

## SHORT RESIDENCE TIME (SRT) COAL HYDROLYSIS

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### INTRODUCTION:

For the last two years, Cities Service R & D has been investigating the Short Residence Time (SRT) Hydrolysis Process which noncatalytically hydrogenates dry coal to produce directly, in a one-step process, light aromatic liquids (essentially benzene), and high Btu gas ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ )<sup>(1)</sup>. In addition, heteroatoms in the coal are removed as  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_x$ . The product char can be used to produce make-up hydrogen or hydrogasified further in another reactor to make additional high Btu gas.

A continuous, bench-scale unit to process 1 to 2 lb/hr. coal has been constructed at the CSR&D laboratories in Cranbury, N.J., and has been in operation since the summer of 1975. Coal conversions of the order of 50-80 wt.% MAF coal have been routinely attained with a light aromatics yield of the order of 12-16 wt.% MAF coal and a gas yield ( $\text{C}_1 + \text{C}_2$  and  $\text{CO}$ ) of the order of 34-68 wt.% MAF Coal.

### EXPERIMENTAL PROGRAM:

The Cities Service program was as follows:

1. Design, construct and operate a 2 lb/hr. experimental unit.
2. Perform cold flow model studies to determine optimum nozzle designs.
3. Derive mathematical models to predict experimental results.
4. Identify scaleable coal feeder designs.
5. Define metallurgical requirements.

A relatively simple free-fall, dilute phase reactor system was designed to utilize as simple an apparatus as possible to prove or disprove the intrinsic chemistry for producing light aromatics directly from coal. Operation of the unit has demonstrated that coal can be converted directly to light aromatic liquids without the intermediate production of high boiling tars.

The bench-scale unit, as designed, is also being utilized to carry out the following objectives:

1. Determination of the role of major process variables on conversion and selectivity.
2. Development of commercially scaleable equipment necessary for the successful operation of an SRT Hydropyrolysis unit.
3. Development of a simple, working kinetic model of SRT Hydropyrolysis experimental data.
4. Determination of the critical scaleup parameters and their effect on product yields and selectivities.

The unit is performing essentially trouble-free and is giving the necessary smooth operation required to perform process variable studies. About three dozen runs each of four to five hours duration have been completed.

#### DESCRIPTION:

Figure 1 is a schematic of the bench scale unit. Hydrogen is supplied from a tube trailer to a diaphragm compressor capable of recompressing the hydrogen to 3000 psi. The hydrogen is then metered to the controller valves which control the flow of hydrogen to the preheater and to the quench cooler. These hydrogen streams then enter the reactor assembly as indicated in the schematic. Dried, pulverized coal is fed batchwise to a hopper which is then pressurized to reactor pressure with hydrogen. A star-wheel feeder then delivers the coal through a standpipe into the reactor. The coal then mixes with the hydrogen, which has been heated to the approximate reaction temperatures desired. The mixing occurs in a manner formulated to achieve very high heating rates of the coal which is necessary for a high degree of coal conversion. The coal then falls in free-fall through the four-foot reactor pipe into the char pot devolatilizing as it traverses the reactor. The temperature-time history of the coal is controlled by the introduction of a cold quenching medium (cryogenically cooled hydrogen) through a variable length probe within the reactor. The variable length probe allows for the change in reactor length easily thus providing the mechanism for varying residence time without changing the reactor. The entire reactor is immersed in an adiabatic enclosure (electrical furnace). The resultant quenched hydrogen-product gas mixture exits the char pot at a temperature between 440-880°F which is below the reaction temperature of the product stream. The residual char remains in the char pot until removal at the completion of a run. The hydrogen-product gas stream then passes through three stages of indirect heat exchange where the liquid products are sequentially condensed from the hydrogen stream. Condensation temperature can be controlled between -200°F and +200°F by the use of suitable coolants. The non-condensable hydrogen stream is then depressured, metered, analyzed by gas chromatography and then vented to the atmosphere.

