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REACTION, PROCESS, AND COST ENGINEERING FOR THE FLASH HYDROPYROLYSIS (FHP) OF COAL

by

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Abstract

The latest experimental data on the Flash Hydropyrolysis of North Dakota lignite in the 2 lb/hr entrained tubular reactor experimental facility are summarized. The range of conditions investigated covers reactor pressures from 500 psi to 4000 psi, temperatures from 500° to 900°C, and coal particle residence times in the reactor from 1 to 10 seconds. The major effects of the process variables on the yields of liquid hydrocarbons consisting mainly of BTX and heavy oils ($\geq C_9$) and hydrocarbon gases consisting mainly of methane and ethane and small amounts of carbon oxides are summarized. The product yield for maximum carbon conversion to liquid was obtained at 725°C and 2000 psi and amounts to 10% BTX, 10% oils, 25% methane, 10% ethane, and 6% CO. A maximum gaseous yield was obtained at 875°C and 2500 psi and amounts to 88% methane, 0.5 ethane, 1.3% CO and < 1% BTX. The optimum coal residence time in the tubular reactor for the liquid condition is ~ 7 seconds and for gases it is ~ 2 seconds. Possibilities exist for improving liquid yields at higher pressures and for improving gas effluent compositions under dense phase operation. A three-step reaction model is developed in an attempt to obtain generalized expressions of the

hydrocarbon component yields as a function of pressure, temperature and residence time. The experimental data have been fitted to Arrhenius type rate equations taking into account formation and decomposition of major products. Activation energies indicate mainly a chemical reaction controlled mechanism. The use of these rate equations in conjunction with heat balance expressions are described for the design of a hydropyrolysis reaction vessel. Additional experimental, design, and analysis work is needed to obtain a much more detailed understanding of the reactor engineering. Process design and preliminary economic estimates are made for three versions of the FHP process system: (1) producing only liquid products for motor gasoline fuel, (2) producing both liquid and gaseous hydrocarbon products for motor gasoline and pipeline gas, and (3) producing only gaseous products for pipeline gas. For comparable overall values of coal conversions (62%), the minimum production cost is obtained for the combined production of motor gasoline and pipeline gas. The largest factor (∿ 35%) in the capital cost of the FHP plant is the equipment needed for recycling and conditioning the hydrogen process gas. The FHP process has the advantage of allowing effective gas-solid and gas-liquid separation operations for producing hydrocarbon products from the unconverted char, oils, and process gas. The FHP system also has the distinct advantage of versatility and process flexibility for varying the product slate and the production rate of gaseous and liquid hydrocarbon fuel products in the same reactor depending on reactor operating conditions.

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I. Introduction

Following early work, in the 1960's, on the rapid gas phase hydrogenation of coal for the synthesis of liquid hydrocarbons, preliminary bench scale experiments in a 3/4-in. diameter x 8-ft long downflow reactor was undertaken at Brookhaven National Laboratory in 1974.(1) When hydrogenating lignite at temperatures and pressures up to 700°C and 1500 psi, the results indicated significant yields of liquids, especially benzene, and gaseous hydrocarbons, particularly methane and ethane. The liquid yields increased for reaction residence times less than 30 seconds.

Preliminary process design and economic evaluation of a flash hydropyrolysis process(2) indicated a reasonable return on capital investment especially for chemical feedstock production. This gave encouragement to the further investigation and development of a flash hydropyrolysis process (FHP) which featured a one step, non-catalytic, rapid deep hydrogenation system for conversion of coal to synthetic liquids and gaseous fuels. In late 1976 a larger, versatile, and highly instrumented entrained downflow tubular reactor was constructed and placed into operation.(3)

During this period several university research laboratories have contributed to an understanding of the rapid coal hydrogenation reaction, notably, R. Graff et al.(4) at City University of New York and J. B. Howard et al.(5) at MIT. In addition, three federally-supported industrial programs have been undertaken at Cities Service Research and Development Company on a short residence time (CS-SRT) hydrogenation process,(6) at the Institute of Gas Technology on a high speed riser cracking process (using a coil reactor)(7) and at Rocketdyne Corp. on a rocket type reactor system.(8) Other private industrial oil and chemical companies also appear to be actively interested in the FHP systems.

The purpose of this paper is to summarize the Brookhaven experimental results on FHP, to present correlations of data and models which would represent the data, to indicate how these correlations can be used for reactor and process designs, to present several flow sheets, (one for maximizing liquid, another for maximizing gas, and a third for gas and liquid coproducts) and to update and present further preliminary economic estimates and evaluations.

II. Experimental Results

A 1-in. tubular reactor, 8-ft long equipped with four sectional clam shell electric heaters and 4-ft of cooling section was constructed of Inconel 617, a high Cr-Ni alloy. A 4-lb capacity pressurized coal feed hopper mounted on top of the reactor tube can feed coal up to 2 lbs/hr downflow to the reactor. Hydrogen can be supplied up to 5 lbs/hr and preheated to a maximum of 850°C in a 1/4-in. diameter electrical resistance heated hairpin tube. The reactor tube maximum operating conditions are 4000 psi and 800°C or 2500 psi and 900°C. An on-line process gas chromatograph can analyze 10 chemical components every eight minutes with sample taps every two feet along the length of the reactor and in the traps and vent lines. A char trap maintained at 300°C separates out the char and avoids condensation of liquid hydrocarbons. This is followed by a water-cooled trap which separates the oils ($\geq C_9$) and a low temperature trap (-40°C) which separates the condensable BTX ($\leq C_9$). The remaining gases are vented up a stack.

A schematic of the apparatus is shown in Figure 1 and a summary of the operating characteristics of the equipment is given in Table 1. Mass balances and yields are computed based on the analyses and the liquid product and char collected. Initially, a non-caking North Dakota lignite was chosen for extensive study. Several exploratory runs have been made with higher rank coals, including treated caking coals. A typical computer data reduction and material balance printout sheet is given in Table 2 and includes the analysis of feed lignite and resulting char in addition to product yield data. The details of the experimental results to date are published in five quarterly reports.(9) Approximately 180 independent runs have been made with North Dakota lignite. The principal experimental results are summarized below.

The coal was usually ground to 50-150 μ particle size and dried to < 3% moisture in an inert atmosphere. Where not specifically noted the computed total residence time of the coal due to free fall and imposed hydrogen velocity down through the reactor tube is in the order of 9 to 12 seconds. Attempts at experimental measurement of residence time have also been made with capacitor plates at the entrance and exit of the reactor.

The major gaseous hydrocarbon products formed are methane and ethane. CO and CO_2 are also formed in minor amounts. The major liquid products formed are BTX, containing mainly (90 to 100%) benzene, and heavier hydrocarbons referred to either as oils ($\geq C_9$) or heavier liquid hydrocarbons. The latter consist mainly of polynuclear aromatic hydrocarbons (PAH's) the composition of which is shown typically in Table 3. It is interesting to note that under the present experimental conditions, no detectable amounts of aliphatic or oxygenated compounds (phenol and cresol) have been found. Due to the high boiling range of the $\geq C_9$ hydrocarbons (see Figure 17), a satisfactory analytical method for an on-line measurement for these has not as yet been developed. The yield of the $\geq C_9$ product fraction is determined by collection and analysis of the total liquid produced at the end of a run. Generally, the limit of accuracy for the analysis of the solid coal and char (C, H, N, S, ash, etc.) and the BTX by the on-line gas chromatograph, is considered to be within ± 2% of the absolute value. Calculations of hydrogen consumption, effective carbon conversion (carbon in liquid and gaseous products divided by total carbon including carbon required to produce hydrogen) and energy conversion efficiency (the ratio of the heating value of the products to the heating value of the coal feed including that for producing hydrogen) are also given in Table 2.

One of the first questions which had to be answered was the effect of hydrogen on the coal conversion reaction in comparison to an inert gas pyrolysis. Figure 2 indicates that over a series of reactor pressures from 100 to 167 atm and 750°C temperature, the presence of hydrogen increases the total hydrocarbon yield by at least six times and the liquid hydrocarbon yield by at least eight times. The yields are expressed in fraction of carbon in the feed coal converted to product. Thus, hydropyrolysis unequivocally improves the yields of liquid and gaseous hydrocarbon products.

A series of dilute phase (C/H weight feed rates of 0.5 to 1.5) coal hydrogenation experiments was performed to obtain the parametric process chemistry. The effects of the major process parameters, which includes hydrogen pressure, hydrogen preheat, reactor temperature, and gas and coal particle residence times were determined on the product yields and distribution.

The general trend characteristics of the FHP conversion of coal to products collected at the exit of the tubular reactor are shown for the main liquid product BTX in Figure 3, and the main gaseous hydrocarbon (methane and ethane) in Figure 4. It appears that the yield of liquid remains at a relatively low level at any given pressure until temperatures in the order of 650°C is reached. The BTX yield tends to rise and reach a maximum in the order of 10% at temperatures ranging from 725° to 800°C after which the yield declines. Thus, a dynamic equilibrium appears to be established between the formation and the decomposition of the liquid hydrocarbons. In the case of the gaseous hydrocarbons, the yield appears to continually rise both as a function of pressure and temperature reaching values as high as 50 to 60%. However, it should be pointed out that these are not maximum yields since they have been measured at the exit which is across the entire length of the reactor at coal residence times ranging from about 9 to 12 seconds. The maximum yields along the length of the reactor and the effect of residence time are presented later.

Concerning the flash hydropyrolysis operation, it is calculated that the average coal particle heat-up rate from ambient feed temperature to reactor temperature is approximately 50,000 °C/sec when mixed at the entrance to the reactor with 750°C preheated hydrogen. The calculated heat-up rate for the coal particle to reach devolatilization temperature (∿ 500°C) is significantly greater, being approximately 150,000 °C/sec. The average cool-down or quench rate of the reaction mixture from the heated reaction zone, through the air cooled quench zone to the 300°C char trap is approximately 200 °C/sec. However, the initial cool-down rate at the exit of the reaction zone may be higher.

Figure 5 shows the experimental curves for the average maximum BTX yields observed as a function of both temperature and pressure. The maximum yields were determined from the highest measured value along the length of the reactor using the sample taps. The maximum yields increase with an increase in both variables reaching a maximum of approximately 10% under two sets of conditions, i.e., at 2000 psi and 800°C and at 2500 psi and 750°C. The product yields as a function of residence times are given in Figure 6 for 2000 psi and 775°C and in Figure 7 at 2500 psi and 775°C. The maximum yields for BTX peak out respectively at about 4 and 7 seconds coal particle residence time along the reactor. When the temperature is raised to 800°C at approximately the same pressure of 2000 psi as shown in Figure 8, the benzene yield is seen to have already reached its maximum by 2 seconds residence time and has started to decompose at a more rapid rate.

Generally, as shown in Figure 9, when using North Dakota lignite at temperatures in the range of 725° to 750°C and 2000 psi, the maximum yield of the heavier liquid hydrocarbons ($\geq C_9$), is approximately the same as the BTX yield. However, above 750°C, the $\geq C_9$'s decrease much more rapidly with increasing temperature than the BTX. Since one of the probable products of decomposition or cracking of the heavier liquids is BTX, there appears to be a strong relationship between the measured yields of these two liquid products. At even higher temperatures, (> 775°C) the heavier liquids ($\geq C_9$'s) decrease rapidly primarily due to hydrogenation and rapid formation of gaseous hydrocarbons.

Figure 10 summarizes the results of experiments designed to maximize the gaseous hydrocarbon ($CH_4 + C_2H_6$) yields as a function of temperature and pressure. The data shows that the yield of these products can reach values in excess of 80% at 2500 psi and 875°C. The figure also indicates the strong dependency of the yield on operating pressure, the yield increasing at the rate of approximately 17% of the available carbon converted for every 500 psi increase in system pressure at temperature in the range of 875°C. A cross plot of HC gas yield as a function of pressure is further discussed in conjunction with Figure 15.

Figures 11 and 12 show the typical decrease in all product yields observed at 875°C as the coal particle residence time exceeds 4 to 5 seconds. Note how at approximately 9 seconds residence time, the only products found left are methane and small amounts of oxides of carbon, mainly CO.

As the temperature is increased to 900°C given in Figure 13, the rate of decomposition of the HC products, which now consist mainly of methane, increases markedly. This is observed to hold true even at pressures down to 1000 psig as shown in Figure 14.

The maximum gaseous hydrocarbon yield occurs between 2.4 and 7 seconds coal particle residence time over a range of pressures as given in Figure 15. At residence times greater than this, the yield decreases as indicated previously. The almost linear nature of the curves shows a yield increase of 2.8 to 3.8% per 100 psi of total system pressure. This pressure effect is thermodynamically in agreement with that predicted for the hydrogen-carbon reaction for formation of CH_4 and C_2H_6.

The production of carbon oxides, $CO + CO_2$, is seldom greater than 10%, and under conditions producing the greatest hydrocarbon yields it is usually in the order of about 5%. As shown in Figure 16, very little CO_2 is formed and the CO concentration is reduced considerably as the system pressure is increased which again is in agreement with thermodynamic equilibrium.

A number of experimental runs were also conducted at pressures of 3000 and 4000 psig. At these higher pressures, the non-caking lignite tended to agglomerate, causing plugging of the reactor. The reason for the agglomeration of a non-caking coal such as lignite under higher hydrogen system pressure is not clear. Although these high pressure runs were not fully successful because of the difficulty in making an accurate material balance, nevertheless, some observations can be made. First, the results obtained at 3000 psig did not appear to differ significantly from those obtained at 2500 psig whether operating in a mode to optimize liquid yields at a lower temperature or in a mode to optimize gaseous yields at higher temperatures. Second, at 4000 psig and 725°C, BTX yields as high as 17% were indicated in conjunction with ethane yields of approximately 30%. These ethane yields are about three times greater than those observed at lower pressures. The methane to ethane ratio at the higher pressure is about 1.5 compared to a value of three usually obtained at the lower pressures. Further investigation is necessary to confirm these data.

The flash hydropyrolysis of lignite is an exothermic process under most conditions. When operating at conditions to maximize liquids, although the reaction to produce these aromatic liquids may be endothermic, (based on the heat of formation of benzene from hydrogen and carbon, +20 kcal/mole) the reactions producing water (by hydrogenation of the relatively high oxygen content (23.4%) in lignite) and the co-products methane and ethane (heats of formation are -18 and -20 kcal/mole, respectively) make the overall process exothermic (∿ -0.66 kcal/gm of coal). As conditions are changed to reduce liquid yields and increase the yields of methane and ethane, the overall process becomes even more exothermic, reaching approximately -1.2 kcal/gm of coal at high methane yields.

Since the feed ratio of hydrogen to coal is usually in the order of 1 lb of hydrogen to 1 lb of coal, the product concentrations in the process gas stream are far below thermodynamic equilibrium values. Due to this dilute phase, the methane gas usually is below 5 mole % concentration in the equipment while the equilibrium concentration is 84% at 700°C and 4000 psig and 32% at 900°C and 500 psig. In a recent experiment designed to study the effect of hydrogen to coal ratio, a methane concentration of approximately 33% was observed. The experimental conditions were 2500 psig and 875°C with a hydrogen to coal feed ratio of 0.2. Under these conditions, the equilibrium concentration is about 61%, thus, the methane reached 54% of the equilibrium value. It should be further mentioned that for these denser phase experiments, correlations should be made with partial pressure of hydrogen which decreases rapidly as equilibrium is approached.

A distillation curve was made on the total liquid product collected from a liquid mode run and is shown in Figure 17. The sharp break in the curve after approximately 50% of the liquid had distilled over is due to the almost 50% concentration of BTX usually found in the liquid. The last drop came over at 314°C after 84% of the material had distilled over. The remaining 16% was solid residue.

Tables 4 and 5 give the approximate distribution in the products of the nitrogen and sulfur initially found in the coal. The N and S content in the feed is generally low (0.9% and 0.5%, respectively). As shown in Table 4, very small amounts of nitrogen, ∿ 4% of the N in the feed is found in the liquid hydrocarbon. The absolute concentration of nitrogen in this product is less than 0.2%. The aqueous liquid produced by the hydrogenation reaction usually has a pH of ∿ 9, was found to contain as much as 3.3% NH_3. Although the quantity of nitrogen found in the water produced and the char varies considerably as indicated in the table, the sum is usually between 70 and 75%, thus leaving approximately 21 to 26% unaccounted for, which is assumed to be vented to the atmosphere as NH_3.

The sulfur balance, given in Table 5, shows the major portion (48-77%) remaining in the char. Generally, the greater the overall carbon conversion to products, the higher the sulfur retention in the char. The sulfur concentration in the liquid hydrocarbon product is usually < 0.1% which indicates that less than 1% of the sulfur in the coal finds its way into the liquid. The water produced in the hydrogenation reaction contained approximately 12-15% sulfur as H_2S and the remaining 15-35% was assumed to have been vented to the atmosphere as H_2S. The low S concentration in the liquid product is beneficial when considering blending and hydrocracking for producing motor gasoline.

The results of two exploratory runs are given in Tables 6 and 7. In the first run, the feed to the reactor was made up by blending an equal weight of char from previous runs with freshly ground lignite. Table 6 indicates that the BTX increased 61% and the ethane more than doubled. This could be attributed to either a catalytic effect of the char or since the yields were calculated on the carbon contained in the coal feed alone, some of the yield could have come from reaction with the char itself. The 49% reduction in CO (from 8.1% to 4.1%) could be attributed to the fact that the char is almost completely devoid of any oxygen.

The run given in Table 8 was made by feeding fresh lignite impregnated with 5 wt% iron. The results obtained with this coal were slightly greater than those obtained with untreated coal run at the same conditions, except for an increase in BTX (+61%) at the expense of the light oils (-49%) and a substantial increase in ethane (+80%). Further work needs to be performed to determine the trade off of increased yield due to catalysis and the cost of the catalyst or its recovery.

III. Summary of the Experimental Observations

1. The presence of hydrogen in the reactor significantly improves the yield of both liquids and gaseous hydrocarbon products compared to straight pyrolysis.

