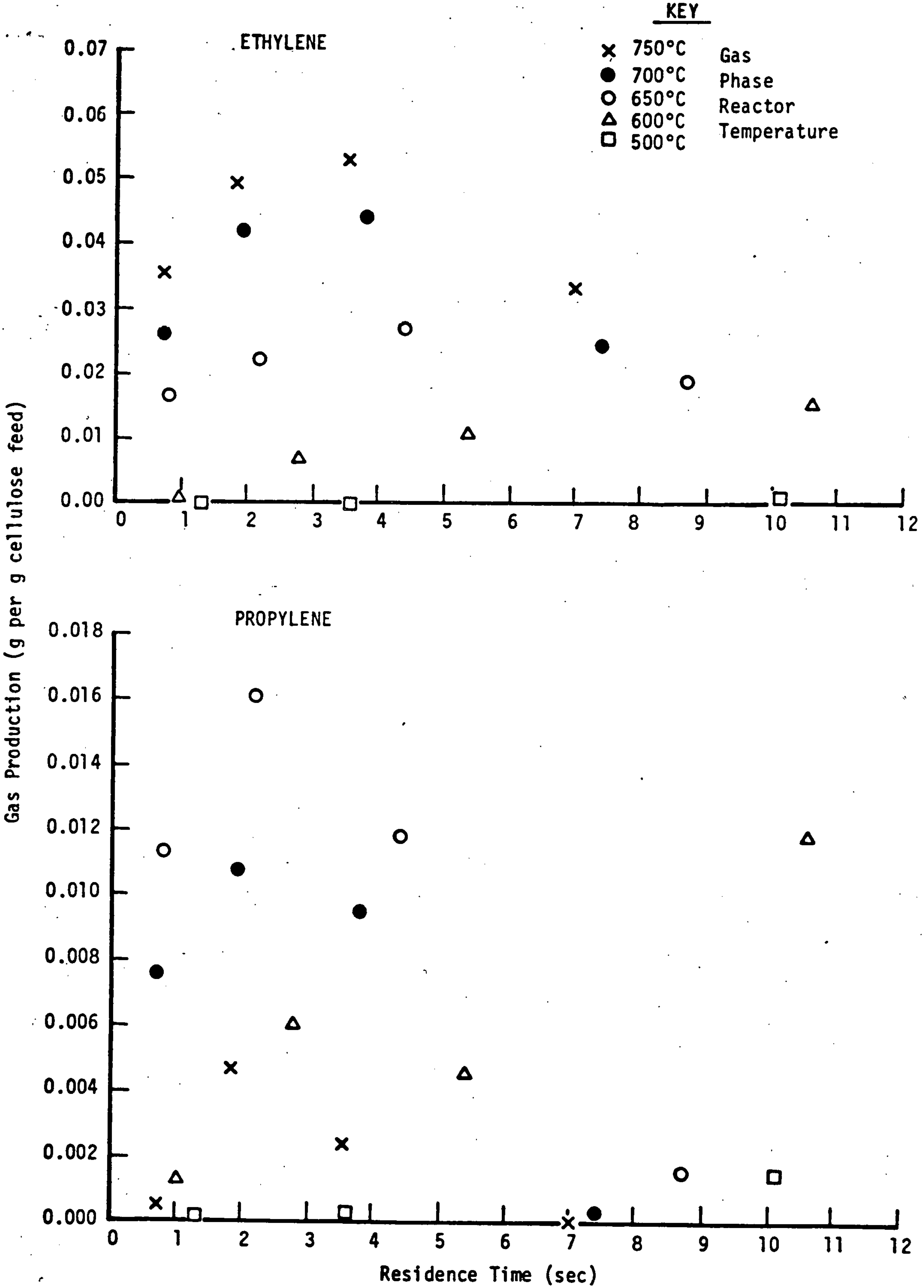

Figure 4 Olefin production vs. residence time as a function of gas phase reactor temperature.

