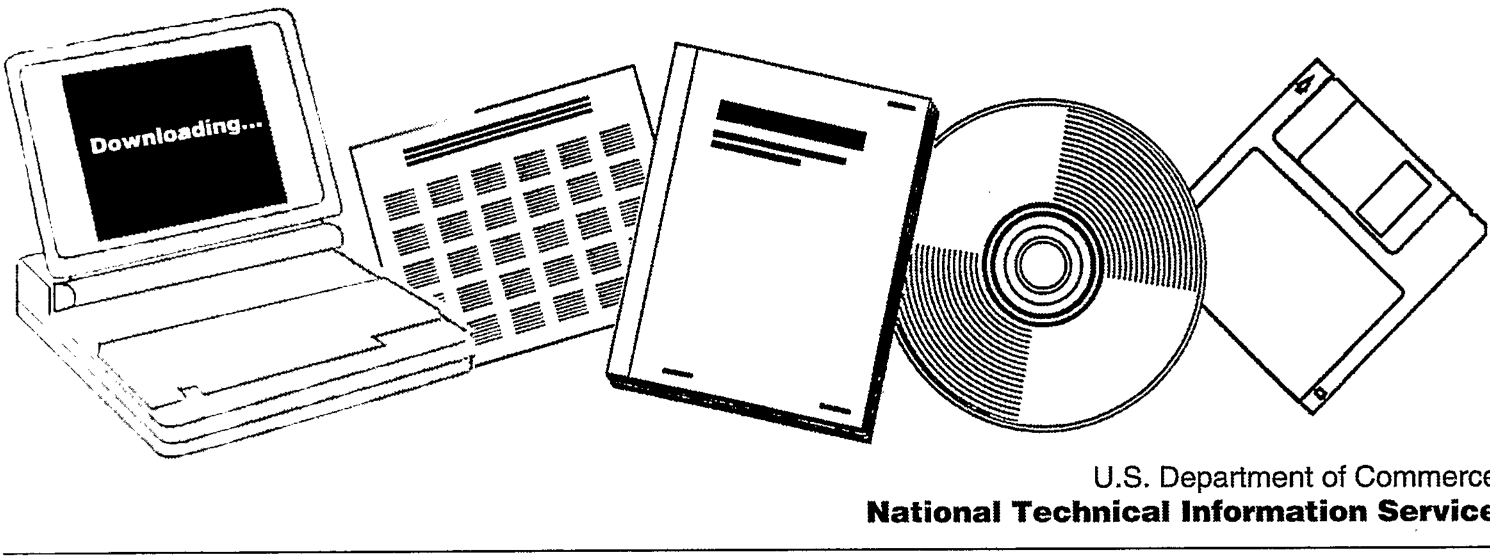
DE82009832

EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL-LIQUEFACTION REACTOR. PROGRESS REPORT, SEPTEMBER 1, 1981-FEBRUARY 28, 1982

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING

FEB 1982



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AN EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL-LIQUEFACTION REACTOR

DOE/PC/30243--T3

DE82 009832

Progress Report

September 1, 1981 - February 28, 1982

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Work Performed Under Contract Number

DE-FG22-80PC30243

February 1982

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AN EXPERIMENTAL STUDY OF MULTIPLE STEADY STATES IN AN ADIABATIC COAL LIQUEFACTION REACTOR

<u>Summary</u>

The objective of this particular work was to get experimental data and analyze the thermal behavior of a bench scale adiabatic continuous stirred coal liquefaction reactor. This report briefly describes the progress on this project during the period September1, 1981 to February 28, 1982.

The reactor was a 1 liter autoclave with two zones of 'adiabatic heaters' to reduce the temperature gradients at the wall of the reactor. Detail analysis (Shah et al., 1981), has been done to estimate the total heat loss from the reactor. The total heat loss from the reactor was calculated to be always less than 10% of the total heat input to the reactor. Therefore, the results and conclusions drawn from the present study can be utilized to predict the thermal behavior of a large scale adiabatic coal liquefaction reactor. Experiments were carried out with 30 wt% Ireland bituminous coal in process solvent for three different severity conditions,

(a) low severity at $703^{O}K$, 10.2 MPa and 2 wt% ash.