2. The liquid yields which consist of BTX (mainly benzene) and heavier oils ($\geq C_9$) become significant at temperatures above 650°C and

go through a maximum and then decrease above temperatures of 800°C.

3. Liquid yields of approximately 20% (∿ 10% BTX and ∿ 10% oils ($\geq C_9$)) are obtained in the temperature range of 725° to 800°C and hydrogen pressures of 2000 psig or greater.

4. Although increased hydrogen pressure tends to cause increases in liquid yields, the effect becomes less pronounced above 2000 psig.

5. For the production of liquids, coal residence times in excess of 5 to 7 seconds are not necessary; at temperatures > 775°C, longer residence times tend to cause decomposition of the liquids resulting in a lower yield.

6. Potentially high BTX yields (∿ 17%) observed at 4000 psig hydrogen indicates that further study is necessary at high pressures, however, difficulties in agglomeration are encountered.

7. The gaseous hydrocarbon yields, principally consisting of methane and ethane, continually rise both as a function of both pressure and temperature.

8. A maximum of approximately 90% carbon conversion to gaseous hydrocarbons was observed at 875°C and 2500 psig hydrogen pressure.

9. Hydrogen pressure has a significant influence on the gaseous HC yield; a linear increase in yield of as much as 3.4% for each 100 psi increase in hydrogen pressure is obtained.

10. Maximum gaseous yields occur at coal particle residence times of 2 to 5 seconds and mainly towards the shorter residence times. Increased residence time causes significant decomposition of the products, particularly at temperatures greater than 850°C.

Two definitive maximum point runs obtained to date are shown in Table 8. One run listed, is the highest liquid yield run (19.9% liquid and 64.5% total conversion) and the other is the highest gaseous yield run (88.5% HC and 90.5% total conversion).

The accumulation of experimental yield data over a wide range of temperature, pressure, and residence time is a continuing effort. The correlation of this process chemistry data is of vital importance to the confident design of a hydropyrolysis reactor and its integration into a coal refinery operation.

IV. Reaction Modelling and Correlation of Experimental Data

The following assumptions were made for modelling the reaction system:

1. The system is considered to be isothermal, based on the thermal measurements along the length of the reactor.

2. Chemical reactions are the rate determining steps.

3. Due to the complex nature of coal, the reaction kinetics are based on a semi-empirical approach based on experimental observation rather than on a pure mechanistic model alone.

4. Experimental weight fractions of BTX, methane, and ethane increase and then decrease as well as decomposition of these species and is taken into account in the model. The quantities of methane and ethane produced from BTX are assumed, in the first approach to the model, to be small compared with those from the direct hydrogenation of the coal.

5. Carbon oxides and all other chemical species are not considered in the model because of their relatively small quantities. The heavy oil product is considered in this model to be an intermediate species. These products can be taken into account in a more complete model in the future.

6. Free carbon formed by the decomposition of the products, has lower reactivity with the hydrogen than the carbon in coal.

7. Dilute phase operation in an excess hydrogen atmosphere is assumed so that the partial pressure of hydrogen approximates the total pressure.

8. The model can be considered as a lumped parameter model with all the unknown phenomena accounted for by the kinetic constants.

The reaction scheme is then:

$$\text{C(in coal)} + H_2 \xrightarrow{k_1} \text{BTX (benzene, toluene, xylene)} + H_2 \xrightarrow{k_2} CH_4 + C_2H_6 \qquad (1)$$

$$\text{C(in coal)} + 2H_2 \xrightarrow{k_3} CH_4 + H_2 \xrightarrow{k_4} \text{C(free carbon)} \qquad (2)$$

$$\text{C(in coal)} + H_2 \xrightarrow{k_5} C_2H_6 + H_2 \xrightarrow{k_6} \text{C(free carbon)} \qquad (3)$$

Reaction (1) shows that benzene, toluene, and xylene (BTX) in coal are devolatilized upon heating which can then decompose in the presence of hydrogen to methane, ethane, and free carbon. Reactions (2) and (3) are the hydrogenation of coal to form methane and ethane which can then decompose to form free carbon upon further reaction. k_1 to k_6 are the kinetic constants of the reaction and are functions of temperature and pressure. This three-step sequence, which admittedly does not describe the entire reaction chemistry, represents an initial attempt in a comprehensive correlation of the experimental results.

Representing the concentration of carbon, BTX, methane, and ethane in the reactor as [C], [BTX], $[CH_4]$, and $[C_2H_6]$, one can then write the mass balance equation for these species.

$$-U_s \frac{d[C]}{dx} = (k_1 P_{H_2}^{\ n_1} + k_3 P_{H_2}^{\ n_3} + k_5 P_{H_2}^{\ n_5})[C] \qquad (4)$$

$$U_g \frac{d[BTX]}{dx} = k_1 P_{H_2}^{\ n_1} [C] - k_2 P_{H_2}^{\ n_2} [BTX] \tag{5}$$

$$U_g \frac{d[CH_4]}{dx} = k_3 P_{H_2}^{\ n_3} [C] - k_4 P_{H_2}^{\ n_4} [CH_4] \tag{6}$$

$$U_g \frac{d[C_2H_6]}{dx} = k_5 P_{H_2}^{\ n_5} [C] - k_6 P_{H_2}^{\ n_6} [C_2H_6] \tag{7}$$

U_s and U_g are the solid and gas velocity, respectively, where U_s can be determined from a stochastic model by Waslo and Gal-Or(11) and the inlet conditions are:

$$[C](o)=C_o,\ [BTX]=0,\ [CH_4]=0,\ [C_2H_6]=0 \tag{8}$$

A list of the nomenclature used in the kinetic model is given at the end of this paper. Equations (4)-(8) can be solved for the weight fraction conversions. For BTX, methane and ethane, the weight fraction conversion expressions are correlated in the following form.

$$Y_1 = \frac{A}{-\alpha_{1i}+\alpha_{2i}} \left(e^{-\alpha_{1i}t} - e^{-\alpha_{2i}t}\right) \tag{9}$$

Where i designates the components BTX, methane and ethane; α_{1i}, α_{2i} and A relate to the kinetic constants k_1 through k_6. Applying the nonlinear estimation method criteria of obtaining good calculated values is based on reducing the sum of the square of the deviation of the calculated value from the observed value to a minimum. To apply the method of Box, one needs to have reasonably good initial estimates of these parameters. Parameter A can be found from the first data point (i.e. the lowest residence time conversion).

$$A = \left.\frac{dy_i}{dt}\right|_{t=0} = \frac{Y_{i1}-0}{t_i-0} = \frac{Y_{i1}}{t_i} \qquad (10)$$

α_{1i} and α_{2i} are found from the maximum point, i.e., by setting $\frac{dy}{dt} = 0$ in equation (9) and combining the result with equation (9) evaluated at $Y_{i\ max}$ and t_{max}, one obtains:

$$\exp(-\alpha_3/\nu_{max}) + \nu_{max}\ \ln\ \alpha_3 = 0 \qquad (11)$$

and

$$\alpha_1 = -\ln\alpha_3/t_{max} \qquad (12)$$

where $\nu_{max} = Y_i$, $max/(A\ t_{max})$ and $\alpha_3 = \alpha_2\ Y_i$, max/A. One can use the Newton-Raphson technique to determine α_3 (hence α_2). α_1 is then found from equation (12).

Correlation of experimental data have been made using the eighteen experimental runs in which hydrocarbon yields were measured at 2-ft intervals along the reactor length to obtain the residence time data. These data are mainly at 2000 and 2500 psi total pressure. The data have been correlated and coupled with the model to give the kinetic constants.(13) An example of fitting the data to the kinetic reaction model expression is shown for a run in Figure 18. The theoretical model indicates that at a given temperature and pressure, α_{1i} in the first experimental term in equation (9) should be constant for all the weight fraction conversions of BTX, CH_4 and C_2H_6. However, correlation of the data does not indicate this behavior. This may be due to the fact that other reactions in addition to the three-step reaction sequence assumed in equations (1) through (3) may be taking place. This indicates that further modification of the model is required, however, it is not clear as yet as to what key reactions should be considered. Other than this limitation, the final expression for the yields of BTX, CH_4 and C_2H_6 are given in Table 9. It is noted that equations (16) through (21) will vary depending on the data correlated in the present form are based on the results of eighteen runs at pressure of 2000, 2500 psi and temperature of 725° to 900°C.

The standard error for the estimated conversion of BTX, methane, ethane with coal residence time, at constant temperature and pressure is within $\pm$ 10% of the mean values.

The activation energies of all these reactions (equations (16) through (21)) are found to be in the order of 30 kcal/g-mole or more, ranging up to 87.9 kcal/gm mole with the exception of equation 19, which has a lower value. This largely indicated that the reaction mechanism within the particle size range investigated is largely, kinetically (chemical reaction) controlled as opposed to heat or mass transfer (diffusion) controlled. These activation energies are in general the same order of magnitude as the activation energies found for the pyrolysis of coal.(5) This might indicate that the rate controlling step in flash hydropyrolysis is the initial devolatilization of the coal.

V. Reactor Design

The reaction model and the conversion equations derived above can be applied to the design of an FHP reactor. Only a preliminary example of the application to the design of an entrained downflow reactor operating under isothermal conditions, in approximately the experimental range investigated, is presented here. An FHP liquefaction plant producing 50,000 bbl/day of liquid distillate product will require approximately 25,000 tons/day of lignite (e.g., gas to solid particle velocity

U_{gs} of 0.2) pressure of 2000 psi and temperature of 775°C and fractional conversion of coal to BTX of 10%, then applying equations (13) through (18) and (20) to the coal particle residence time is calculated to be 18 seconds. The reactor diameter can be determined by the following equation.

$$d = \left(\frac{4M}{U_s \rho_s \Pi \phi} \right)^{1/2} \tag{22}$$

Where M is coal flow rate, U_s is velocity of the solid particle, ρ_s is solid density, ϕ is volumetric solid fraction in a reactor (ϕ is 0.03 for the present calculation). The reactor length can be obtained by the product of velocity of the solid particle and its residence time. The velocity of the solid particle can be approximated by Stokes' free fall velocity.

The calculation indicates that the diameter of the reactor should be 21.6 ft and the length 17.2 ft. However, the design of the reactor is also limited by the ability to construct high pressure and high temperature thick-walled vessels. Therefore, to limit wall thickness to a reasonable size (∿ 6") the number of vessels would be increased to four which would then decrease the diameter to 10.8 ft. The length remains at a value of 17.2 ft.

Further work is needed to design an adiabatic flash hydropyrolyzer to deal with the heat transfer in the reactor.

VI. Process Design and Selection of Process Conditions

Having developed some of the experimental data for the FHP process chemistry and correlating the results which includes expressions for the yields of the major products, i.e., gaseous methane (CH_4) and ethane (C_2H_6) and liquids (aromatics BTX ($\leq C_9$) and heavier oily liquids ($\geq C_9$)) as a function of the major process variables, i.e., pressure, temperature, and reactor residence time, an FHP reactor design and process design can be obtained. However, since the product mix varies with the reactor conditions there are at least three modes of operation of the FHP process as a synthetic fuel producer as follows: (1) a maximum amount of liquid product, (2) both liquids and gases, maximizing the coal conversion, and (3) a maximum amount of gases. The FHP process is, thus, a highly versatile product oriented system depending on the operating conditions of the reactor. The basic concept of the reactor and process design has been discussed previously emphasizing the chemical feedstock aspects.(2) In this paper we will in a similar manner evaluate the process as a fuel producer in the three modes outlined above.

The coal refinery in any of the production modes consists of the following common sections.

1. Coal preparation.
2. Flash hydropyrolysis
3. Product separation and gas recycling.
4. Hydrogen production.
5. Product separation.
6. Services
7. Environmental control.
8. Land, working capital, and facility development.

Process block diagrams for FHP are given in Figure 19 for liquid motor gasoline production alone, in Figure 20 for combined product motor gasoline and pipeline gas, and in Figure 21 for pipeline gas alone. Details of the complementary and auxiliary process units are given in reference 10. The major differences between the three processes besides the operating conditions in the flash hydropyrolyzer are as follows.

(a) Liquid Production

The main plant features consists of the FHP unit, cryogenic separation of gaseous products, recycling hydrogen and a conventional refinery complex. Liquid products are recovered in the quench tower unit and processed through the fuel refinery complex. Methane produced in the FHP unit is steam reformed to produced the hydrogen for performing the hydropyrolysis. All the char from the hydropyrolyzer is used to fuel the recycle hydrogen preheat furnace and to produce the steam for methane reforming. Methane reforming eliminates the need for an oxygen plant.

A process advantage over other liquefaction processes such as synthoil and SRC II is that the products are condensed out of the gaseous phase eliminating the need for a difficult high temperature liquid-solid separation operation. A process disadvantage is that large amounts of hydrogen must be recycled and made up for high temperature and pressure operation of the FHP.

(b) Combined Liquid and Gas Production

In this case the main process departure from (a) is that the char from the FHP unit is gasified using an oxygen plant and a steam generator is needed to feed the BCR (Bituminous Coal Research) gasifier.

(c) Gas Production

The plant consists of the FHP unit combined with cryogenic separation of methane, and recycling hydrogen. Char from the hydropyrolyzer, together with make-up coal, is gasified with oxygen and steam in a BCR gasifier. The methane gas is also used for plant fuel requirements.

A parametric study would be desirable for determining capital and manufacturing cost as a function of the yields at different pressure, temperature and coal residence times in the flash hydropyrolyzer. In lieu of a detailed optimization, the present study deals with a point determination for each of the three modes of operation. In Table 10, specific product yields were selected based on the experimental results described above. It is noted that the gas product yield condition was limited to approximately the same value as for the liquid (total conversion of 62%). Further estimates will be made in the future based on the maximum experimental results obtained for gas yields.

VII. Plant Capacity and Material and Energy Balances

Typical plant capacities for coal conversion to pipeline gas have been selected to produce an equivalent of 250 million cubic feet per day of gas. This corresponds to a fuel oil equivalent (FOE) of approximately 50,000 bbl/day of fuel oil. These capacities were used to size the three plants studied here. It would take about 40 of these large plants to provide motor fuel equivalent to 25% of the current U. S. consumption and 50 of the gasification plants to provide 20% of the natural gas consumption. For the yields given in Table 10 the coal feed rate required is in the order of 25,000 to 30,000 tons per day of lignite for production of 47,700 bbl/day of motor gasoline in the liquid process or 395 MM SCFD of pipeline gas for the gas process. Table 11 gives the materials and energy balance for each of the three plants.

Although the overall energy efficiency (based on products from FHP) varies from 79% to 94% from an all gas to an all liquid process, the net thermal efficiency (accounting for internal plant energy needs) varies from 60.9% for all gas to a high 72% for the combined gas and liquid plant, but decrease to 50% for the liquid plant. The reason for the lower net efficiency for the liquid plant is that the methane produced in the FHP reactor is reformed with steam to produce hydrogen.

VIII. Capital and Manufacturing Cost

A modularized unit capital cost estimate was made.(10) Table 11 summarizes these costs. The subunits under each of the major sections are listed below.

1. Coal preparation

    Pulverizer-dryer
    Storage
    Feed system

2. Flash hydropyrolysis

3. Product separation and gas recycle

    Char and solid separation system
    Iron oxide tower
    Quench tower
    Decanter for gas plant
    MEA and CO sorbent system for gas plant
    BTX extraction unit for liquid plant
    Ethylene plant for liquid plant
    Dryer
    Gas separation unit
    Selexol and Cosorb systems for liquid plant
    H_2 furnace
    Recycle gas/superheat steam generator
    Feeding gas compressor
    H_2 recycle compression
    Pre-quench steam generator
    Recycle gas/H_2 exchanger
    H_2 furnace steam generator
    Quench cooler for liquid plant
    Post quench cooler for liquid plant

4. Hydrogen production

   Hydrogen feed compression
   Oxygen plant for gas and combined plant
   BCR H_2 generator
   Shift convertor
   Selexol
   Claus plant
   Post-BCR gasifier steam generator
   Post-shift steam generator
   Quench water cooler

   For liquid plant only:

   Steam reformer
   Shift convertor
   MEA unit
   Claus unit
   Refrigeration unit
   Reformer waste heat steam generator

5. Product preparation

   For liquid plant only:

   Dimerization
   Olefin hydrogenation
   Isomerization
   Alkylation
   Hydrocracker
   Gasoline blending

6. Services

7. Environmental control

8. Land, working capital, and facility development.

The highest capital investment is in the all pipeline gas plant, amounting to $936 million. The next highest is in the combined gas and liquid plant at $892 million and the least costly is in the all liquid plant at $839 million. The main difference for the liquid case is due the need for an oxygen plant for the all gas and the combined liquid and gas plant. There are also significant differences in the size of hydrogen recycle and steam generation equipment between the processes.

The following observations are made concerning the distribution of capital investment.

1. The largest fraction of the plant capital investment is in the product separation and hydrogen gas recycle being about 35% of the plant.

2. The next highest investment is in the hydrogen production part of the plant which amounts to 20 to 25% of the plant.

3. Land, working capital, and facility development comes next at about 13 to 15%.

4. One of the lowest fractions is for the flash hydropyrolyzer itself which is about 5%.

5. The environmental control capital investment; amounts to only about 3.4%.

A summary of the manufacturing costs are given in Table 13. Depreciation and mortgage finacing is estimated using a high debt leveraged utility economy. The lowest estimated cost is for the combined liquid and gaseous plant at \$3.83/MMBTU (0.54/gallon or \$23/bbl for motor gasoline). The next highest is for the all-gas plant at \$4.53/MMBTU pipeline gas (\$30.17/bbl FOE (Fuel Oil Equivalent)). The liquid only plant comes out highest at \$5.13/MMBTU (0.77/gas or \$32.34/bbl) reflecting the low net overall efficiency.

IX. Conclusions

It is concluded that the high net efficiency combined liquid and gaseous fuel product plant should be further developed. Further analysis should also be made at higher temperature conditions where higher yields of gases are obtained. Additional experimental kinetic data and modelling correlations are needed to gain confidence in the proper design of of flash hydropyrolysis reactors. The FHP process has the advantage of ease of separation of liquid and solid products from the reactor compared to other coal conversion processes. It also has the decided advantage of versatility and flexibility in producing a range of liquid and hydrocarbon products in one unit by varying the process conditions without the need for a costly catalyst system.