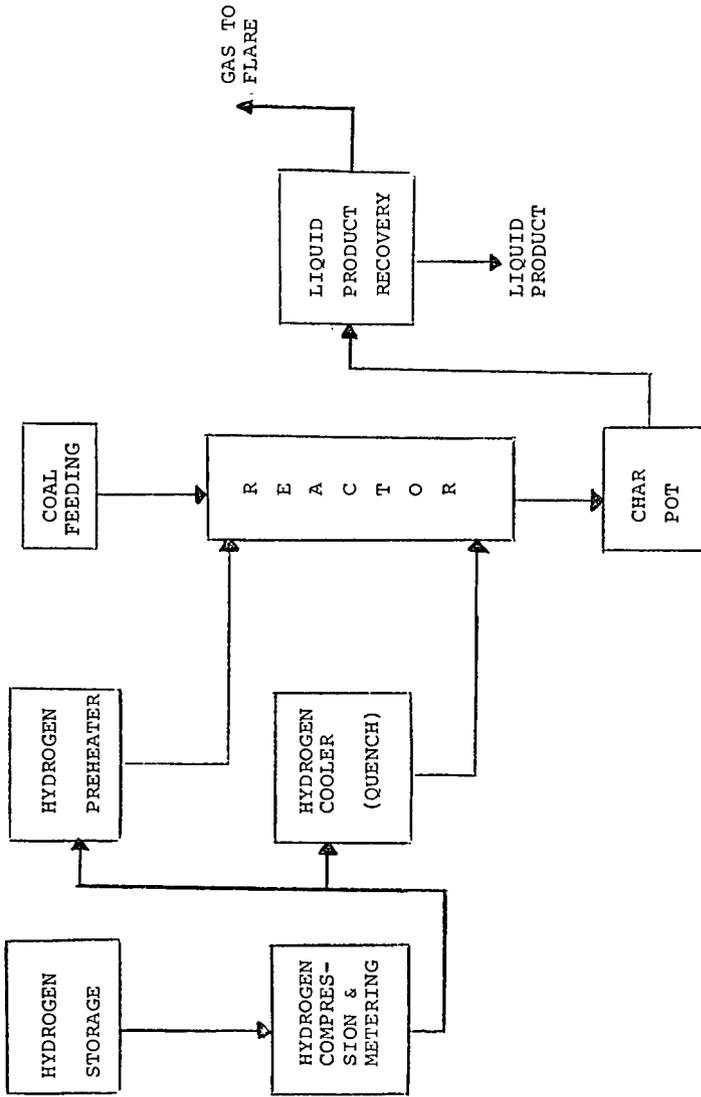


FIGURE 1: SCHEMATIC OF CITIES' COAL LIQUEFACTION 2 LB/HR. UNIT

Figure 2 is a schematic of the reaction section. It shows the coal hopper delivering coal to a star-wheel feeder similar in design to one that has been used for a number of years by the Pittsburgh Energy Research Center. The coal flows from the star-feeder into the reactor in which hot hydrogen is made to intimately mix with the cold coal. The coal then free-falls through the reactor into the char pot where the products are separated from the char by the use of a simple filter. The reactor contains a variable length quench probe which has been perfected by Cities Service and allows for the residence time to be explicitly defined by moving the probe to varying lengths within the reactor. For the initial studies, hydrogen was used as a quench medium because it did not complicate the analysis of the products.

Table 1 shows the range of operating conditions studied using North Dakota lignite. Although Western Kentucky bituminous coal has been run, this paper will be confined to discussions on lignite. The Table shows coal has been run continuously from 1.25-8.0 hours. Most of the runs, however, have been in the 4-5 hour range. The reactor temperatures were varied from 1150° to 1575°F average hydrogen-coal temperatures. This reactor temperature was indirectly measured from the skin temperature of the reactor by using a mathematical model generated by Cities Service. The residence time has been varied from 100-3000 milliseconds by the use of this variable length quench probe. One of the more critical parameters on this Table is heatup rate; this parameter has been varied from 50,000-150,000F°/sec.

Table 2 is the analysis of the lignite that was used. The coal was dried to 3% moisture before it was used in the experiment. Table 3 shows the range of conversion and yields obtained using North Dakota lignite. Carbon conversion of 80% have been achieved and the liquid yields have been as high as 16 wt.% based on moisture and ash free coal. This liquid is essentially 94% pure benzene with smaller amounts of naphthalene and anthracene. Above about a 1200°F reactor temperature, only light aromatic liquids are produced. The gas produced is essentially composed of methane and ethane. These products are identified by using a gas chromatographic system designed so that a thermal conductivity detector is in series with the flame detector. Using this system, carbon balances are calculated.

The following are the pilot plant achievements to date:

1. Continuous, steady-state operation with coal feeding for 8.0 hours.
2. No pressure drop buildup in nozzles, reactors or recovery system.
3. Preheating, reacting and quenching of coal--hydrogen mixtures at total residence times of less than one second.
4. Coal heatup rates of the order of 50,000-100,000F°/sec.
5. Quenching of reaction products within reactor vessel.
6. No tar formation with principal hydrocarbon products being benzene, methane, ethane.
7. Exceeded Fisher assay coal and carbon conversions at all three operating severities.