(b) moderate severity at $723^{O}K$, 13.6 MPa and 10 wt% ash.

(c) high severity at $743^{O}K$, 20.4 MPa and 10 wt% ash.

It was observed that the rate of hydrogen consumption for moderate and high severity conditions can well be expressed by the correlation developed by Singh et al. (1980, 1981). Experimentally it was observed that for low severity conditions, no ignition of the reactor temperature was observed whereas for other cases, the ignition temperature

increased significantly as the severity conditions decreased.

One interesting dynamic feature of the reactor was its slow time response for changes in feed temperature. For a feed temperature of approximately 685^{O}K, there was a temperature excursion beyond the safety limits of the system which is approximately equal to 465^{O}K when there is every possibility of coking in the reactor. HOwever, it took close to seven hours to exceed the safety limit.

I. Introduction

Theoretical studies on the thermal behavior of gas-liquid reactor (Huang and Varma, 1981, Shi-Ping Ho, 1980; Raghuram et al., 1977, Raghuram et al., 1979; Luss and Amundson, 1977) had been done quite extensively, but the experimental data are still scarce (Ding et al., 1974). On the other hand, theoretical studies on the thermal behavior of gas-liquid-solid system (Singh et al., 1982; Shah et al., 1982) is a recent phenomenon and to our knowledge, no experimental data had been reported so far.

Coal liquefaction is a highly exothermic reaction and heat of reaction is approximately 5000-7000 cal/gm of hydrogen consumed (Singh et al., 1980). Theoretical studies have shown the possibility of existence of multiple steady states in gas liquid (Raghuram et al., 1977; Raghuram et al., 1979; Luss and Amundsson, 1977) and gas-liquid-solid (Singh et al., 1982; Shah et al., 1982) reactors. Industrial reactors are preferentially designed for adiabatic mode of operation, in contrast to laboratory reactors which are more convenient to operate in isothermal mode, bascially because of their low surface area to volume ratio. Therefore, reliable data on the thermal behavior of an adiabatic bench scale reactor are essential for the proper scale-up and actual design of an industrial coal liquefaction reactor.

In this report, experimental data on the thermal behavior of a bench scale adiabatic coal liquefaction reactor are presented. The results of this study were further analyzed to evaluate our understanding of the thermal behavior of an actual commercial scale coal liquefaction reactor.

II . Experimental System

A. Reactor

In Figure 1 we show a schematic diagram of the adiabatic CSTR used for our present study. The main elements of the reactor system are: (1) an "Autoclave Engineers" reactor of capacity 1 liter, two turbines, baffles, thermowells and an extended shaft on the magnetic drive; (2) two zones of "adiabatic heaters" each being controlled so as to reduce the temperature gradient to zero in the radial direction outside the reactor; (3) high wattage "Calrod" heaters to be used for the start-up period; (4) thermocouples inside the reactor and the inlet line to measure the temperature inside the reactor and the feed slurry. Details of the reactor assembly are given by Shah et al. (1981).

B. Process Flow Description

A block diagram given in Figure 2 describes the process flow system used during experimentation. A continuous supply of pure hydrogen was available at a supply pressure of 34 MPa which was reduced to the system pressure through an array of high pressure regulator, needle valves and rotameters. The system pressure was recorded at several points within the system; i.e., preheater inlet, reactor outlet and at the separator system. The feed tank which was provided with an accurately formulated slurry blend was equipped with an agitator and a baffle system in order to insure that the slurry mixture would remain uniform. The slurry feed rate was determined by the weight loss of the slurry from the feed tank. Gas rate calibrations were made before and after each experimental run.