Nomenclature

A	empirical constant defined by equation (10)
[BTX]	dimensionless weight fraction of benzene, toluene and xylene normalized to initial carbon concentration
[C]	dimensionless weight fraction of carbon in coal normalized to initial carbon concentration
C_o	initial carbon concentration (weight fraction) in coal
$[CH_4]$	dimensionless weight fraction of methane normalized to initial carbon concentration
$[C_2H_6]$	dimensionless weight fraction of ethane normalized to initial carbon concentration
k_1 to k_6	reaction rate constants in equations (1) to (3)
M	coal flow rate, lb/sec
n_1 to n_6	reaction rate order of hydrogen partial pressure in equations (1) to (3)
U_s	velocity of solid particle
U_g	velocity of gas
U_{gs}	U_g/U_s
t_1	the solid residence time corresponds to measurement at the first 2-ft of reactor
t_{max}	the solid residence time corresponds to maximum yield of species measured.
x	axial coordinate along the reactor
Y	weight fraction conversion of species
Y_{max}	maximum weight fraction conversion of species

Greek Symbols

α_1	empirical constant in equation (9)
α_2	empirical constant in equation (9)

Nomenclature (Cont'd)

α_3	$\frac{\alpha_2 Y_{i,max}}{A}$
ν_{max}	$\frac{Y_{i,max}}{A\ t_{max}}$
ρ_s	coal density
ϕ	volumetric solid-phase fraction in reactor
Θ_B	dimensionless weight fraction of benzene, toluene, and xylene
Θ_4	dimensionless weight fraction of methane
Θ_6	dimensionless weight fraction of ethane

Subscript

i	species subscripts; i=1 for BTX; i=2 for CH_4; i=3 for C_2H_6

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Table 1

DESIGN AND OPERATING CHARACTERISTICS OF THE 1" TUBULAR ENTRAINED DOWNFLOW REACTOR EXPERIMENT

Reactor size	1-in. i.d. x 12 ft long (8 ft heated)
Material	Inconel 617
Coal flow capacity	Up to 2 lb/hr (down to 0.1 lb/hr)
Max. run time	∿ 2 hrs (hopper capacity ∿ 4 lb)
Hydrogen flow	Up to 5 lb/hr (down to 0 flow)
Design pressure	Up to 4000 psi
Design temperature	Up to 900°C
Coal residence time	∿ 0.5 sec (min.) ∿ 20 sec (max.) (free fall for 50 μ particles)
Instrumentation	Full pressure, temperature, and flow rate remotely controlled
Analytical	On-line gas chromatograph measuring 10 components every 8 min. with integrator and direct readout and compositional analysis. H_2, CO, $(+N_2)$, H_2O, CO_2, CH_4, C_2H_6, C_6H_6, C_7H_8, C_8H_{10} and total HC.
Sample taps	Every 2 ft along reactor
Production collection	Trap - char Water condenser - oils Low temp. condenser - BTX Batch gas sampler - gas

Table 2

TYPICAL RUN DATA, MASS BALANCES AND YIELD

North Dakota Lignite
Run No. 115, Sample No. 3, Date: 2/28/78

Coal residence time - measured --
calculated - 7.070 (sec)

Nominal Conditions		
Coal feed rate	0.8675	lb/hr
Hydrogen flow rate	0.9250	lb/hr
Hydrogen velocity	0.1861	ft/sec
Reactor temp.	750.0	°C
Preheat temp.	750.0	°C
Hydrogen pressure	2500.0	psi

Total Accumulated Wts. (gm)	
Coal feed	584.0
Char	227.4
Light oils	32.00
BTX	37.50
Water	150.0

	Coal Analysis (wt%)	Char Analysis (wt%)
Carbon	61.08	68.70
Hydrogen	4.080	2.200
Oxygen (by difference)	23.44	3.950
Nitrogen	0.870	0.660
Sulfur	0.530	0.990
Ash	10.00	23.50

Proximate Analysis (wt%)	
Volitile matter	43.1
Fixed carbon	46.9
Ash	10.0

Moisture Content of North Dakota Lignite as Mined is 30% by Wt

	Product Conc. in Gas, lb/C. ft	% Carbon Conv. to Product	% MAF Coal Conv. to Product
Carbon Monoxide	.1890E-03	2.672	4.228
Carbon Dioxide	-0-	-0-	-0-
Methane	.8910E-03	21.99	19.93
Ethylene	-0-	-0-	-0-
Ethane	.3430E-03	9.033	7.674
Benzene	.3140E-03	9.550	7.025
Toluene	.2700E-05	.8122E-01	.6041E-01
Xylene	-0-	-0-	-0-
Light Oil	.2540E-03	8.034	5.906
Water	.1190E-02	-0-	26.62
	Total	51.36	

Table 2 (Cont'd)

Total Material Balance, %

	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	MAF Coal
Liquids	17.7	22.1	0	0	0	13.0
Hydrocarbon gases	31.0	145.0	0	0	0	27.6
Carbon oxides	2.67	0	9.27	0	0	4.23
Water	-0-	65.2	90.9	-0-	-0-	26.6
Ammonia	-0-	3.22	-0-	70.5	-0-	0.827
Hydrogen sulfide	-0-	0.221	-0-	-0-	27.3	0.171
Char	43.8	21.0	6.56	29.5	72.7	33.1
Total	95.2	256.0	107.0	100.0	100.0	106.0

Hydrogen consumption - .6379E-01 lb hydrogen/lb coal
1.253 Mole hydrogen/mole Carbon

Heat of reaction - .6624 kcal/gm of coal fed

Effective carbon conversion (%) - 51.36
Effective energy efficiency (%) - 67.11

Table 3

TYPICAL COMPOSITION OF OILS AND HEAVIER LIQUID HYDROCARBON PRODUCT ($\geq C_9$) FROM THE FLASH HYDROPYROLYSIS OF LIGNITE

	Wt%
Naphthalene	38.1
Other 2 ring aromatics (methyl naphthalene fluorene, etc.)	19.5
Three ring aromatics (phenanthrene, etc.)	11.1
Four ring aromatics (pyrene, etc.)	5.1
Five ring aromatics (chrysene, etc.)	3.1
High boiling fraction (asphaltenes)	23.1

Table 4

FLASH HYDROPYROLYSIS OF LIGNITE

Nitrogen Balance

Nitrogen Conc. in Lignite Feed - 0.87% N

	% Distribution in Product	Concentration in Product Stream (wt%)
Contained in liquid HC product	4	0.16
Contained in char	30-55	0.6-1.1
Dissolved in water produced	15-40	2.7-5.0
Vented to atmosphere	21-26*	-0-

* By difference

Table 5

FLASH HYDROPYROLYSIS OF LIGNITE

Sulfur Balance

Sulfur Conc. in Lignite Feed - 0.53% S

	% Distribution in Product	Concentration in Product Stream (wt%)
Contained in liquid HC product	1	0.09
Contained in char	48-77	0.85-1.7
Dissolved in water produced	12-14	0.54-0.73
Vented to atmosphere	15-35*	-0-

* By difference

Table 6

FLASH HYDROPYROLYSIS OF LIGNITE

Effect of Char Addition to Lignite Feed

Fraction Carbon Converted at 750°C and 2000 psig (Based on Lignite Only)

	100% Lignite Feed	50% Lignite-50% Char*	% Change Over 100% Lignite
CO	0.081	0.041	- 49%
CH_4	0.275	0.293	+ 7%
C_2H_6	0.055	0.120	+118%
BTX	0.076	0.122	+ 61%
Oils ($\geq C_9$)	0.104	0.070	- 33%
	0.591	0.646	

* Char added to lignite obtained from previous runs.

Table 7

FLASH HYDROPYROLYSIS OF LIGNITE

Effect of Treating Lignite with Iron Oxide

Fraction Carbon Converted at 2000 psig and 750°C

	100% Lignite Feed	5 wt% Fe Added* to Lignite	% Change Over 100% Lignite
CO	0.081	0.052	-36%
CH_4	0.275	0.302	+10%
C_2H_6	0.055	0.099	+80%
BTX	0.076	0.122	+61%
Oils ($\geq C_9$)	0.104	0.051	-49%
	0.591	0.626	

* Fe added as $Fe_3(SO_4)_2$ and dried.

Table 8

FLASH HYDROPYROLYSIS OF NORTH DAKOTA LIGNITE

Maximum Liquid and Maximum Gas Yield Runs

	Max. Liquid Run	Max. Gas Run
Run No.	134	135
Date	4/20/78	4/25/78
Reactor temp. (°C)	775	875
Reactor pressure (psig)	2000	2500
H_2 feed rate (lb/hr)	0.82	0.88
Coal feed rate (lb/hr)	0.98	0.95
Residence time (sec)	7.1	4.7
Product Yields (% Carbon)		
CO	3.4	1.3
CH_4	30.9	88.0
C_2H_6	10.3	0.5
Total HC gas	41.2	88.5
BTX	10.2	0.7
$\geq C_9$	9.7	0.0
Total liquid	19.9	0.7
Total	64.5	90.5
Heat of reaction (kcal/gm coal)	- 0.70	- 1.3
Hydrogen consumption (lb/lb coal)	0.077	0.20
Effective carbon conv. (%)	58.8	62.4
Effective energy eff. (%)	75.9	100.0

Table 9

REACTION MODEL AND EXPLICIT EXPRESSIONS FOR THE KINETIC CONSTANTS

Yield BTX, CH_4 and C_2H_6 as a Function of Kinetic Constants, Hydrogen Pressure Time and Gas to Solid Relative Velocity

	Equation No.
$\Theta_B(t) = \frac{k_1P_{H_2}^{n_1}}{U_{gs}(-kP_{H_2}^{n_1} - k_3P_{H_2}^{n_3} - k_5P_{H_2}^{n_5} + \frac{k_2P_{H_2}^{n_2}}{U_{gs}})}\left[e^{-(k_1P_{H_2}^{n_1} + k_3P_{H_2}^{n_3} + k_5P_{H_2}^{n_5})t} - e^{-\frac{k_2P_{H_2}^{n_2}t}{U_{gs}}}\right]$	(13)
$\Theta_4(t) = \frac{k_3P_{H_2}^{n_3}}{U_{gs}(-k_1P_{H_2}^{n_1} - k_3P_{H_2}^{n_3} - k_5P_{H_2}^{n_5} + \frac{k_4P_{H_2}^{n_4}}{U_{gs}})}\left[e^{-(k_1P_{H_2}^{n_1} + k_3P_{H_2}^{n_3} + k_5P_{H_2}^{n_5})t - \frac{k_4P_{H_2}^{n_2}t}{U_{gs}}} - e\right]$	(14)
$\Theta_6(t) = \frac{k_5P_{H_2}^{n_5}}{U_{gs}(-k_1P_{H_2}^{n_1} - k_3P_{H_2}^{n_3} - k_5P_{H_2}^{n_5} + \frac{k_6P_{H_2}^{n_6}}{U_{gs}})}\left[e^{-(k_1P_{H_2}^{n_1} + k_3P_{H_2}^{n_3} + k_5P_{H_2}^{n_5})t} - e^{-\frac{k_6P_{H_2}^{n_6}t}{U_{gs}}}\right]$	(15)

<u>Subscripts</u>: Θ (t) is expressed in weight fraction conversion of feed coal to product.
B, 4, and 6 refers to BTX, CH_4 and C_2H_6, respectively.

Table 9 (Cont'd)

REACTION MODEL AND EXPLICIT EXPRESSIONS FOR THE KINETIC CONSTANTS

Data Correlation Based on Temperatures of 725° to 900°C, Pressure of 2000 and 2500 psi

Chemical Reactions	Reaction Rate Expressions $k_m \sim (sec^{-1})$; P_{H_2} (atm) and $T\,^{o}K$	Equation No.
$C(\text{in coal}) + H_2 \xrightarrow{k_1} BTX$ (benzene, toluene, xylene)	$k_1 P_{H_2}^{n_1} = 1.12 \times 10^{12} P_{H_2}^{-0.3} \exp\left(-\frac{61969.3}{RT}\right)$	(16)
$BTX + H_2 \xrightarrow{k_2} CH_4 + C_2H_6$	$k_2 P_{H_2}^{n_2} = 9.34 \times 10^{14} P_{H_2}^{-0.19} \exp\left(-\frac{73154.7}{RT}\right)$	(17)
$C(\text{in coal}) + 2H_2 \xrightarrow{k_3} CH_4 + 2H_2$	$k_3 P_{H_2}^{n_3} = 2.64 \times 10^{4} P_{H_2}^{0.05} \exp\left(-\frac{29012.4}{RT}\right)$	(18)
$CH_4 + 2H_2 \xrightarrow{k_4} C$ (free carbon)	$k_4 P_{H_2}^{n_4} = 9.58 P_{H_2}^{0.85} \exp\left(-\frac{11709.8}{RT}\right)$	(19)
$C(\text{in coal}) + H_2 \xrightarrow{k_5} C_2H_6 + H_2$	$k_5 P_{H_2}^{n_5} = 3.41 \times 10^{13} P_{H_2}^{1.34} \exp\left(-\frac{87856.5}{RT}\right)$	(20)
$C_2H_6 + H_2 \xrightarrow{k_6} C$ (free carbon)	$k_6 P_{H_2}^{n_6} = 8.45 \times 10^{10} P_{H_2}^{-0.003} \exp\left(-\frac{55526.4}{RT}\right)$	(21)

k = kin constants (sec^{-1}); P = pressure in atm; T = absolute temp. (800 psi)

Table 10

FLASH HYDROPYROLYSIS OF COAL

Process Design Conditions

Coal Type - North Dakota Lignite

Main Fuel Product Made	Liquids	Liquids and Gases	Gases
Reactor Conditions			
Pressure, psi	2000 (136 ATM)	2000 (136 ATM)	2500 (170 ATM)
Temperature °C	750°C (1382°F)	750°C (1382°F)	825°C (1517°F)
Coal res. time, sec	8.7 sec	8.7 sec	9.5 sec

Product Yields

	Liquids		Liquids and Gases		Gases	
	% C conv. to product	% MAF Coal conv.	% C conv. to product	% MAF Coal conv.	% C conv. to product	% MAF Coal conv.
Methane (CH_4)	25.00	21.57	25.00	21.57	55.00	47.46
Ethane (C_2H_6)	10.00	8.09	10.00	8.09	1.00	0.81
Benzene C_6H_6)	10.00	7.00	10.00	7.00	0.50	0.35
Light oil ($\geq C_9$)	10.00	7.00	10.00	7.00	0.50	0.35
CO	6.00	9.04	6.00	9.04	5.00	7.53
CO_2	1.00	2.37	1.00	2.37	0.00	0.00
NH_3	-0-	0.96	-0-	0.96	-0-	0.96
H_2S	-0-	0.37	-0-	0.37	-0-	0.37
H_2O	-0-	24.74	-0-	24.74	-0-	27.66
Total	62.00	81.14	62.00	81.14	62.00	85.49
Char	38.00	24.54	38.00	24.54	38.00	24.54

Char Analysis

	Liquids	Liquids and Gases	Gases
C	69.00	69.00	69.00
H	2.53	2.53	2.53
O	0.00	0.00	0.00
N	0.55	0.55	0.55
S	1.80	1.80	1.80
Ash	26.12	26.12	26.12

Factors

	Liquids	Liquids and Gases	Gases
H_2 consumption lbs/100 lbs coal	6.75	6.75	10.7
H_T of reaction kcal/gm coal	- 0.79	- 0.79	- 0.95
Energy conversion efficiency - %	69.3	69.3	82.7

Table 11

FLASH HYDROPYROLYSIS OF COAL

Material and Energy Balance

Main Fuel Product Made	Liquids		Liquids and Gases		Gases	
Reactor Operating Conditions						
Pressure, psi	2000 (136 ATM)		2000 (136 ATM)		2500 (170 ATM)	
Temperature, °C	750°C (1382°F)		750°C (1382°F)		825°C (1517°F)	
Feed to Plant	tons/day	10^9 Btu/day	tons/day	10^9 Btu/day	tons/day	10^9 Btu/day
Lignite to FHP reactor	28,000	636.0	29,140	661.9	25,000	568.4
Lignite to BCR gasifier	-0-	-0-	-0-	-0-	3,946	89.6
Oxygen to BCR gasifier	-0-	-0-	9,729	-0-	11,464	-0-
H_2O for plant (net)	2,115	-0-	864	-0-	4,604	-0-
Total	30,115	636.0	39,733	661.9	45,014	650.0
Product from Plant						
Pipeline gas (CH_4)	2,562*	114.6*	5,583	250.5	11,020	493.3 (395.8 net
LPG (C_3H_8)	134	24.7	134	24.7	80 (oil)	2.9 (oil)
Motor gasoline (RON 90)	5,481	286.2	5,481	286.2	80 (Benz.)	3.2 (Benz.)
Tar	55	1.7	55	1.7	-0-	-0-
Sulfur (S)	186	1.5	201	1.6	203	1.6
Ammonia (NH_3)	184	3.6	184	3.6	192	3.7
Phenol & cresols	3	0.1	3	0.1	3	0.1
Ash	-0-	-0-	2,477	-0-	2,474	-0-
Char	9,114*	164.1*	-0-	-0-	-0-	-0-
CO	-0-	-0-	2,315*	19.6*	1,706*	14.8*
CO_2	12,396	-0-	23,300	-0-	29,256	-0-
Total	30,115	596.5	39,733	588.0	45,014	519.6
Efficiency - overall	94.0		88.8		79.0	
Net thermal %	50.0		72.0		60.9	
Product Values						
Pipeline gas	-0-		159 MM SCFD		395 MM SCFD	
Motor gasoline (90 RON)	47,700 BB/D		47,700 BB/D		-0-	
LPG	134 tons/D		134 tons/D		134 tons/D	

* Th streams are used internally for fuel in making up heat balance.