REACTION SECTION

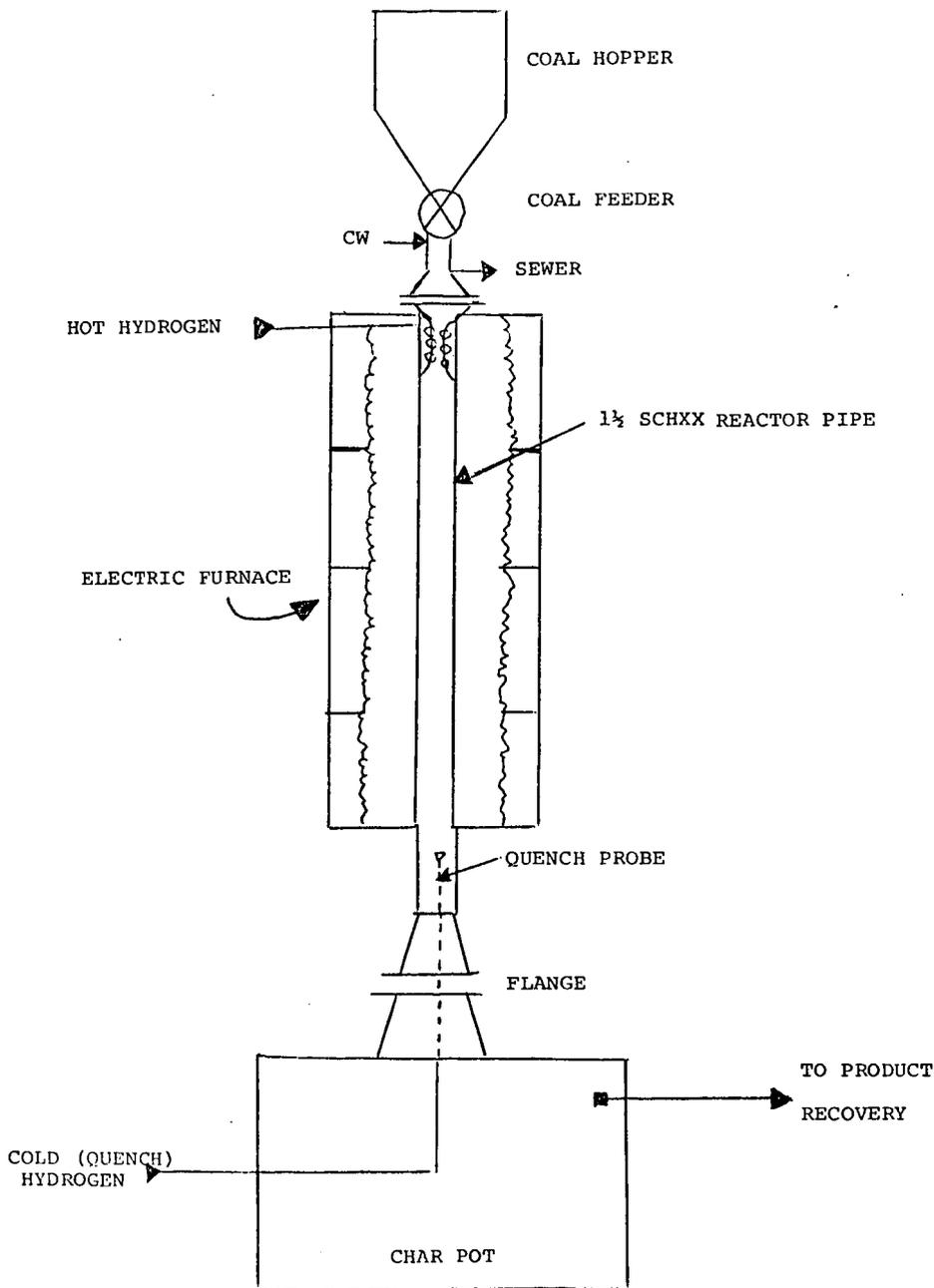


FIGURE 2 158

TABLE 1

RANGE OF OPERATING CONDITIONS STUDIED

NORTH DAKOTA LIGNITE

RUN TIME (COAL)	1.25 - 8.0 HOUR
REACTOR TYPE	FREE-FALL
HYDROGEN/COAL RATIO	0.18 - 2.0 LB/LB.
AVERAGE PARTICLE SIZE	50 - 450 MICRONS
COAL HEATUP RATE	50,000 - 150,000F <sup>o</sup> /SEC.
AVERAGE REACTOR TEMPERATURE	1150 - 1575 <sup>o</sup> F
REACTOR PRESSURE	500 - 3000 PSI
AVERAGE PARTICLE RESIDENCE TIME	100 - 3000 MSEC.
MAXIMUM VAPOR RESIDENCE TIME	0.8 - 14 SECONDS
QUENCH TEMPERATURE	450 - 1000 <sup>o</sup> F

TABLE 2  
NORTH DAKOTE LIGNITE COAL ANALYSIS

I.	<u>ULTIMATE WT. % MAF</u>	
	CARBON	68.1%
	HYDROGEN	4.6
	NITROGEN	1.3
	SULFUR	1.6
	OXYGEN	24.4
II.	<u>PROXIMATE (AS RECEIVED) WT. %</u>	
	MOISTURE	38.8%
	ASH	6.1
	VOLATILE MATTER	25.7
	FIXED CARBON	29.4

TABLE 3  
RANGE OF CONVERSION AND YIELDS OBTAINED  
NORTH DAKOTE LIGNITE

CONVERSION

COAL	40 - 85 WT.% MAF BASIS
CARBON	25 - 80 WT.%
DEVOLATILIZATION	60 - 99 WT.%
DEOXYGENATION	30 - 99 WT.%

YIELDS

GAS (C <sub>6</sub> <sup>-</sup> , CO <sub>x</sub> )	14 - 65 WT.%
LIQUIDS (C <sub>6</sub> <sup>+</sup> )	4 - 16 WT.%
LIQUOR	1.1 - 1.4 BBL/TON

HYDROGEN CONSUMPTION

12,000 - 40,000 SCF/TON

SELECTIVITY TO PRODUCTS

LIQUIDS (C <sub>6</sub> <sup>+</sup> )	15 - 50 WT.%
GAS (C <sub>6</sub> <sup>-</sup> , CO <sub>x</sub> )	85 - 50 WT.%