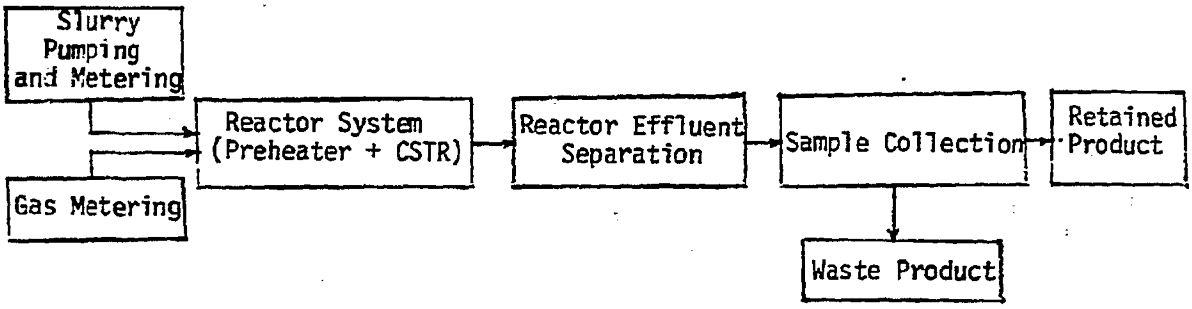

FIGURE 2: Process Flow Diagram

The reactor effluent was separated into two fractions by a high temperature, high pressure separator. These fractions include a heavy product (liquid underflow which contained all of the product solids and overhead vapor stream (hydrocarbon liquids, process water and gas products). The overhead stream was further separated in a low temperature, high pressure separator. The details of the process description are given by Shah et al. (1981).

III. Procedure

The unit was first tested for leaks with nitrogen and then with hydrogen. The "Calrod" heaters were then used to raise the temperature up to 693^{o}K and then the reactor was maintained solely by adiabatic heaters.

If the reactor temperature went beyond 743^{o}K, then the following emergency procedures were adopted:

(1) the preheater temperature was lowered immediately

(2) if this was not sufficient to lower the temperature of the reactor, the heaters were shut-off

(3) if (1) and (2) did not work, nitrogen purge provided in the reactor jacket was turned on.

IV. Results and Discussion

A. Range of Variables

Range of variables covered in the present study are listed below.

TABLE 1

Range of Variables Covered in Present Investigation

Recycle Ash Content (wt%)	2,5 and 10
Slurry Residence Time (SRT)(hr)	0.5, 1 and 1.5
Hydrogen Partial Pressure (MPa)	10.2, 13.6 and 20.4
Feed Temperature (^{o}K)	663-696
Coal Concentration in the Slurry (wt%)	30
Type of Coal	Ireland Mine Bituminous Coal

B. Thermophysical Properties

Based on SRC-II pilot scale data, the heat of reaction (ΔH) values for the Ireland bituminous type of coal has been estimated to be in the range of 5000-7000 cal/gm of hydrogen consumed. An average value of 6250 cal/gm of hydrogen consumed was assumed for our calculation. Other thermophysical properties assumed in the present study are listed below.

TABLE 2

Thermophysical Properties and Parameters used in Calculation

Density (gm/cm^3)

Slurry, $\rho_\ell = 1.2$

Gases, $\rho g = 0.0072$

Reactor Body $\rho R = 7.83$

Specific Heat (cal/gm^oC)

Slurry, $C_{p,\ell} = 0.75$

Gases, $C_{p,G} = 2.43$

Reactor Body $C_{pR} = 0.12$

Heat Content ($Cal/^oC$)

Slurry $V_\ell \rho_\ell C_{p\ell} = 897$

Gases = 0.08

Reactor Body $V_R \rho_R C_{pR} = 900$

Heat Loss Q = 20,000 cal/hr

Reference Temperature $T_o = 300^oK$

C. Kinetic Data

Separate non-adiabatic experiments were performed to measure the kinetics of hydrogen consumption. The experimental data were obtained for three different severity conditions: (1) low severity at 703^oK, 10.2 MPa and 2 wt% ash; (2) moderate severity at 723^oK, 13.6 MPa and 10 wt% ash; (3) high severity at 743^oK, 20.4 MPa and 10 wt% ash. Figure 3 describes hydrogen consumptions vs. nominal slurry residence time (SRT) for these three operating conditions. For moderate and high severity conditions where most coal liquefaction reactors are operated, the data shown in Figure 3 can well be expressed by the correlation proposed by Singh et al. (1980, 1981b) as

$$r_{H_2} = 0.000324 + 3.36 \times 10^4 \, P^{0.28} \, x_{ash} \exp\left(-\frac{9545}{T_R}\right) \quad (1)$$

D. Steady State and Ignition Temperatures

For low severity conditions, no ignition in the reactor temperature was observed for the feed (or preheater outlet) up to 703°K. In the present experimental setup it was not possible to exceed this preheater outlet temperature. For moderate (5% ash, 13.6 MPa) and high severity conditions (10% ash, 20.4 MPa) reaction conditions, the ignition in reactor temperature was observed. In several cases of high severity conditions, once the ignition occurred, the reactor temperature did not achieve a steady state below 740°K, a temperature above which most coal liquefaction reaction cannot be operated under safe non-coking conditions. The ignition temperature significantly increased as the severity of the reaction decreased, however, it was found to be relatively independent of SRT between 0.5 hr and 1.5 hr.