Table 12

FLASH HYDROPYROLYSIS OF COAL

Modularized Installed Cost of Plant

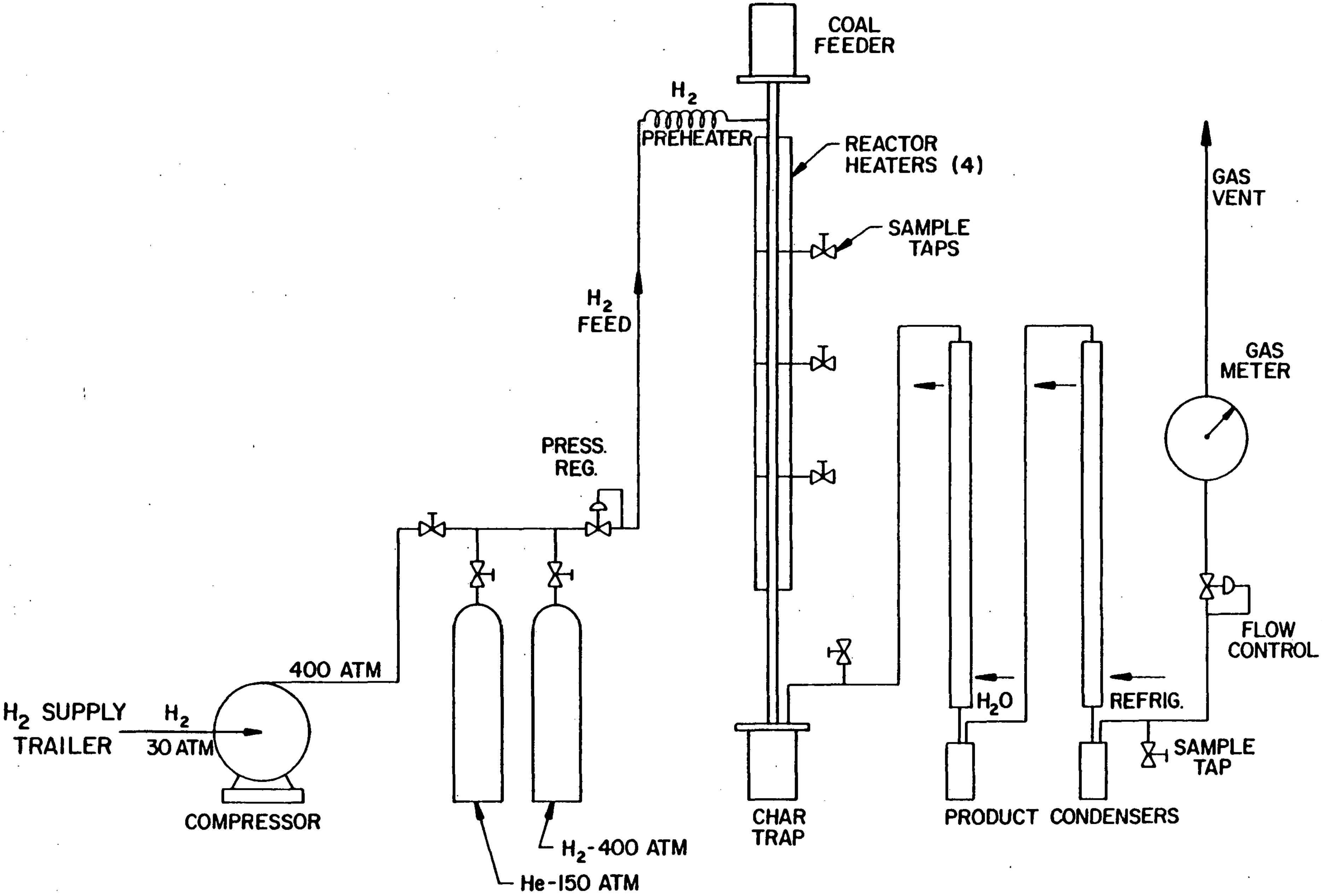
Main Fuel Product Made	Liquids		Liquids and Gases		Gases	
Reactor Operating Conditions						
Pressure, psi	2000 (136 ATM)		2000 (136 ATM)		2500 (170 ATM)	
Temperature, °C	750°C (1382°F)		750°C (1382°F)		825°C (1517°F)	
Product Values						
Pipeline gas (CH_4)	-0-		159 MM SCFD		395 MM SCFD	
Motor gasoline (90 RON)	47,700 BB/D		47,700 BB/D		-0-	
LPG	134 tons/D		134 tons/D		134 tons/D	
Capital Cost Installed 1978 Dollars	$ MM	% of Invest.	$ MM	% of Invest.	$ MM	% of Invest.
1. Coal preparation	92.0	11.0	94.0	10.6	94.0	10.0
2. Flash hydropyrolyzer	44.3	5.3	44.3	5.0	44.3	4.8
3. Product separation gas recycle	290.6	34.6	290.6	32.5	333.1	35.6
4. Hydrogen production	158.2	18.9	177.8	19.9	240.6	25.7
5. Product preparation	60.7	7.2	60.7	6.8	-0-	0.0
6. Services	37.7	4.5	61.3	6.9	61.3	6.5
7. Environmental control	31.2	3.7	38.0	4.2	37.0	4.0
8. Land working capital and facility development	124.3	14.8	125.7	14.1	125.5	13.4
Total	839.0	100.0	892.4	100.0	935.8	100.0

Table 13

FLASH HYDROPYROLYSIS OF COAL

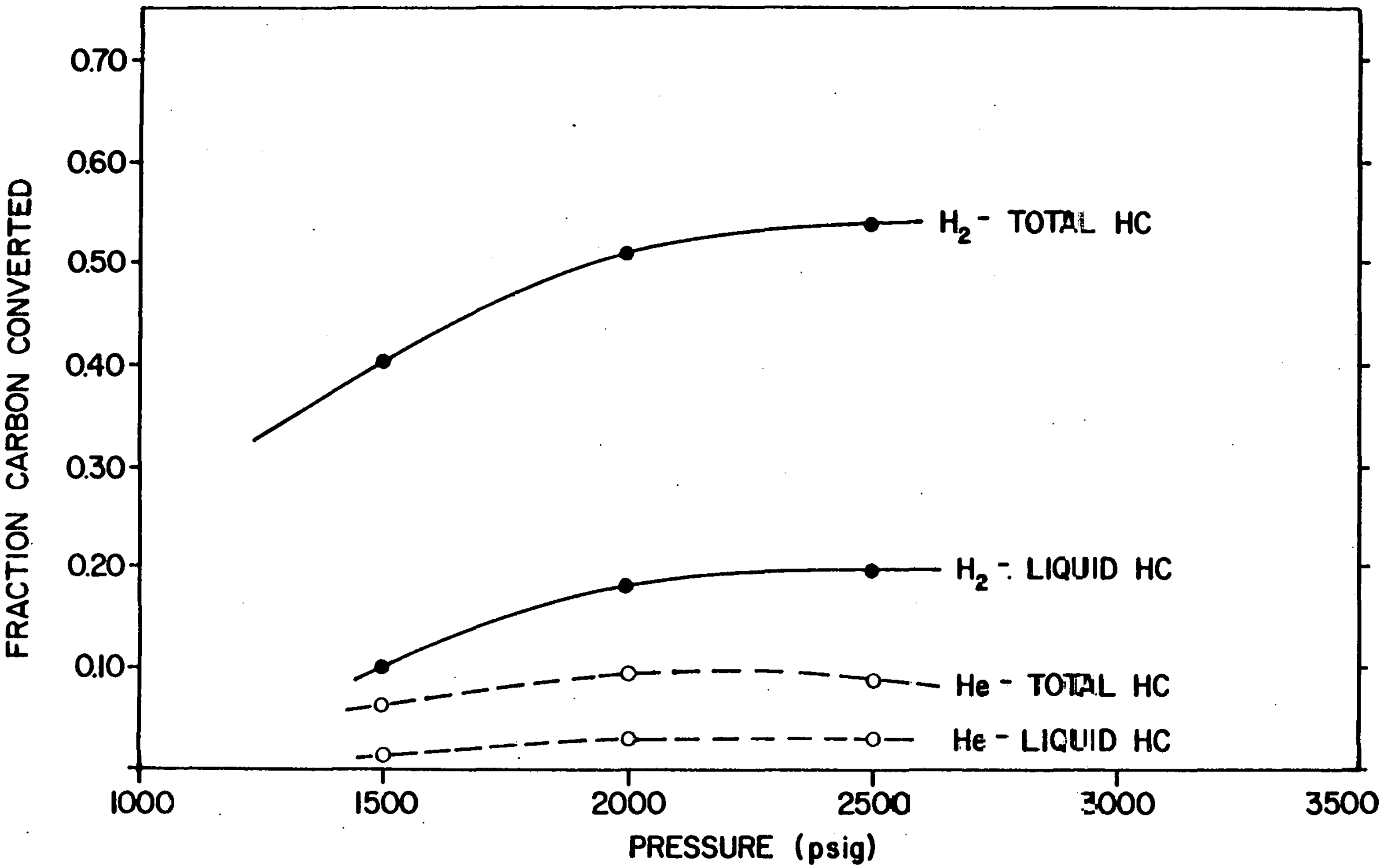
Manufacturing Cost of Product Fuel

Main Fuel Product Made	Liquids	Liquids and Gases	Gases
Reactor Operating Conditions			
Pressure, psi	2000 (136 ATM)	2000 (136 ATM)	2500 (170 ATM)
Temperature °C	750°C (1382°F)	750°C (1382°F)	825°C (1517°F)
Product Values			
Pipeline gas	-0-	159 MM SCFD	395 MM SCFD
Motor gasoline	47,700 BB/D	47,700 BB/D	-0-
LPG	134 tons/D	134 tons/D	134 tons/D
Operating Cost	$ MM/yr	$ MM/yr	$ MM/yr
Lignite @ $20/ton	204.4	212.7	212.5
Catalyst and chemicals	5.5	5.5	5.0
Power @ 15 mills/kwh	1.1	6.8	8.3
Ash disposal	2.6	2.8	2.7
Ins. Maint. GA (8% of capital)	57.2	71.4	74.9
Operating labor	8.0	8.0	8.0
Total operating cost	278.8	307.2	311.4
Mortage 10%	93.4	104.8	109.9
Depreciation @ 5% (20 yrs)	41.9	44.6	44.8
10% ROI and income tax	167.8	178.4	187.1
Total	$581.9	$635.0	$653.2
Selling Price (total FOE)	$5.13/MM BTU	$3.83/MM BTU	$4.53/MM BTU
Pipeline gas, $/MSCF	$5.13/MM BTU	$3.83/MM BTU	$4.53/MM BTU
Motor gasoline, (90 RON)	$ 0.77/gal	$ 0.54/gal	-0-
Fuel oil equivalent (FOE)	$ 32.34/bbl	$ 23.00/bbl	$$30.17/bbl



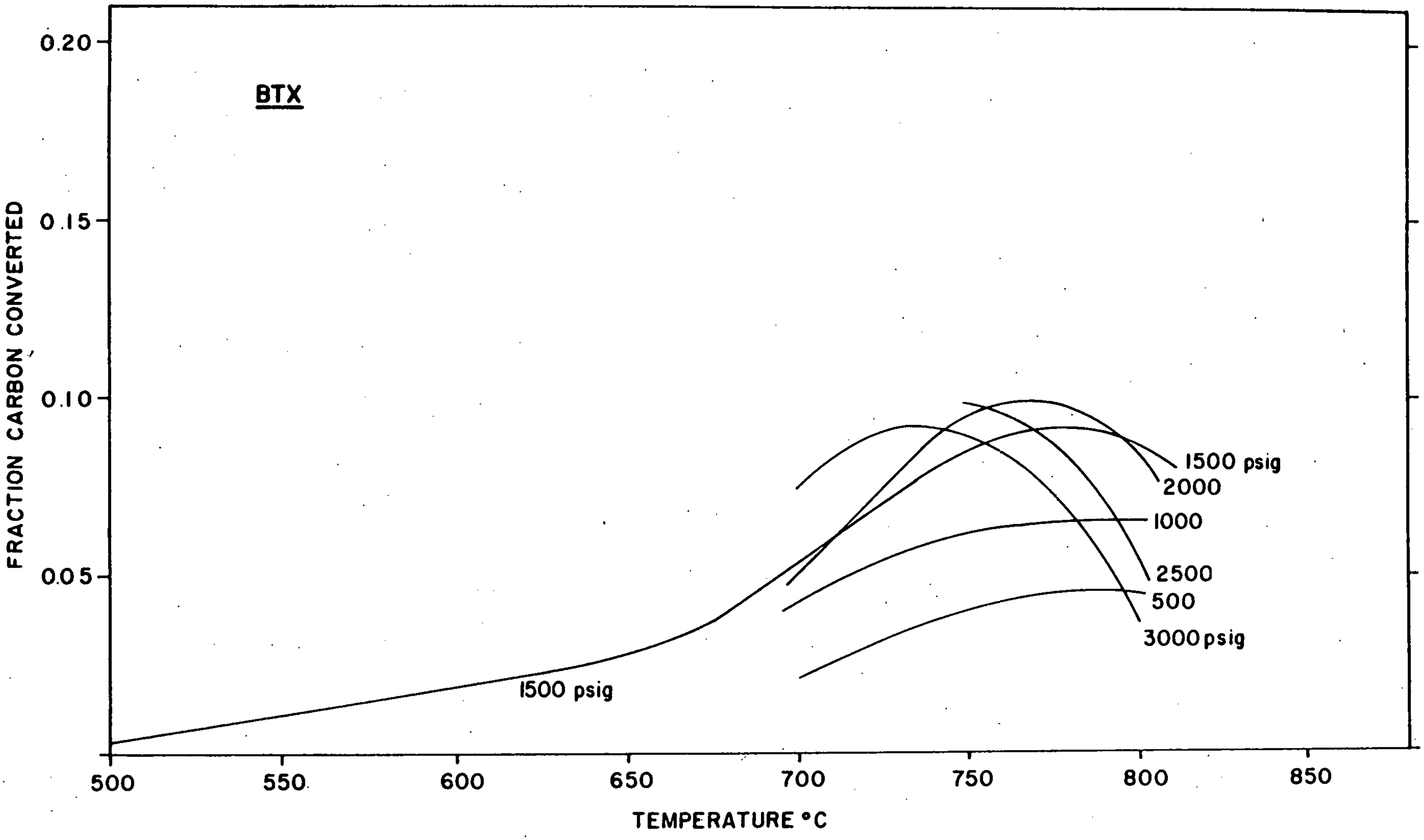
SCHEMATIC FLOWSHEET OF ENTRAINED TUBULAR REACTOR EXPERIMENT

Figure 1



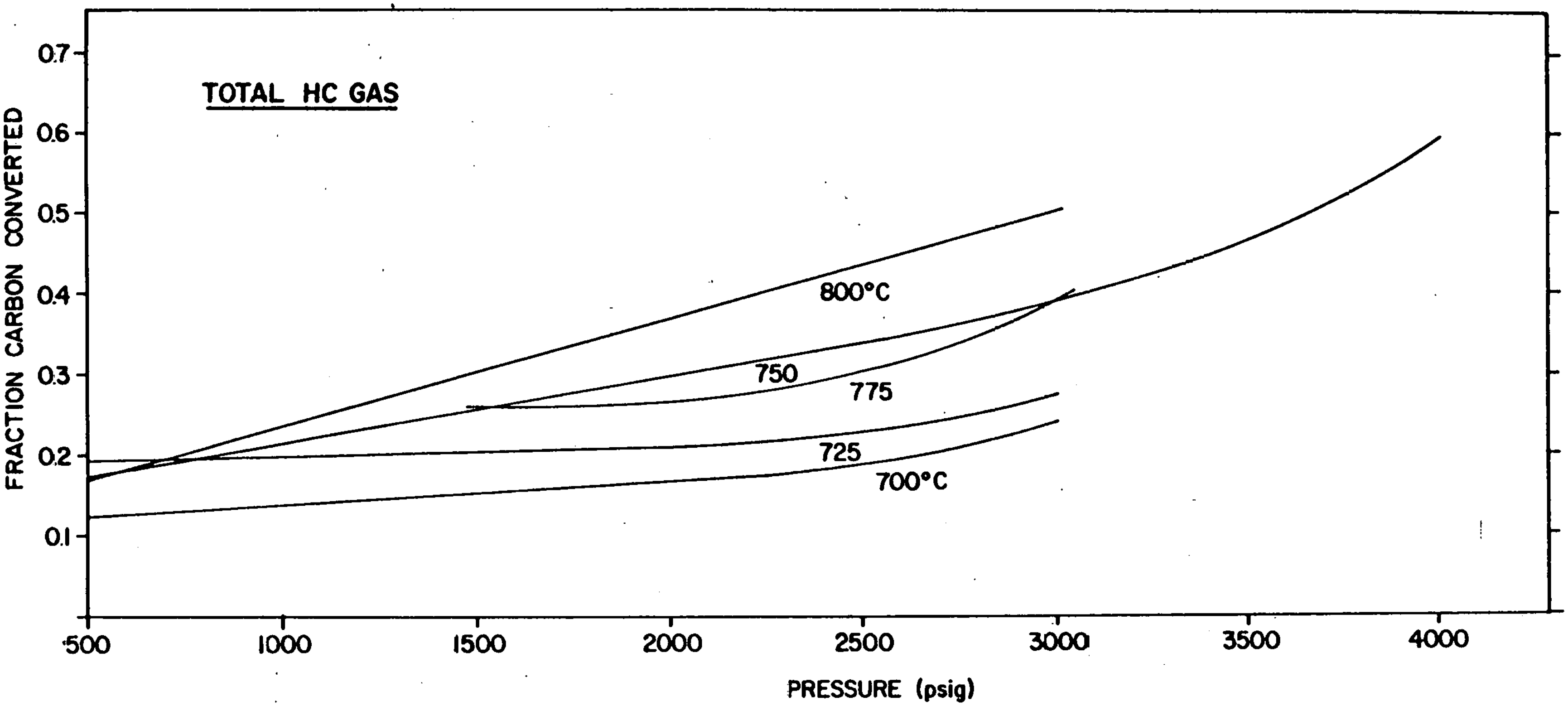
FLASH HYDROPYROLYSIS OF LIGNITE
TOTAL HC AND LIQUID YIELD vs. PRESSURE
TEMP. = 750°C
COAL RESIDENCE TIME 9-12 sec
COAL PARTICLES ≤ 150μ