PRINCIPAL PRODUCTS

GAS

METHANE  
 ETHANE  
 CO (CO<sub>2</sub>)  
 C<sub>3</sub>H<sub>8</sub>

LIQUIDS

BENZENE  
 NAPHTHALENE  
 TOLUENE  
 ANTHRACENE/PHENANTHRENE

## RESULTS:

A approximately three dozen runs have been made with the experimental system. Figure 3 shows the carbon selectivity to gas and liquid as a function of carbon conversion. At a carbon conversion of approximately 45%, carbon selectivity to liquids of 43% is attained. As carbon conversion increases, the lignite is hydrogasified with the principal product being methane. These results were obtained with short residence times in the order of 500 milliseconds. As the residence time is increased, the BTX is cracked to coke and hydrogen rather than converted directly to methane. As a result, if the liquid product is not removed, there is a decided decrease in carbon conversion because the liquid ends up as coke which is deposited onto the remaining char. Kinetic calculations verify these assumptions.

Figure 4 shows the effect of reaction temperature on carbon conversions at residence time in the order of 500 milliseconds. At these medium pressures, the carbon conversion is asymptotic at about 46 wt. %.

Figure 5 depicts a family of curves for the hydrogasification of lignite. It shows how the heatup rates effect carbon conversion. The Cities Service. data fall above IGT<sup>(2)</sup> data because the heatup rates are higher.

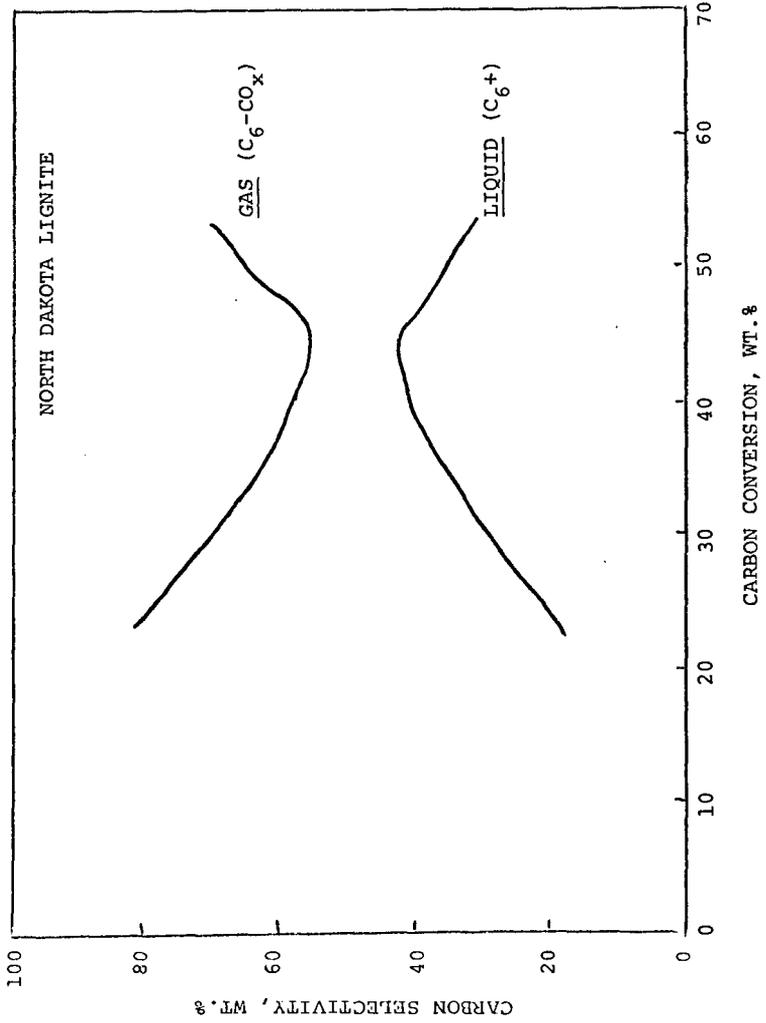
Figure 6 contains the same data as Figure 5, but depicted differently. It shows that as you increase the reaction temperature and also increase the heating rate, carbon conversion increases.

## DISCUSSION:

The experimental results achieved to date suggest that non-catalytic hydroxyprolysis of coal to methane and BTX is technically feasible. Sufficient data has been accumulated to explicitly define the operating conditions necessary to design a commercial unit that will react lignite to methane and BTX. In the commercial design, it is anticipated that an entrained flow reactor would be used. The advantage of this process is that no further hydrotreating of liquid products is necessary and that the products can be sold "as is" from the plant. Several cases have been developed to determine an optimum flow diagram for this process. Two schemes will be shown.

Figures 7 and 8 are process flow diagrams of possible routes. Figure 7 shows a scheme whereby the char is gasified with steam and oxygen. In both schemes, 16,800 T/D of MAF lignite are delivered to the SRT reactor, 324 MM SCFD of CH<sub>4</sub>; 10,600 B/D BTX, 235 T/D NH<sub>3</sub> and 126 T/D S are produced. The overall thermal efficiency for Figure 7, i.e., BTU's out over BTU's in on a nitrogen and sulfur-free basis is 68%. Approximately 10,000 SCF of CH<sub>4</sub> are produced per ton of coal. In this scheme coal is required to supplement the char so that hydrogen and oxygen can be produced.