Table 3 summarizes the experimentally observed steady state and ignition temperature data.

TABLE 3

Summary of Steady State and Ignition Temperature Data

Sl. No.	SRT (hr)	Pressure (MPa)	Ash (%)	Feed Temp. (°C)	Reactor Temp. (°C)	Remarks
1	1.5	3000	10	394	458	S.S.
2	1.0	3000	10	393	453	S.S.
3	1.5	3000	2	414	458	S.S.
4	1.0	3000	10	415	460	I.T.
5	1.0	2000	10	415	435	I.T.
6	1.0	2000	10	420	435	I.T.

S.S. = steady state temperature.

I.T. = Ignition temperature.

E. Multiplicity of Steady States

While in the range of variables studied experimentally, no multiplicity of steady states were observed, the existence of multiplicity of steady states was however confirmed in separate experiments, where different steady state temperatures were obtained for the same feed temperature (Singh et al., 1981) depending on start-up conditions. Similar observations were made in other unpublished pilot scale experiments.

F. Parametric Sensitivity and Transient Behavior

The results shown in Figure 4 clearly indicate that an adiabatic coal liquefaction reactor may exhibit strong temperature sensitivity. In real process this may be controlled by gaseous quench or other feed back control means. Further it has been observed that the thermal behavior of a coal liquefaction reactor is strongly influenced by feed and reactor temperatures, and ash (or catalyst concentration). For the range of variables studied in this particular work, it does not have a pronounced effect on the thermal behavior of the reactor.

One interesting feature of the system was found to be its slow dynamic response for changes in feed temperature. For a feed temperature of approximately 685^{o}K, the reactor temperature exceeded the safety limit. This temperature excursion however took close to seven hours. One can therefore take necessary actions for control within that time e.g. (a) injecting cold hydrogen gas; (b) turning off heating and (3) reducing the feed temperature.

A numerical solution to the transient equation (equation 2) with the feed temperature condition as shown in Figure 5, was found to agree well with the experimentally measured temperature profile. The numerical solution to equation 2 was obtained using Runge-Kutta method.

V. Conclusion

The present study shows that an adiabatic coal liquefaction reactor would exhibit temperature excursions under practical range of operating conditions. The response of the process was, however, slow and the reactor temperature could be controlled by the feed temperature.

Contribution of Gulf Research Center

The authors acknowledge the assistance of Gulf Research and Development Company (subcontractors for the project) for providing facilities for experimental work at their Research Center. Special mention may be made of Dr. Norman L. Carr, Dr. W. E. King, Jr., Mr. W. G. Moon and operators of the unit who extended every possible help in the modification of A-1 coal liquefaction unit, fabrication of the reactor and accessories and carrying out the experimental measurements.

Notations

Cp_g = average specific heat of gas phase (Cal/gm^{o}C)

$C_{p\ell}$ = average specific heat of slurry phase (Cal/gm^{o}C)

ΔH = heat of reaction (Cal/gm-H_2 consumed)

p = hydrogen partial pressure in (psia) =

Q = heat loss from reactor

R = universal gas constant

r_{H_2} = rate of hydrogen consumption (gm/hr·cm^3)

SRT = slurry residence time (hr)

To = reference temperature (^{o}K)

V = volume (cm^3)

X_{ash} = ash mole fraction (-)