Figure 2



FLASH HYDROPYROLYSIS OF LIGNITE
BTX vs TEMPERATURE
PRESS. 500 - 3000 psig
COAL RESIDENCE TIME 9-12 sec

Figure 3



FLASH HYDROPYROLYSIS OF LIGNITE
TOTAL HC GAS vs. PRESSURE
TEMP. 700°- 800°C
COAL RESIDENCE TIME 9-12 sec

Figure 4

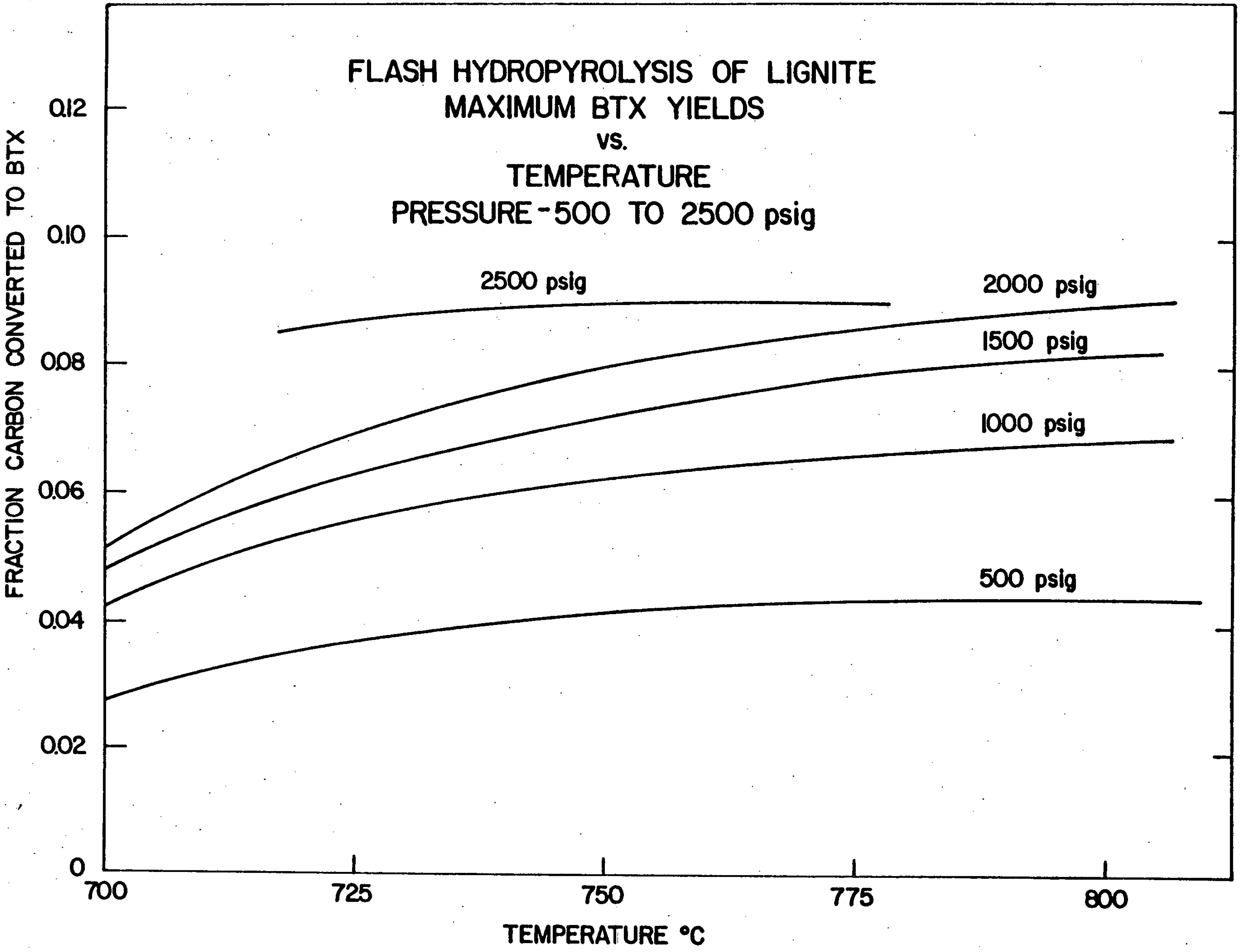

FLASH HYDROPYROLYSIS OF LIGNITE
MAXIMUM BTX YIELDS
vs.
TEMPERATURE
PRESSURE-500 TO 2500 psig
FRACTION CARBON CONVERTED TO BTX
0.12
0.10
0.08
0.06
0.04
0.02
0
700
725
750
775
800
TEMPERATURE °C
2500 psig
2000 psig
1500 psig
1000 psig
500 psig

Figure 5

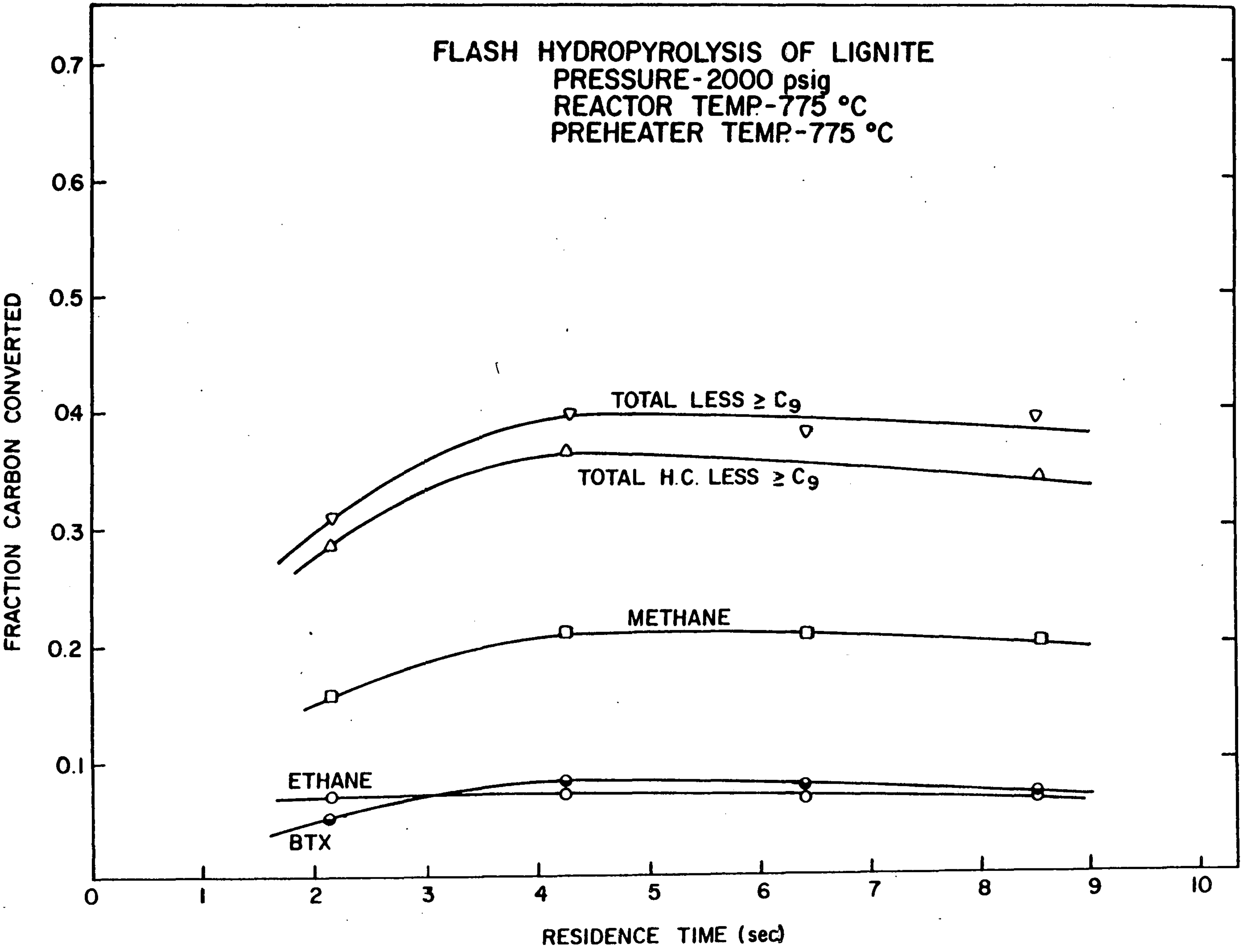

FLASH HYDROPYROLYSIS OF LIGNITE
PRESSURE - 2000 psig
REACTOR TEMP. - 775 °C
PREHEATER TEMP. - 775 °C
TOTAL LESS ≥ C9
TOTAL H.C. LESS ≥ C9
METHANE
ETHANE
BTX
FRACTION CARBON CONVERTED
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
6
7
8
9
10
RESIDENCE TIME (sec)

Figure 6

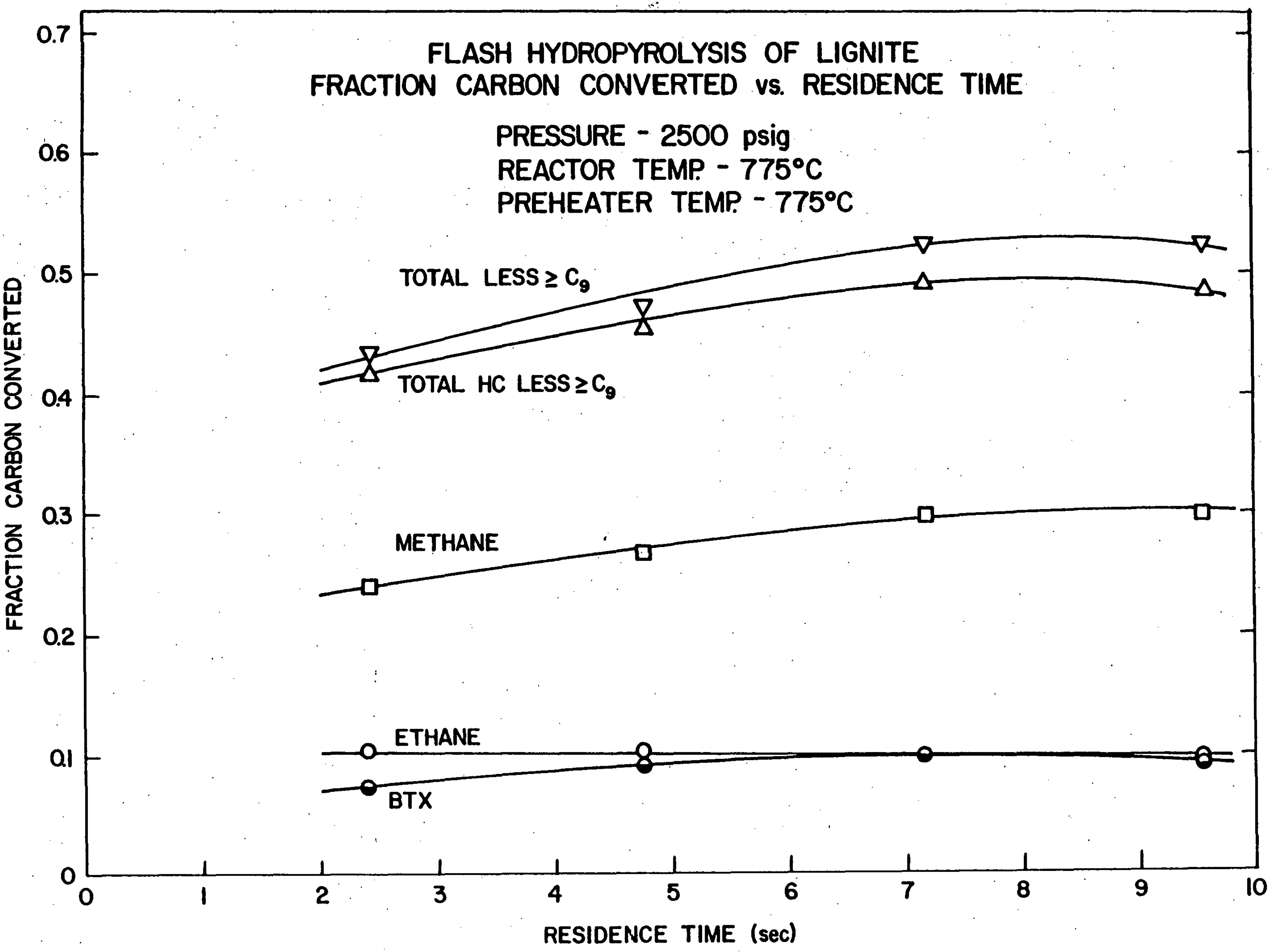

FLASH HYDROPYROLYSIS OF LIGNITE
FRACTION CARBON CONVERTED vs. RESIDENCE TIME
PRESSURE - 2500 psig
REACTOR TEMP. - 775°C
PREHEATER TEMP. - 775°C
TOTAL LESS ≥ C_9
TOTAL HC LESS ≥ C_9
METHANE
ETHANE
BTX
FRACTION CARBON CONVERTED
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
6
7
8
9
10
RESIDENCE TIME (sec)

Figure 7

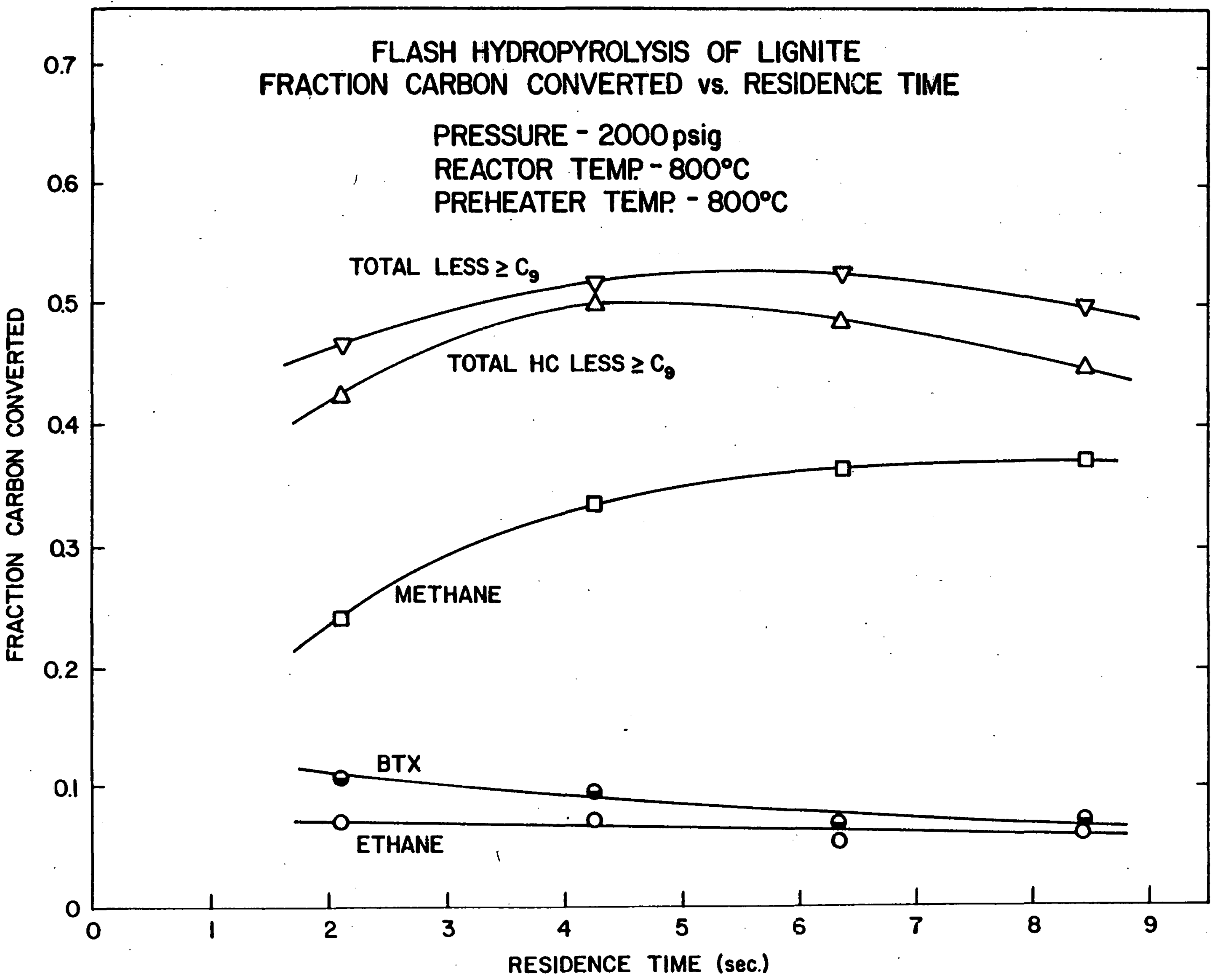

FLASH HYDROPYROLYSIS OF LIGNITE
FRACTION CARBON CONVERTED vs. RESIDENCE TIME
PRESSURE - 2000 psig
REACTOR TEMP. - 800°C
PREHEATER TEMP. - 800°C
TOTAL LESS ≥ C9
TOTAL HC LESS ≥ C9
METHANE
BTX
ETHANE
FRACTION CARBON CONVERTED
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
1
2
3
4
5
6
7
8
9
RESIDENCE TIME (sec.)