FIGURE 3  
CARBON SELECTIVITY DURING SRT HYDROLYSIS



HYDROGASIFICATION OF LIGNITE

EFFECT OF REACTOR TEMPERATURE ON CARBON  
CONVERSION AT  
LOW COAL RESIDENCE TIMES

P: 500 - 1500 psi

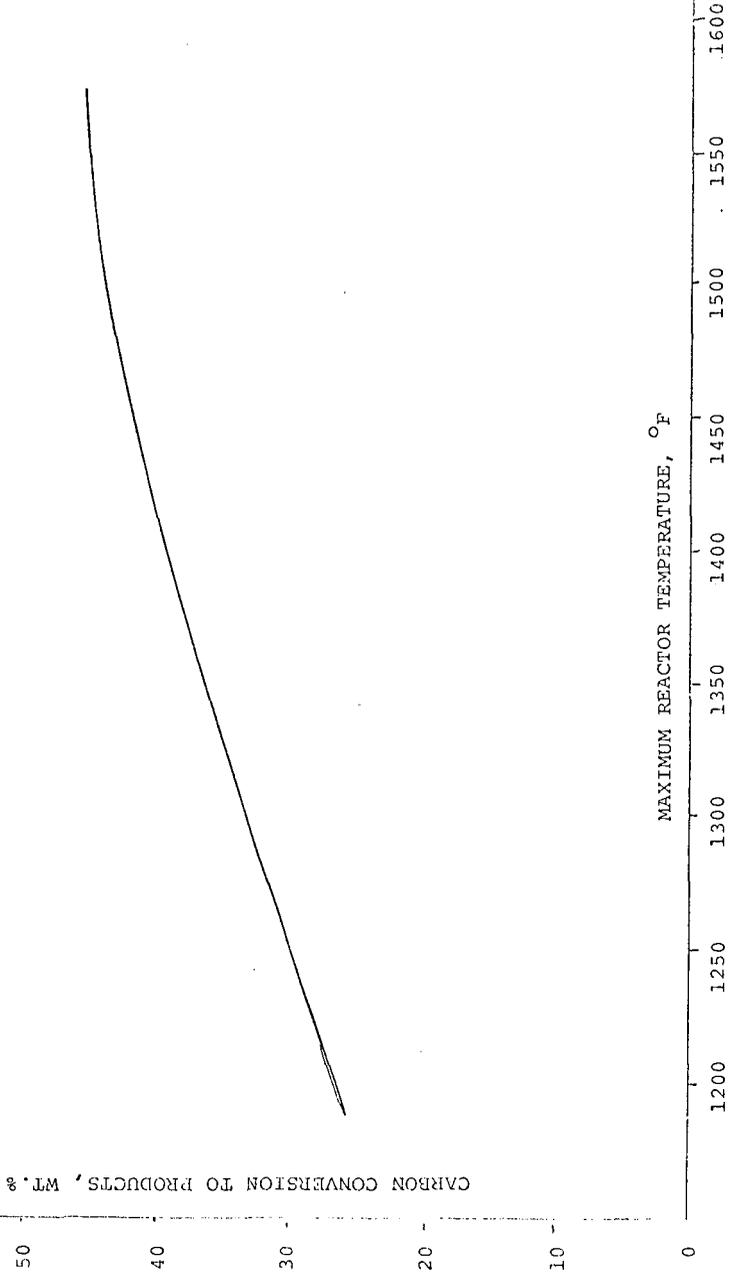