ρ = density

f,R,g refer to feed, reactor and gas respectively

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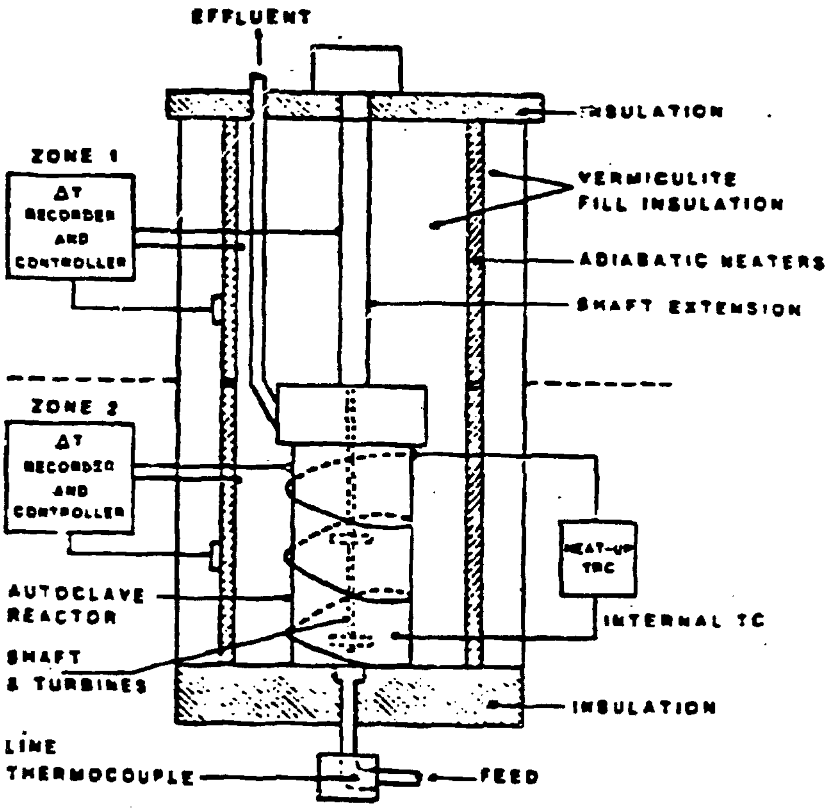