Figure 8

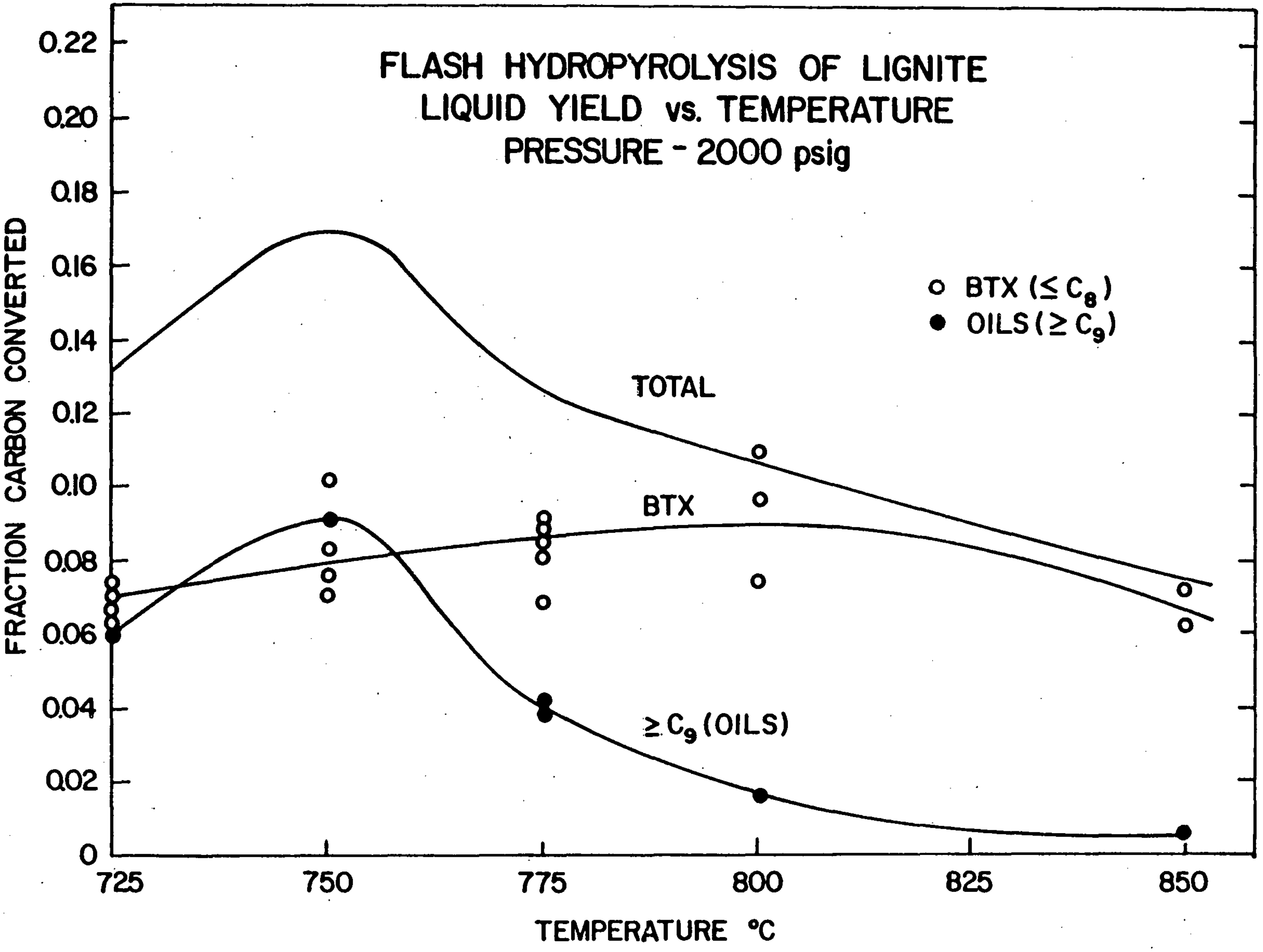

FLASH HYDROPYROLYSIS OF LIGNITE
LIQUID YIELD vs. TEMPERATURE
PRESSURE - 2000 psig
○ BTX ($\leq C_8$)
● OILS ($\geq C_9$)
TOTAL
BTX
$\geq C_9$ (OILS)
FRACTION CARBON CONVERTED
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
725
750
775
800
825
850
TEMPERATURE °C

Figure 9

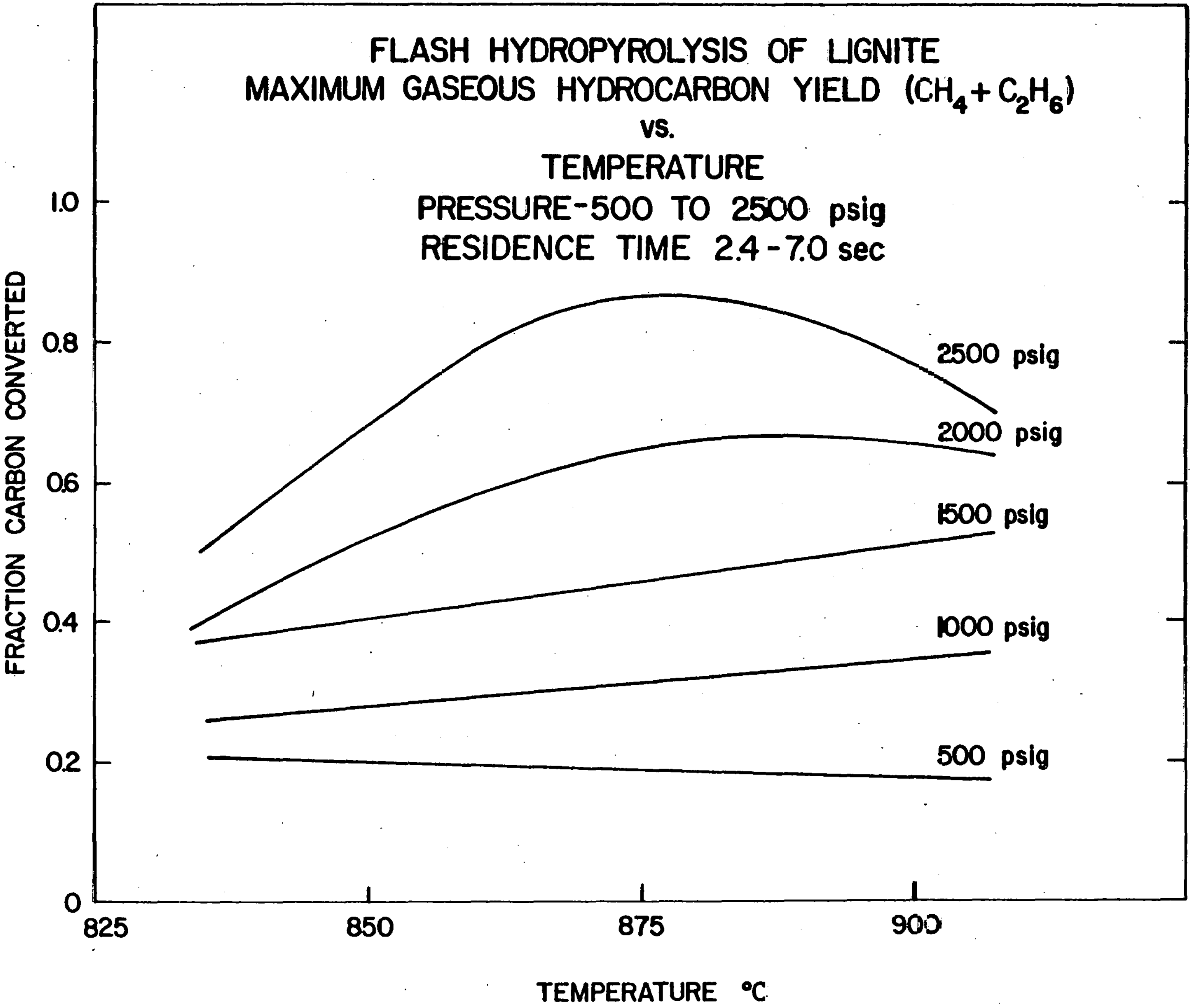

FLASH HYDROPYROLYSIS OF LIGNITE
MAXIMUM GASEOUS HYDROCARBON YIELD ($CH_4 + C_2H_6$)
vs.
TEMPERATURE
PRESSURE-500 TO 2500 psig
RESIDENCE TIME 2.4-7.0 sec
FRACTION CARBON CONVERTED
1.0
0.8
0.6
0.4
0.2
0
825
850
875
900
TEMPERATURE °C
2500 psig
2000 psig
1500 psig
1000 psig
500 psig

Figure 10

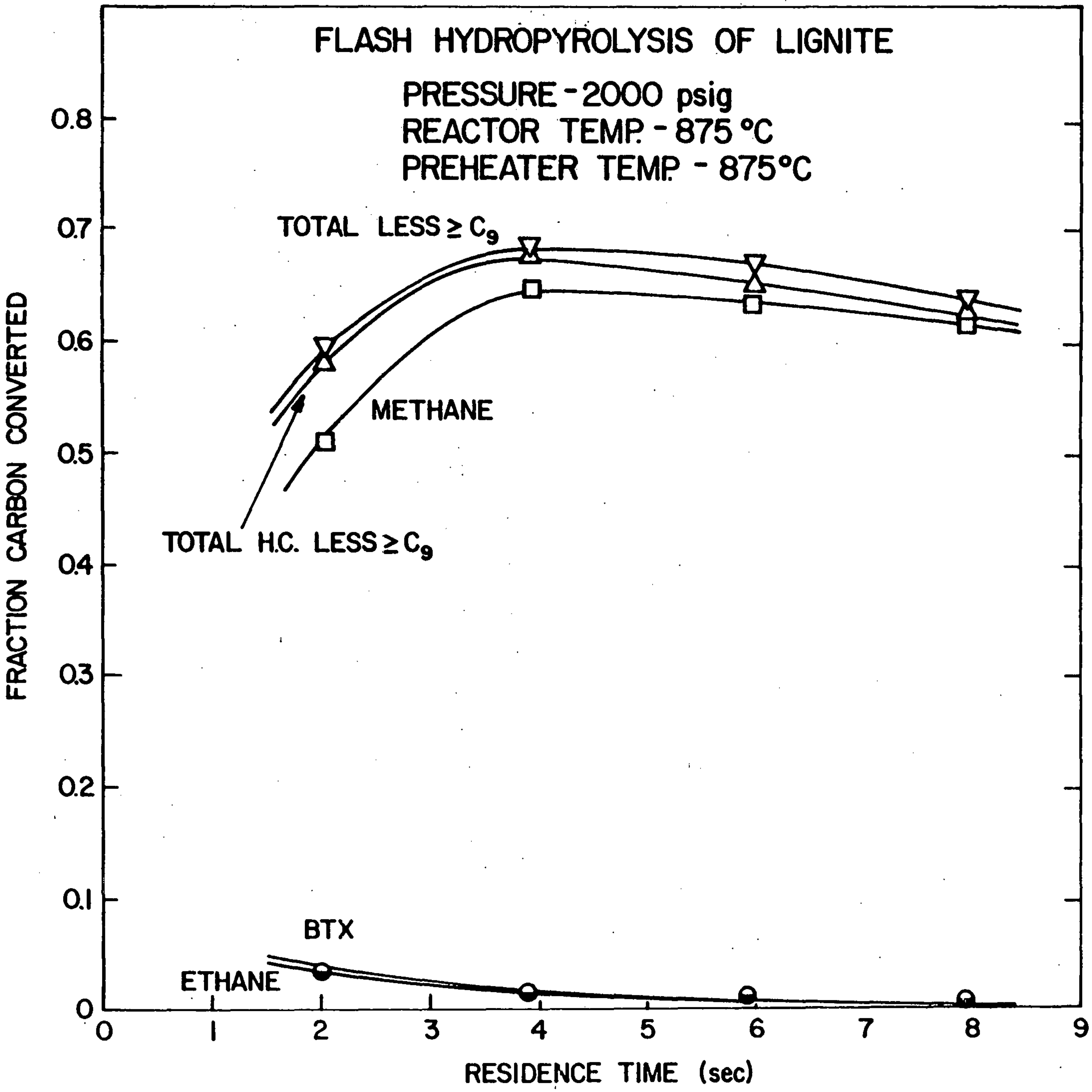

FLASH HYDROPYROLYSIS OF LIGNITE
PRESSURE - 2000 psig
REACTOR TEMP. - 875 °C
PREHEATER TEMP. - 875°C
TOTAL LESS ≥ C_9
METHANE
TOTAL H.C. LESS ≥ C_9
BTX
ETHANE
FRACTION CARBON CONVERTED
RESIDENCE TIME (sec)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
1
2
3
4
5
6
7
8
9

Figure 11

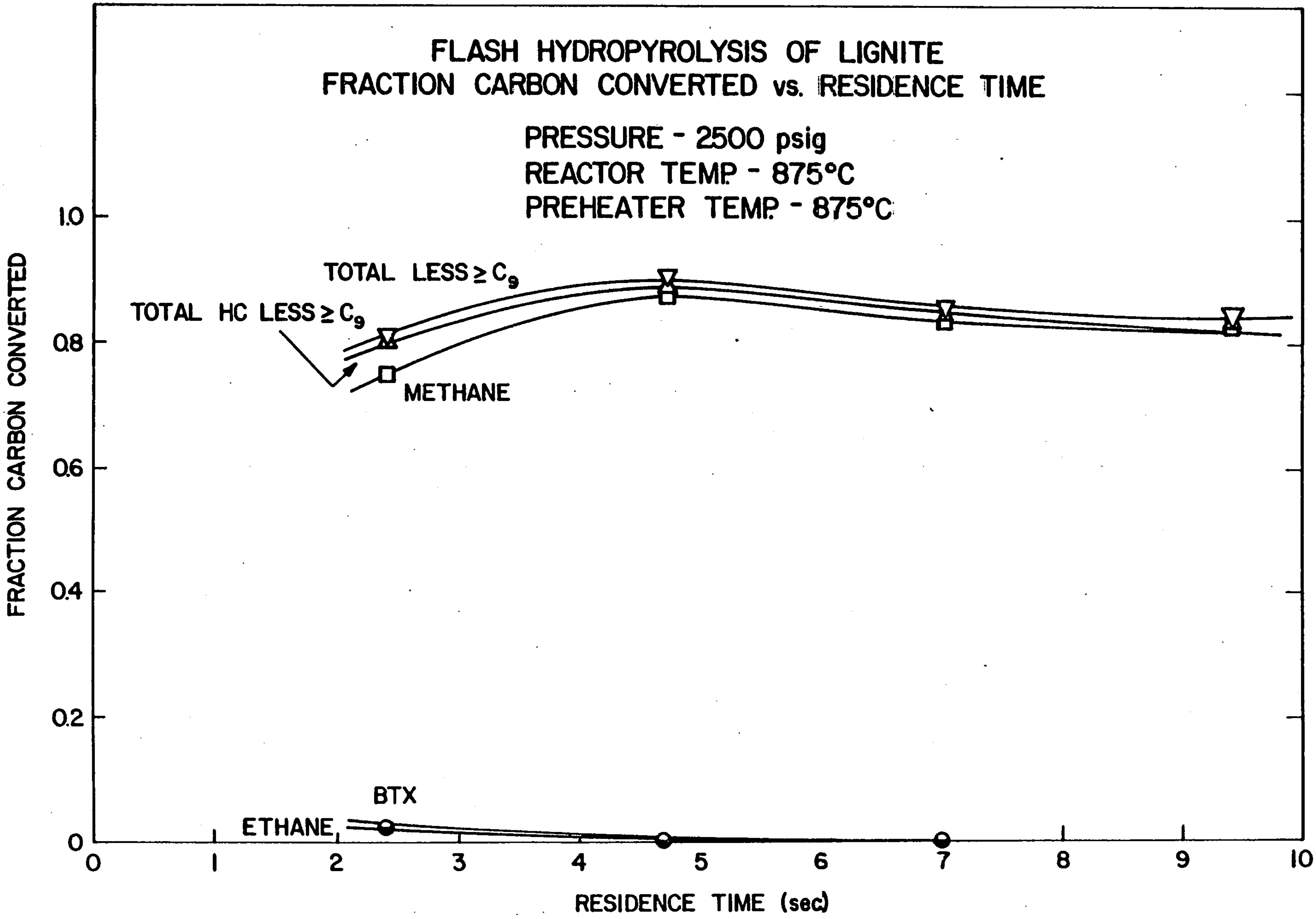

FLASH HYDROPYROLYSIS OF LIGNITE
FRACTION CARBON CONVERTED vs. RESIDENCE TIME
PRESSURE - 2500 psig
REACTOR TEMP. - 875°C
PREHEATER TEMP. - 875°C
TOTAL LESS ≥ C9
TOTAL HC LESS ≥ C9
METHANE
BTX
ETHANE
FRACTION CARBON CONVERTED
1.0
0.8
0.6
0.4
0.2
0
RESIDENCE TIME (sec)
0
1
2
3
4
5
6
7
8
9
10