FIGURE 4

HYDROGASIFICATION OF LIGNITE

EFFECT OF PARTICLE HEATING RATE ON CARBON CONVERSION  
AT SHORT SOLIDS RESIDENCE TIME

P: 500 - 1500 psi

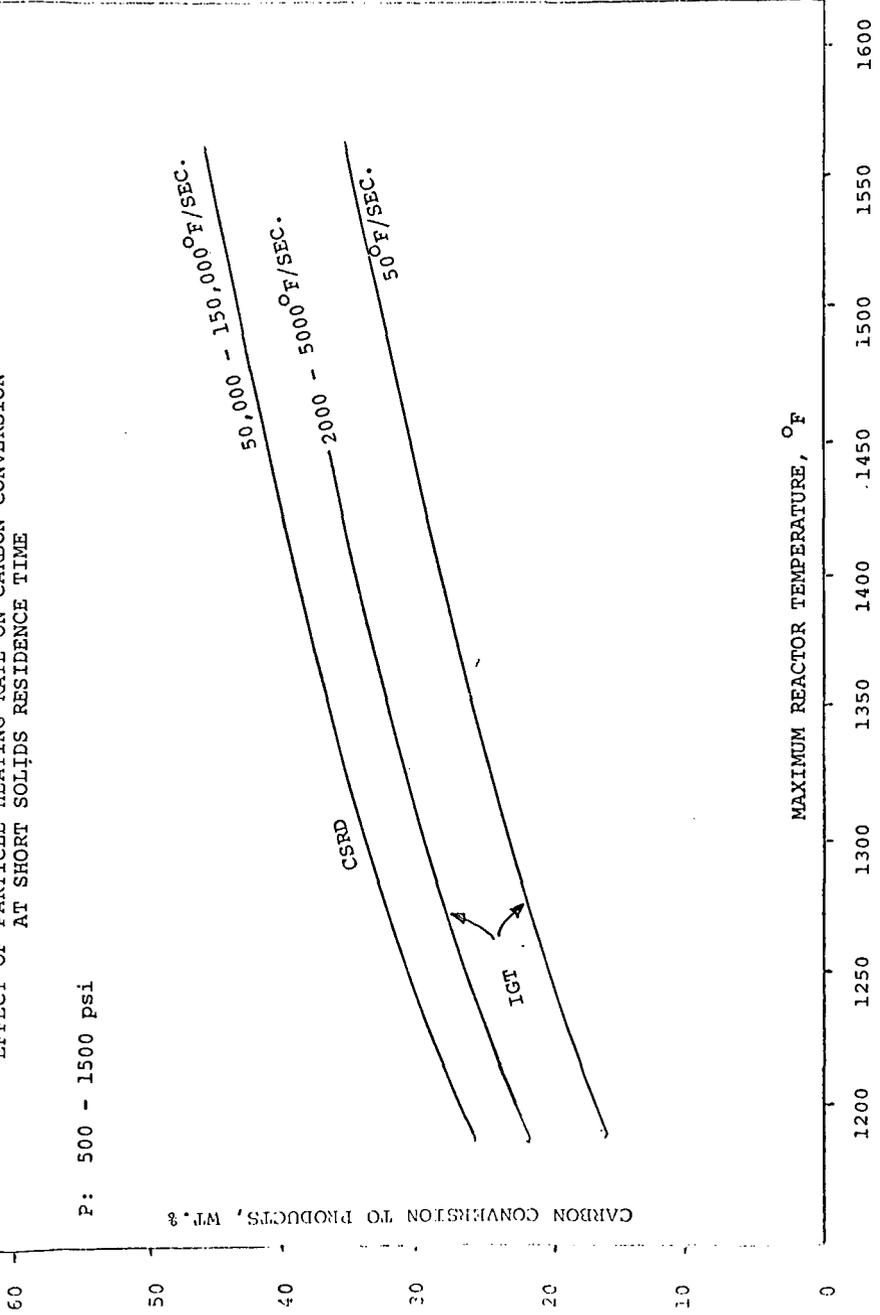
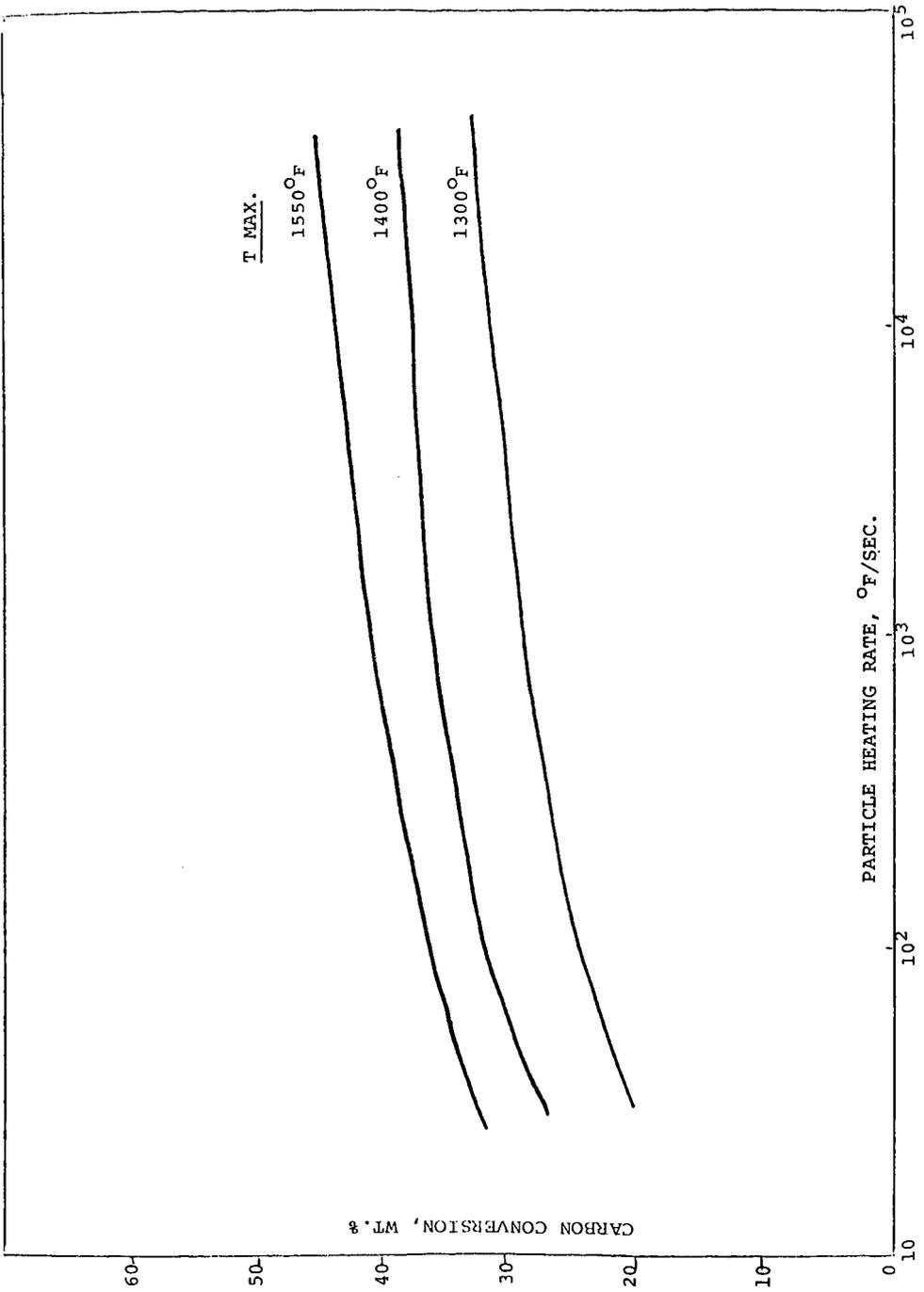