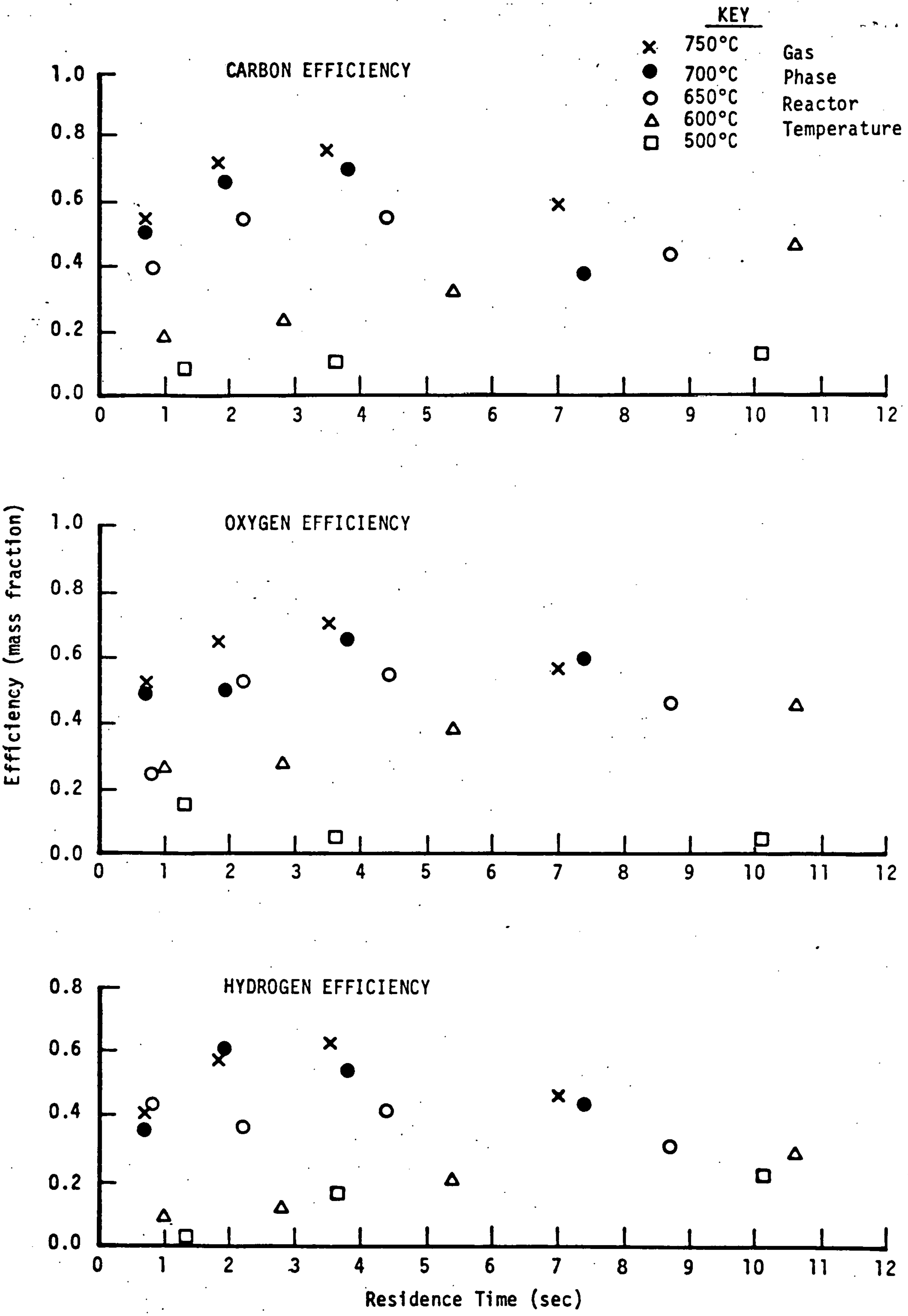

Figure 5 Carbon, hydrogen and oxygen efficiencies vs. residence time as a function of gas phase reactor temperature.

Figure 6

CELLULOSE $\Delta H_{PYROLYSIS}$ VS. PRESSURE