Figure 12

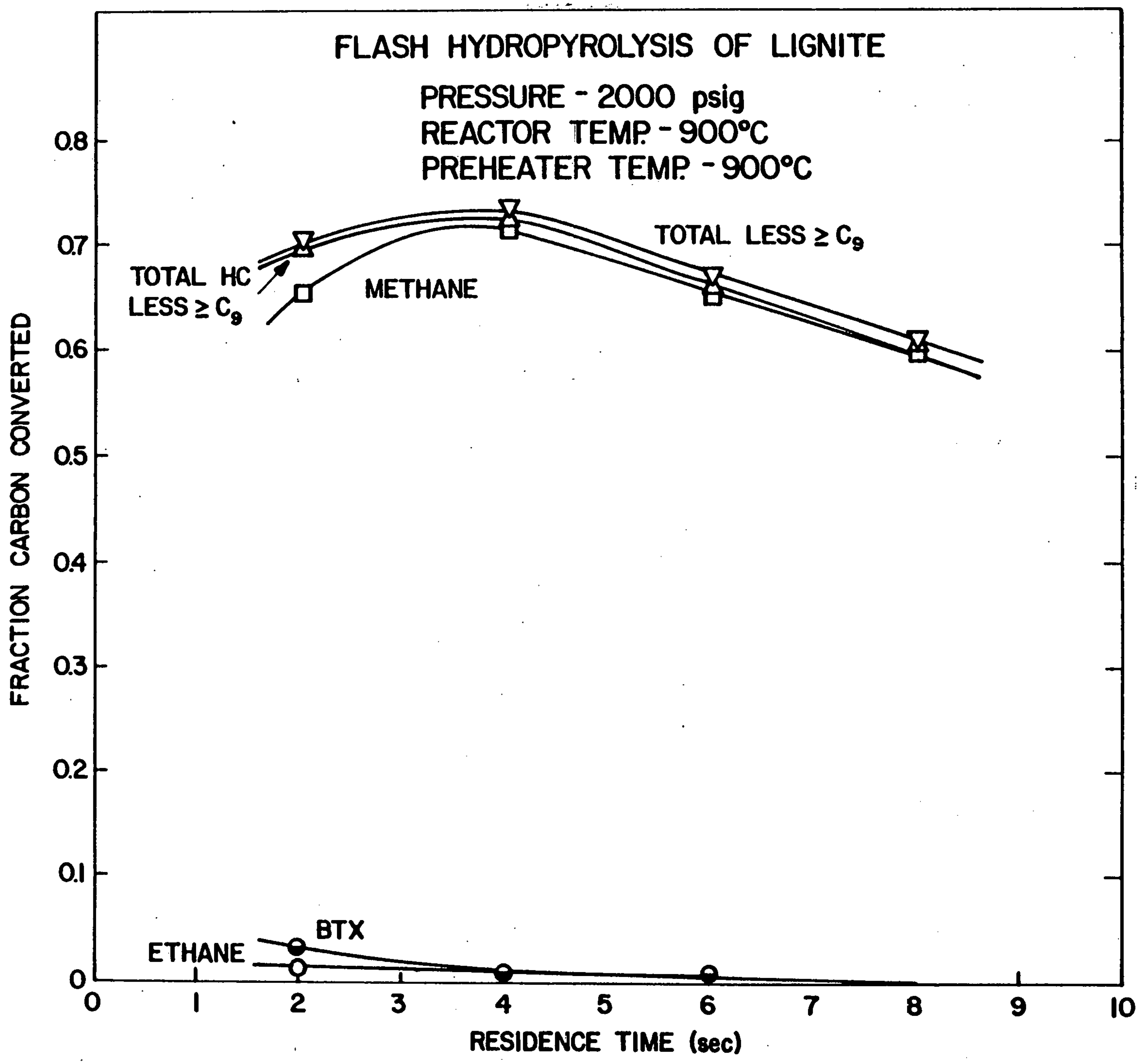
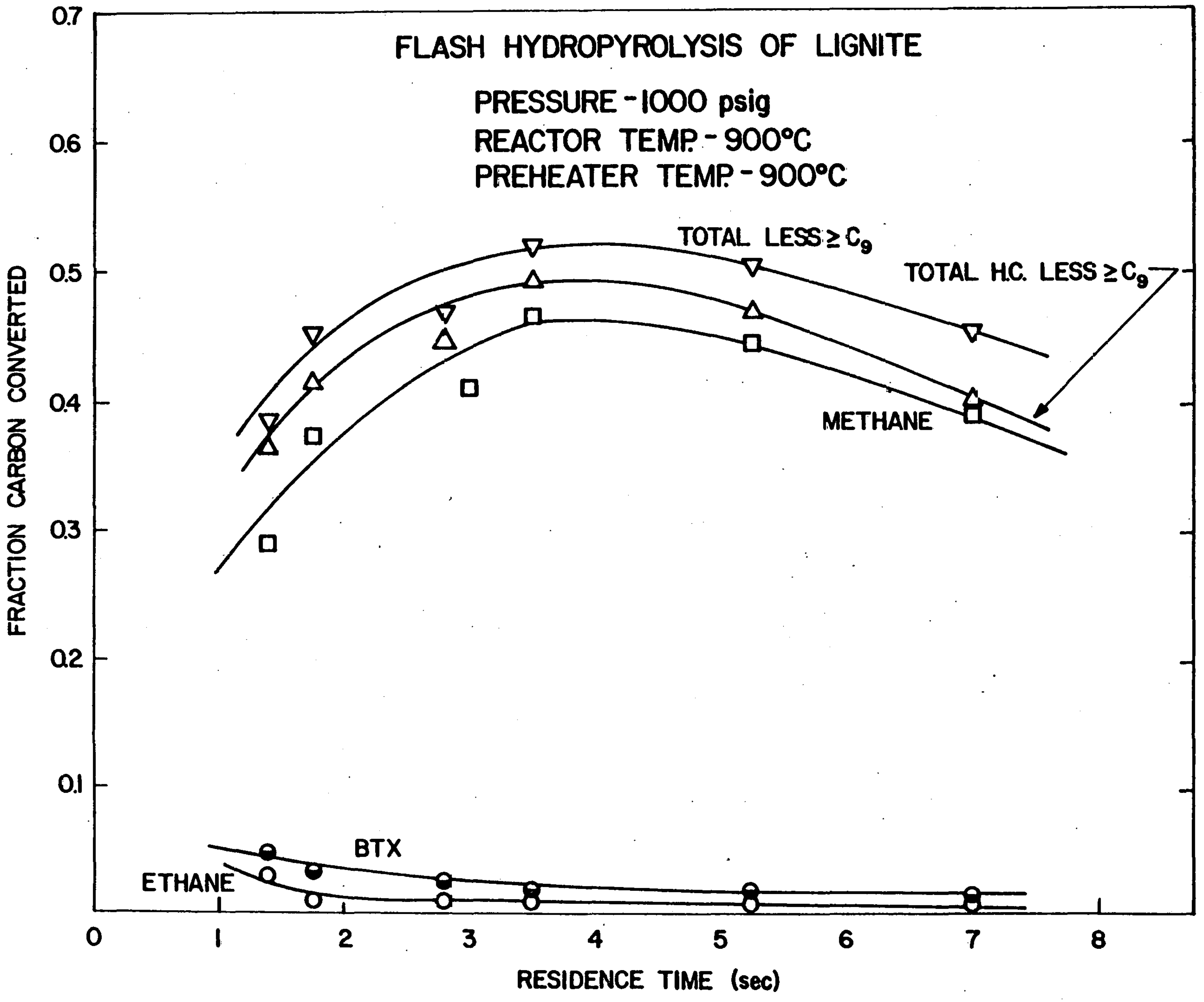

FLASH HYDROPYROLYSIS OF LIGNITE
PRESSURE - 2000 psig
REACTOR TEMP. - 900°C
PREHEATER TEMP. - 900°C
TOTAL HC
LESS ≥ C_9
METHANE
TOTAL LESS ≥ C_9
BTX
ETHANE
FRACTION CARBON CONVERTED
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
1
2
3
4
5
6
7
8
9
10
RESIDENCE TIME (sec)

Figure 13



FLASH HYDROPYROLYSIS OF LIGNITE
PRESSURE - 1000 psig
REACTOR TEMP. - 900°C
PREHEATER TEMP. - 900°C
TOTAL LESS ≥ C9
TOTAL H.C. LESS ≥ C9
METHANE
BTX
ETHANE
FRACTION CARBON CONVERTED
RESIDENCE TIME (sec)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
2
3
4
5
6
7
8

Figure 14

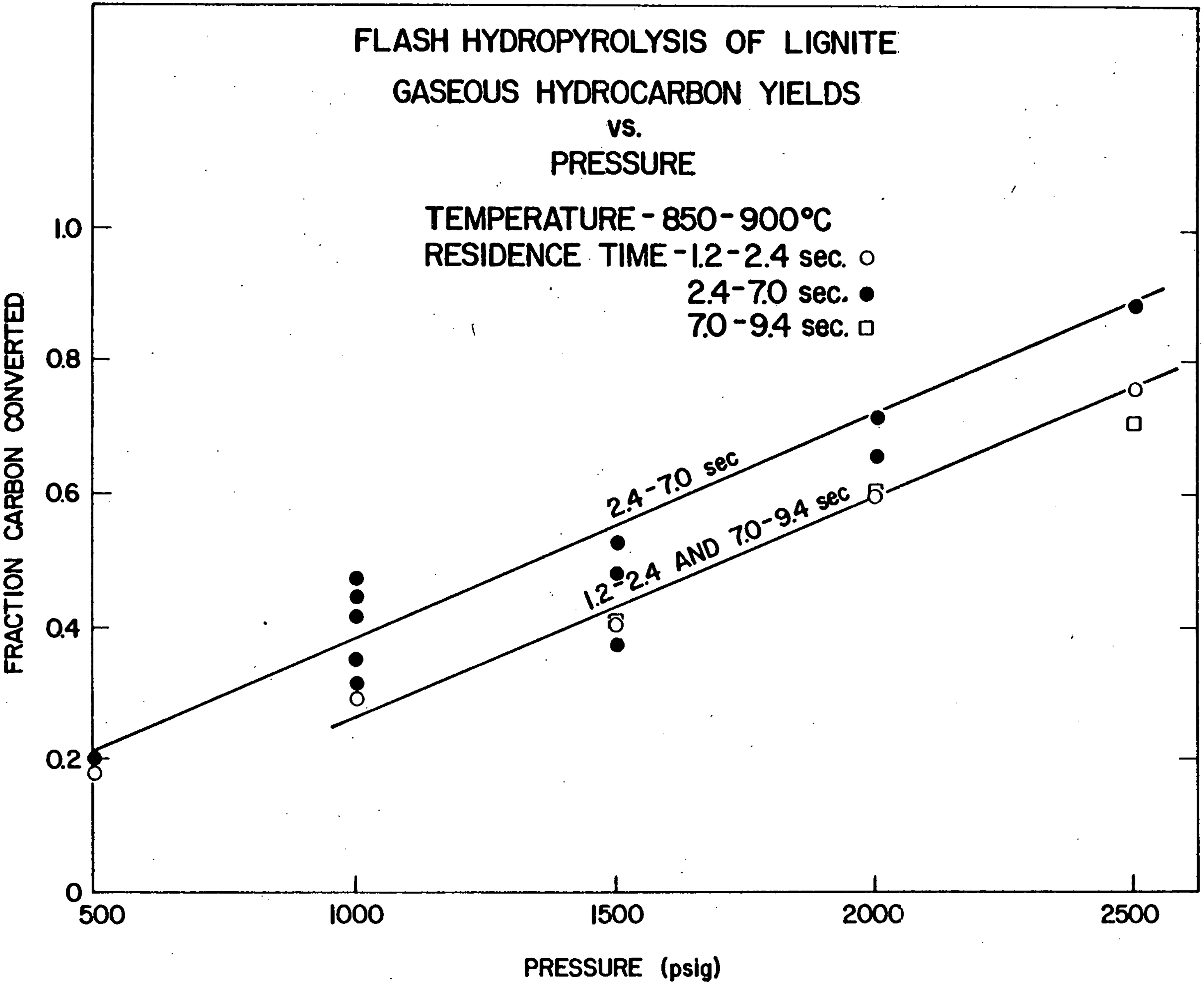
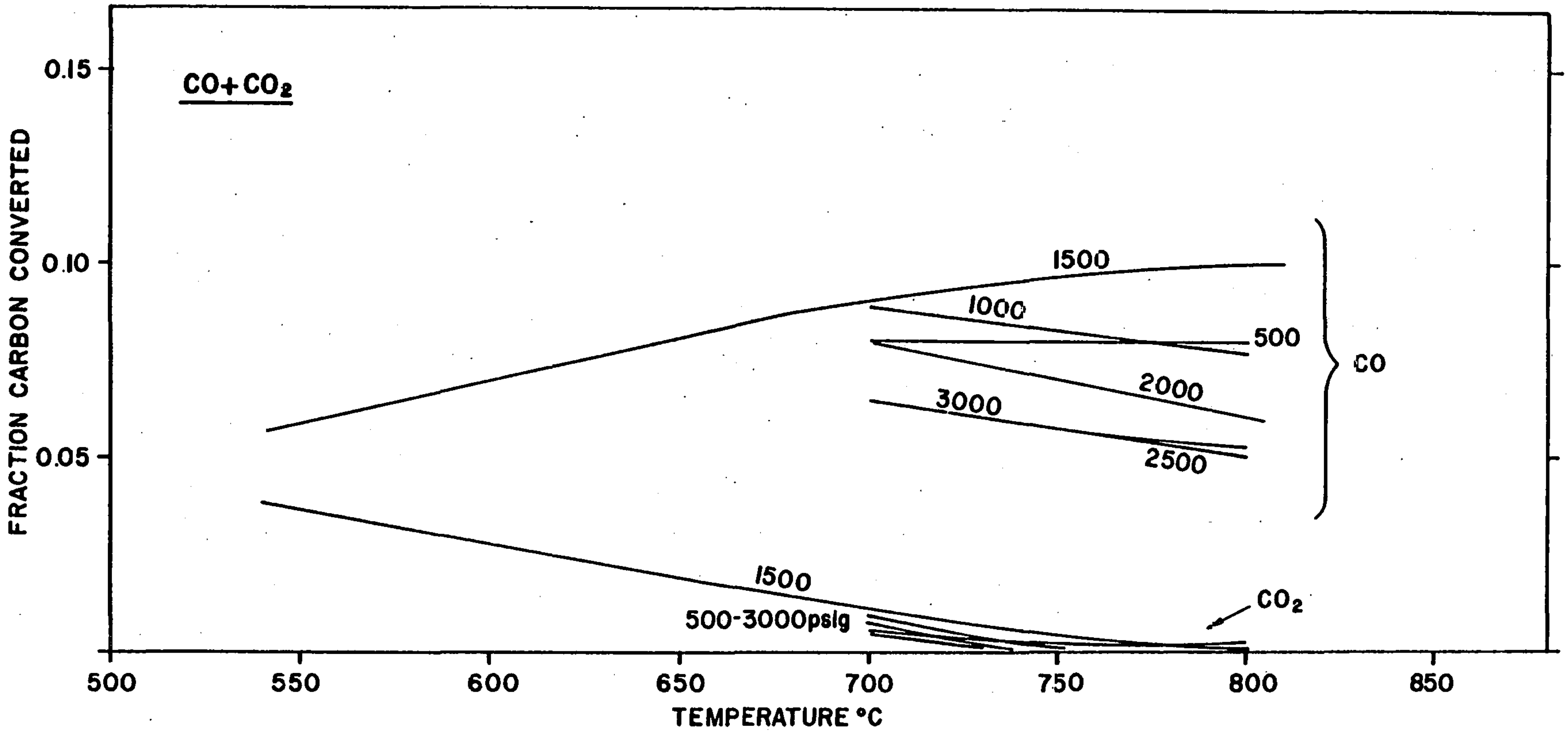

FLASH HYDROPYROLYSIS OF LIGNITE
GASEOUS HYDROCARBON YIELDS
vs.
PRESSURE
TEMPERATURE - 850 - 900°C
RESIDENCE TIME - 1.2 - 2.4 sec. ○
2.4 - 7.0 sec. ●
7.0 - 9.4 sec. □
2.4 - 7.0 sec
1.2 - 2.4 AND 7.0 - 9.4 sec
FRACTION CARBON CONVERTED
0
0.2
0.4
0.6
0.8
1.0
500
1000
1500
2000
2500
PRESSURE (psig)

Figure 15



FLASH HYDROPYROLYSIS OF LIGNITE
$CO+CO_2$ vs TEMPERATURE
PRESS. 500 - 3000 psig

Figure 16

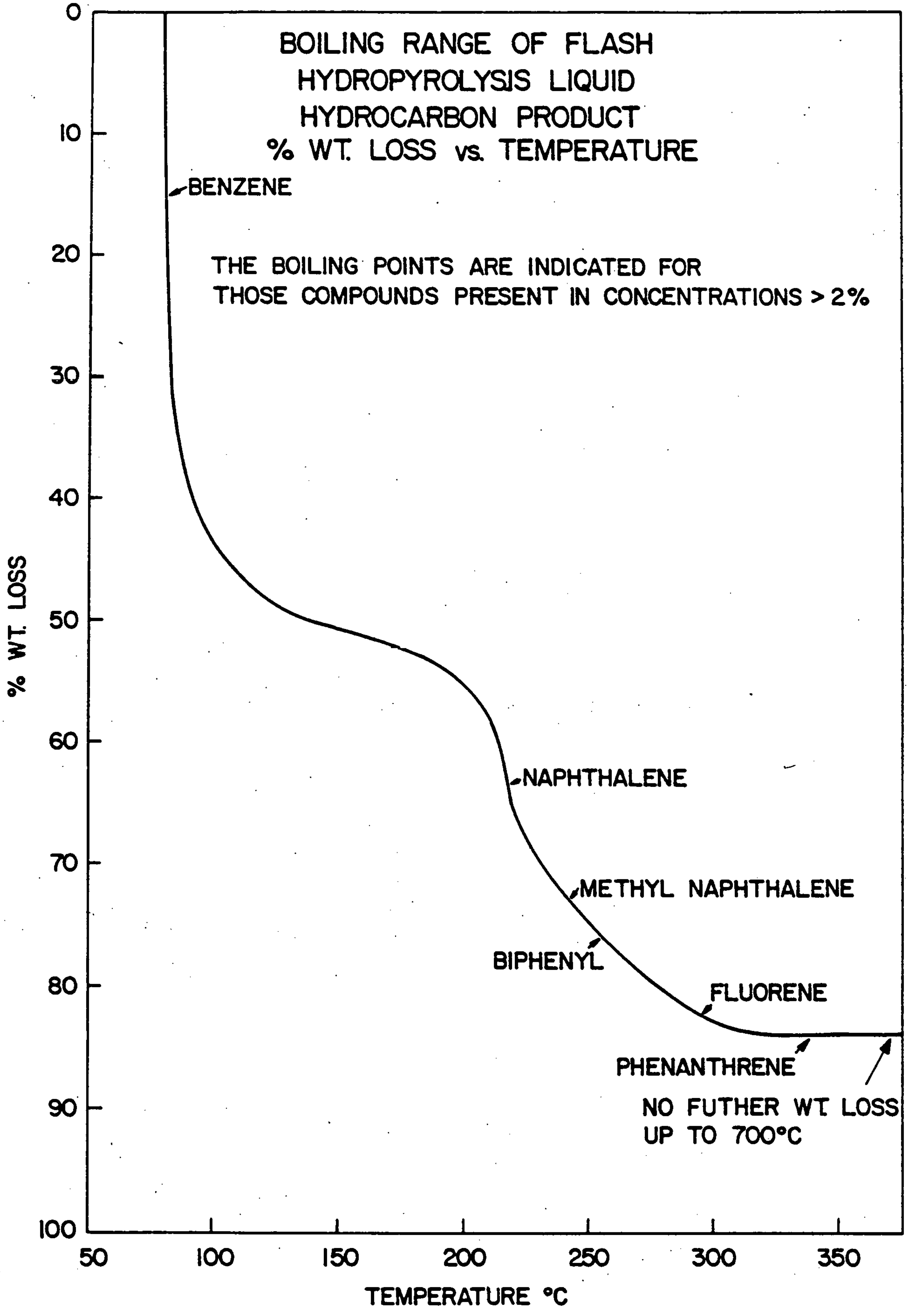

BOILING RANGE OF FLASH
HYDROPYROLYSIS LIQUID
HYDROCARBON PRODUCT
% WT. LOSS vs. TEMPERATURE
THE BOILING POINTS ARE INDICATED FOR
THOSE COMPOUNDS PRESENT IN CONCENTRATIONS > 2%
BENZENE
NAPHTHALENE
METHYL NAPHTHALENE
BIPHENYL
FLUORENE
PHENANTHRENE
NO FUTHER WT LOSS
UP TO 700°C
% WT. LOSS
0
10
20
30
40
50
60
70
80
90
100
50
100
150
200
250
300
350
TEMPERATURE °C