FIGURE 5

FIGURE 6: HYDROGASIFICATION OF LIGNITE



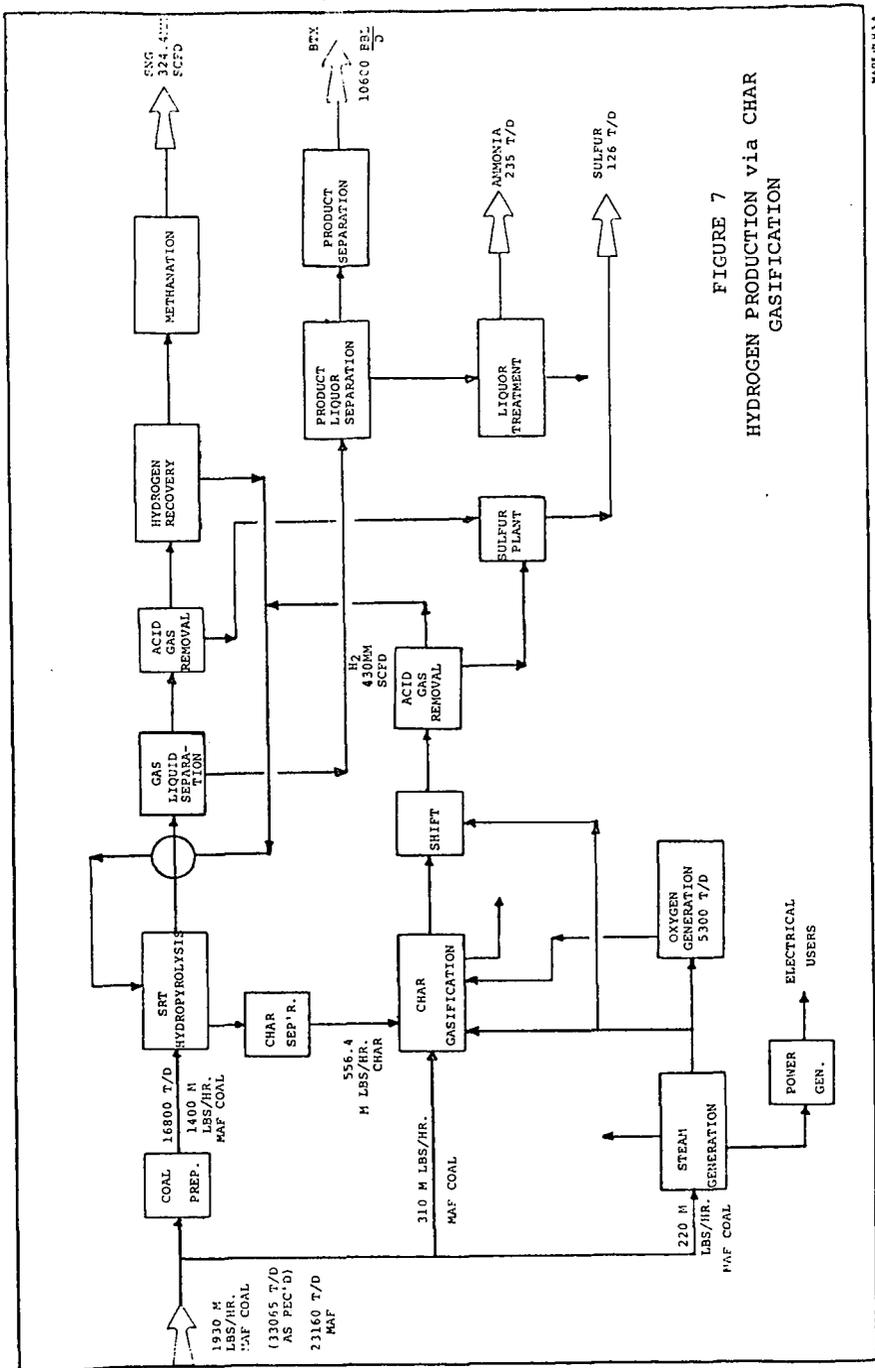


FIGURE 7  
HYDROGEN PRODUCTION via CHAR  
GASIFICATION

SHASTEN, U.S.A.