FIGURE 1: SCHEMATIC DIAGRAM OF THE REACTOR

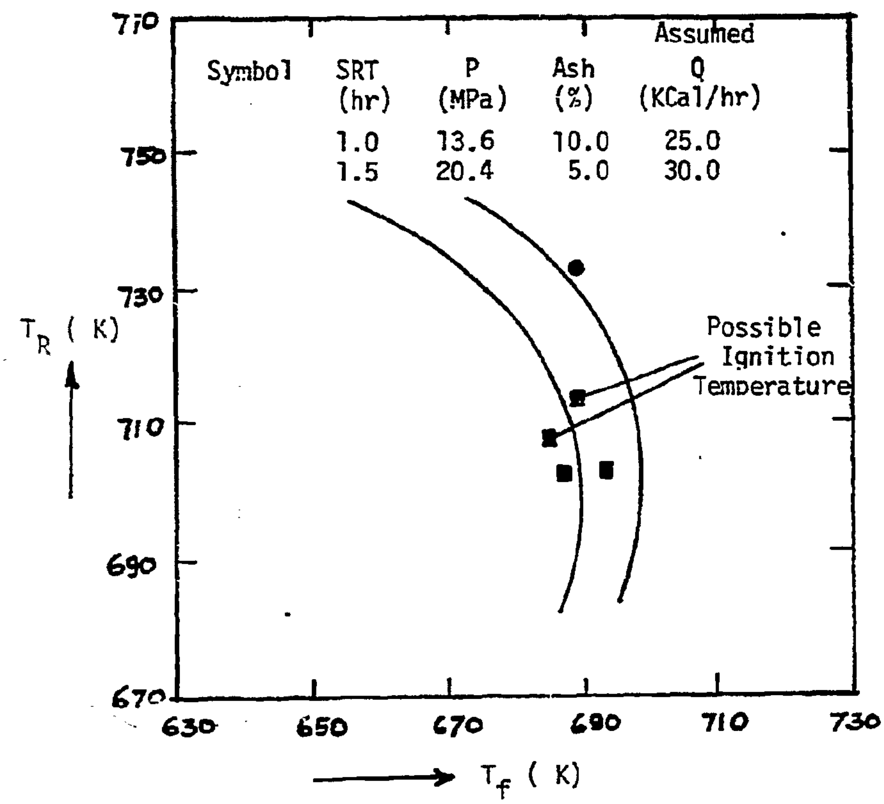

FIGURE 3: Typical Steady State Reactor Versus Feed Temperatures

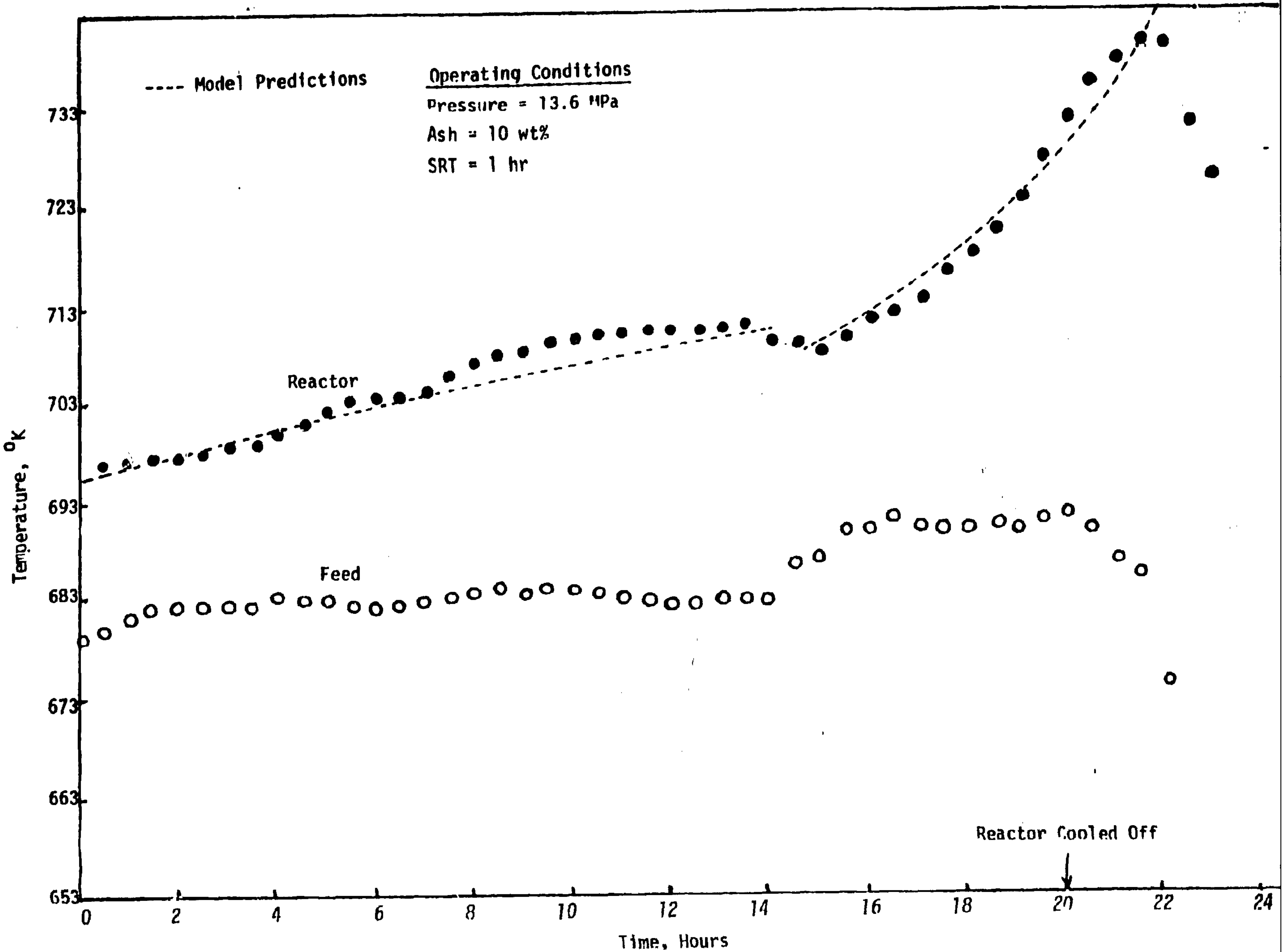

FIGURE 4: Typical Temperature - Time Response

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