Figure 17

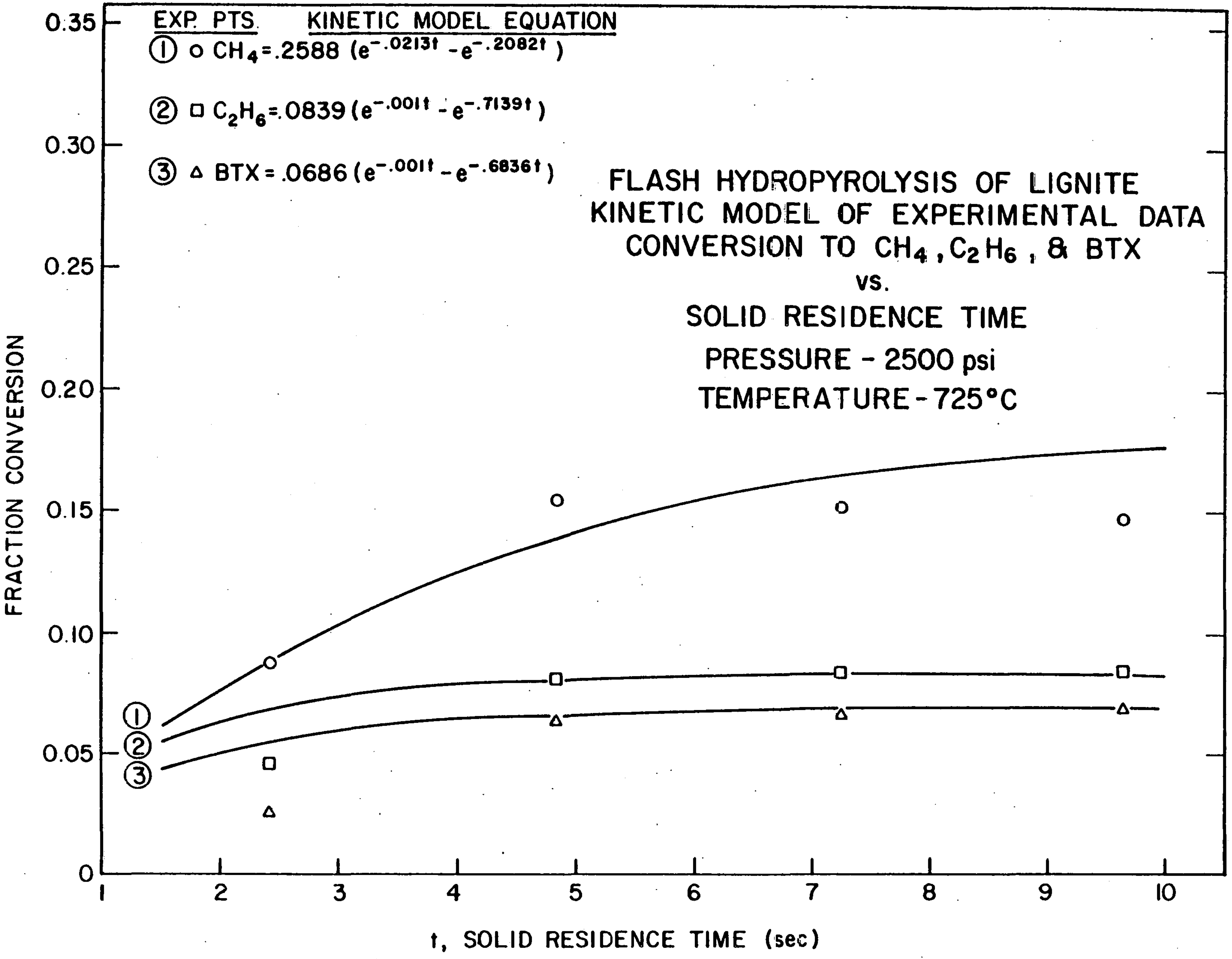
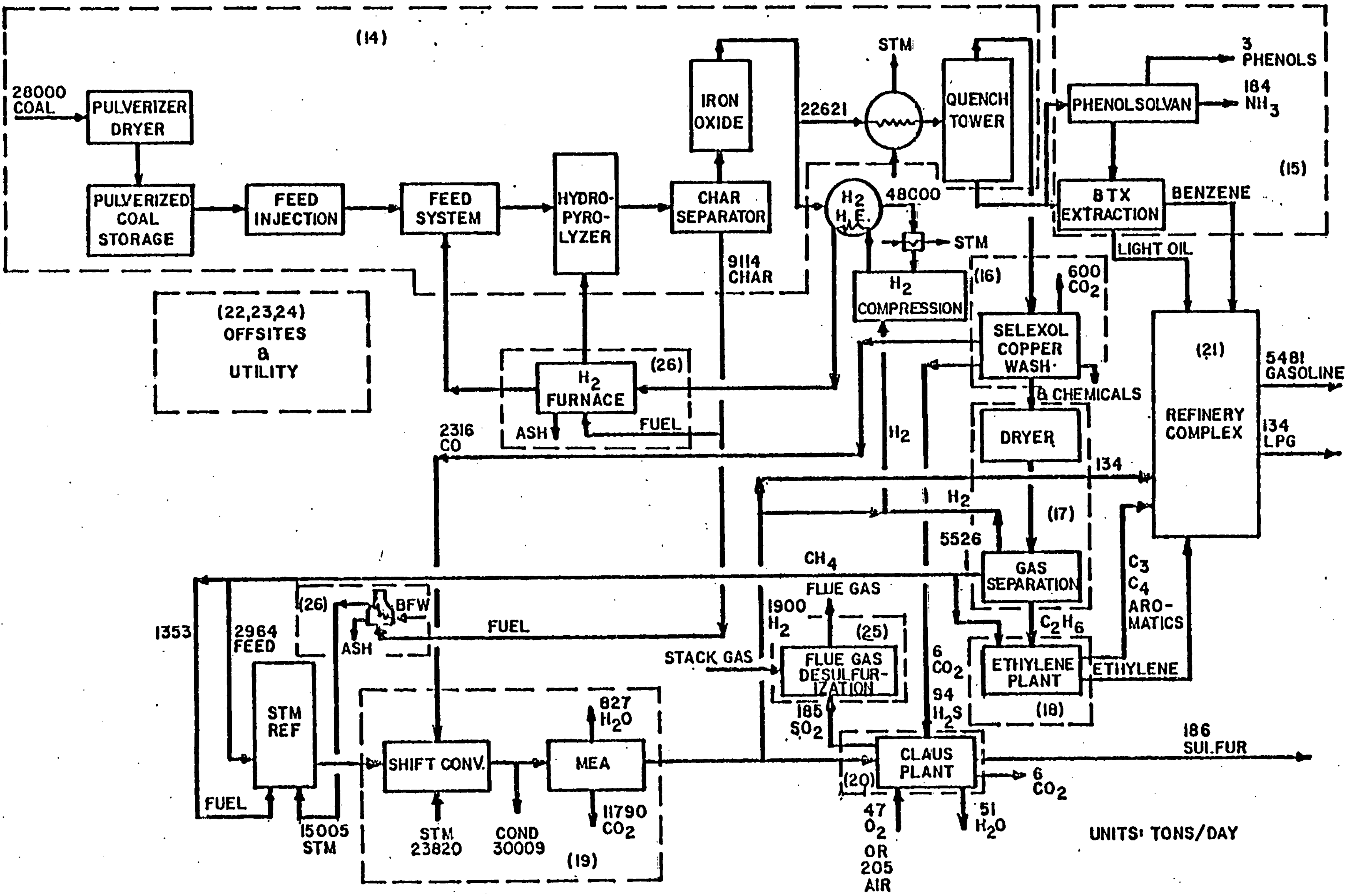
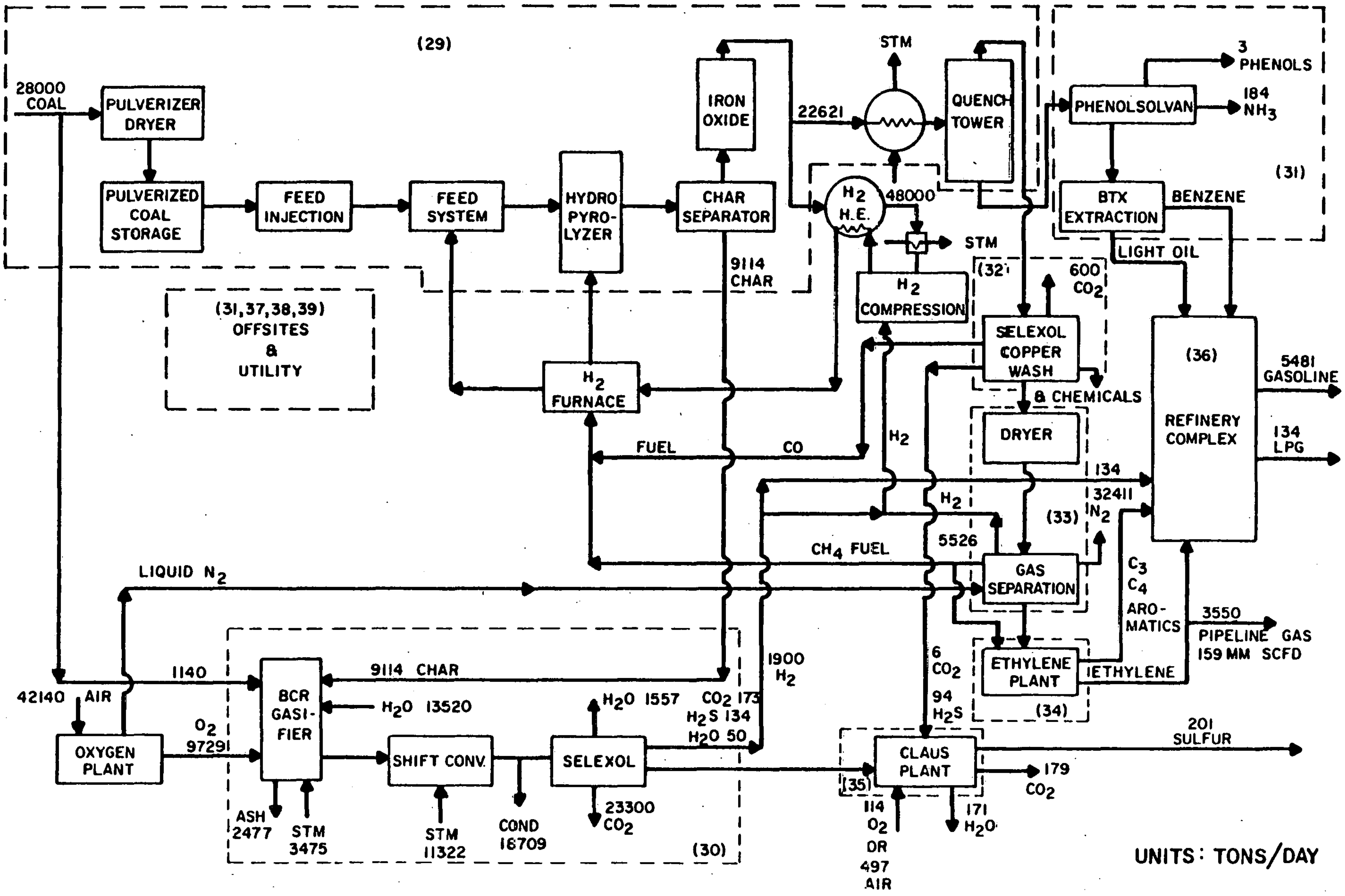

EXP. PTS. KINETIC MODEL EQUATION
① ○ CH4 = .2588 (e^-.0213t - e^-.2082t)
② □ C2H6 = .0839 (e^-.001t - e^-.7139t)
③ △ BTX = .0686 (e^-.001t - e^-.6836t)
FLASH HYDROPYROLYSIS OF LIGNITE
KINETIC MODEL OF EXPERIMENTAL DATA
CONVERSION TO CH4, C2H6, & BTX
vs.
SOLID RESIDENCE TIME
PRESSURE - 2500 psi
TEMPERATURE - 725°C
FRACTION CONVERSION
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
①
②
③
1
2
3
4
5
6
7
8
9
10
t, SOLID RESIDENCE TIME (sec)

Figure 18



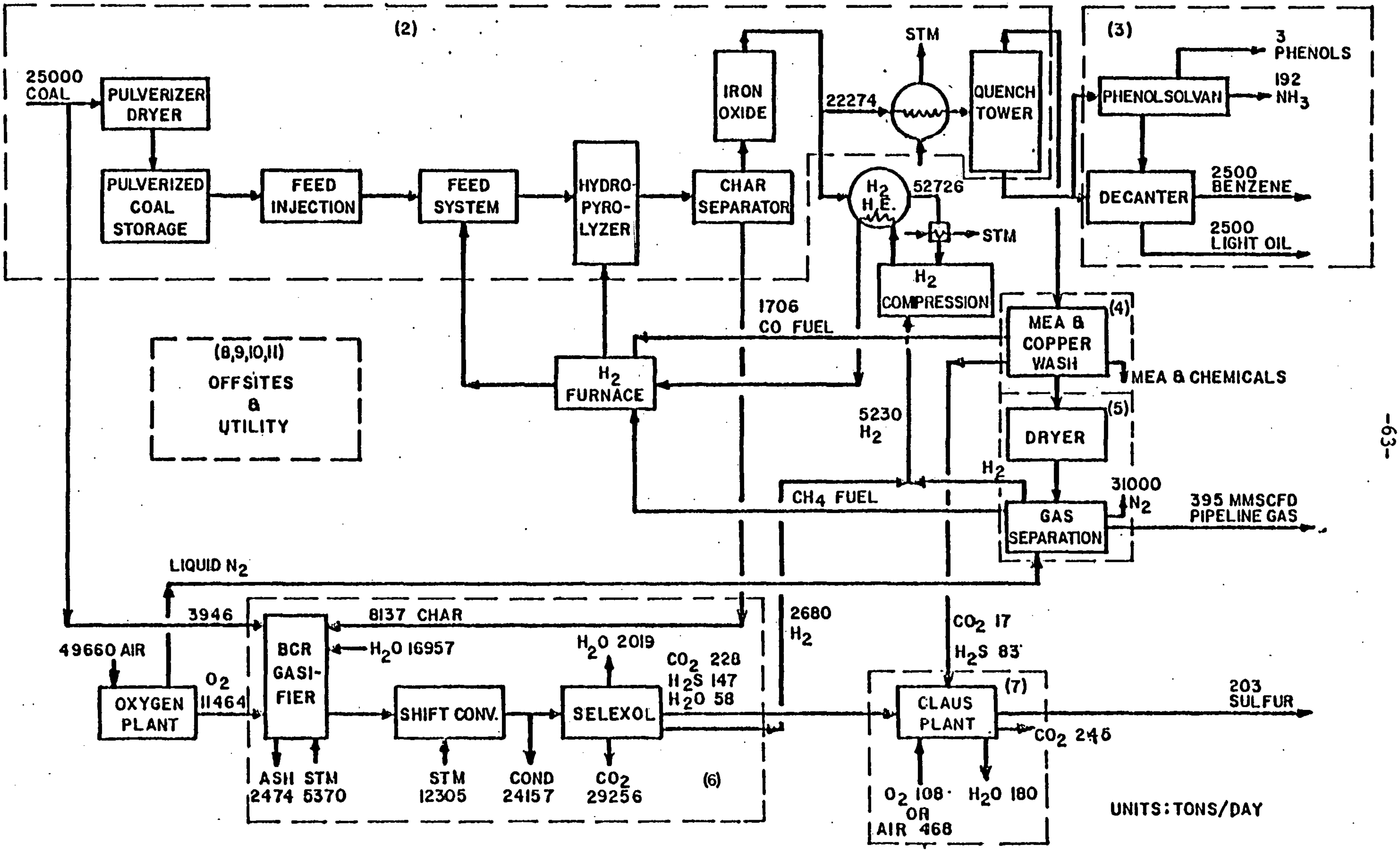
SCHEMATIC BLOCK DIAGRAM OF FLASH HYDROPYROLYSIS OF COAL TO MOTOR GASOLINE

Figure 19



SCHEMATIC BLOCK DIAGRAM OF FLASH HYDROPYROLYSIS OF COAL TO MOTOR GASOLINE AND PIPELINE GAS

Figure 20



SCHEMATIC BLOCK DIAGRAM OF FLASH HYDROPYROLYSIS OF COAL TO PIPELINE GAS

Figure 21