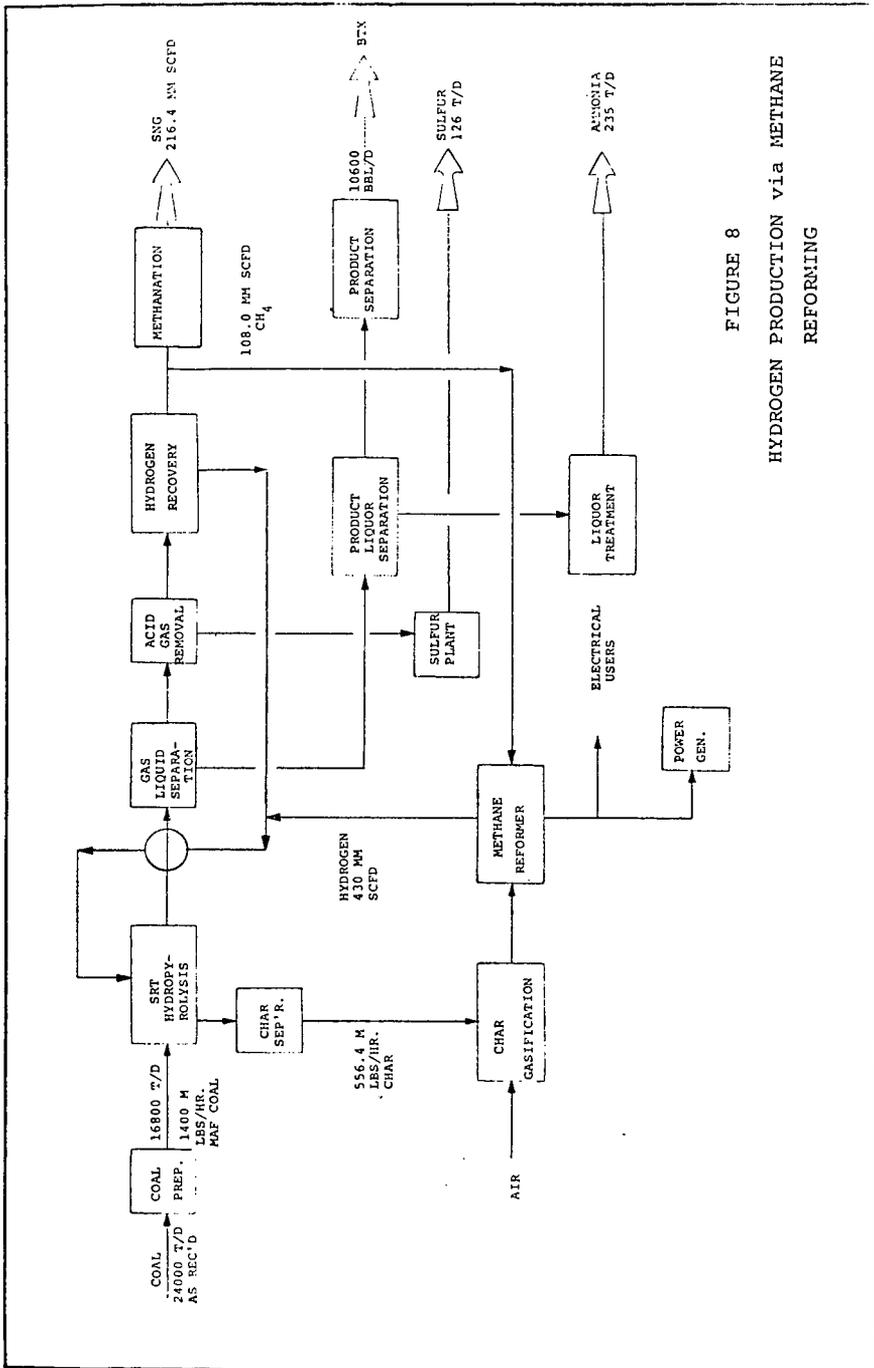


FIGURE 8  
HYDROGEN PRODUCTION via METHANE  
REFORMING

Figure 8 is a flow diagram whereby hydrogen is produced by steam reforming some of the methane that is produced. In this case, the char is gasified with air and the resulting 150 BTU/SCF gas is used to fire the reformer. The thermal efficiency of this scheme is 62% but the capital investment is much less since an oxygen plant is not required. Approximately 9000 SCF of CH<sub>4</sub>/ton of coal are produced. though both schemes are economically attractive, the scheme shown on Figure 8 seems to be the preferred route not only because of the lower capital investment but also because air-blown char gasification is much simpler than char gasification with oxygen and steam.

At present, Cities Service is planning to retain an independent engineering firm to make a detailed engineering analysis so that all alternatives can be evaluated.

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