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EXPERIMENTAL STUDY OF THE MULTIPLE STEADY STATES IN AN ADIABATIC COAL-LIQUEFACTION REACTOR. ANNUAL PROGRESS REPORT, SEPTEMBER 1, 1981-AUGUST 31, 1982

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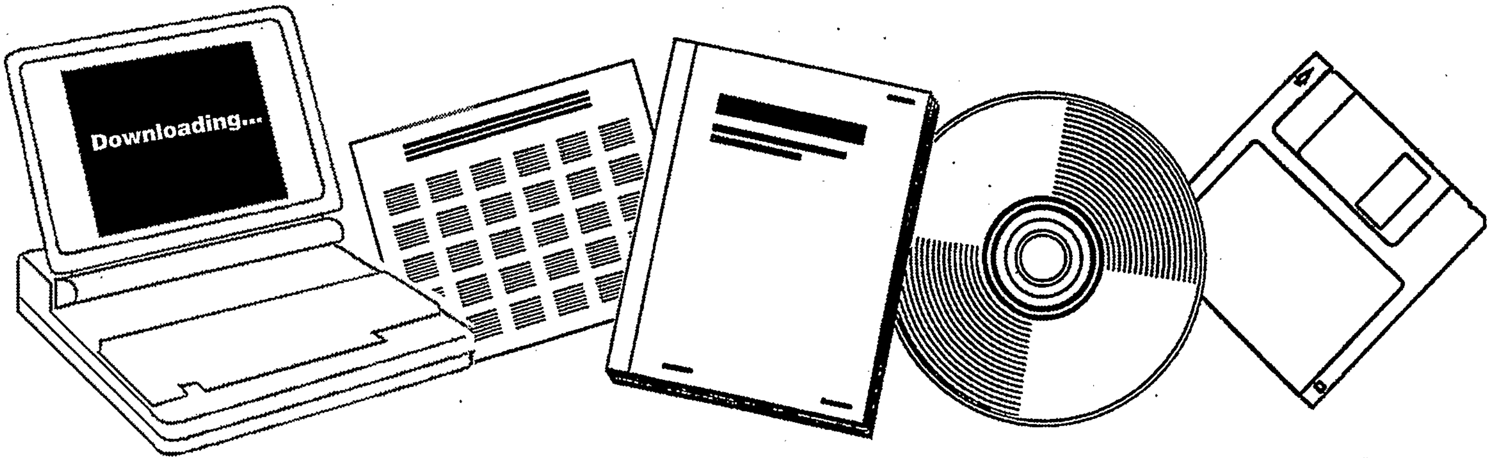

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Introduction

The work being done on this contract by the subcontractor, Gulf Science and Technology Company, has been completed, and a copy of their report is included as the main body of this report.

Analysis of the results is continuing at the University of Pittsburgh and will be presented in the Final Report for the project.

GULF SCIENCE AND TECHNOLOGY COMPANY
Pittsburgh, Pennsylvania

IGNITION BEHAVIOR OF AN EXPERIMENTAL ADIABATIC COAL LIQUEFACTION REACTOR

by

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Chemicals and Minerals Division
Report No. 6003RN036
Project No. 137-1200
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Approved Herman Taylor
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Date Aug 24, 1982

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SUMMARY

Based on an experimental study using an adiabatic CSTR, conditions exhibiting ignition and quench have been found for coal liquefaction. Some factors which affect this kind of thermal behavior have been identified. Under normal feed conditions for SRC-II operation, repeated ignition/quench behavior was demonstrated. No stable steady state was found in the vicinity of 450°C (and below 475°C). Ignition occurred at a feed temperature of about 415°C. The low steady states observed occurred at conditions of no heat generation, presumably at low/no reaction of hydrogen. Some evidence of a preheater effect on reactor ignition was indicated but not systematically studied.

INTRODUCTION

The rational design of a coal liquefaction reactor requires fundamental chemical reaction engineering information. This includes knowledge of the kinetics of the reactions, the hydrodynamics of the reactor, and the thermal behavior of the reactor. Efforts have been made in the development of the reaction kinetics and hydrodynamic areas, although no experimental bench-scale or pilot-scale studies have been reported which elucidate the exothermic nature and behavior of the reactor. In a commercial-scale reactor, the surface area to volume ratio is small and, thus, heat losses to the surroundings are normally small compared to the total heat generated within the reactor. This is not true, however, for most laboratory-scale reactors where the surface area to volume ratio is relatively large and where the heat capacity of the reactor hardware is significant compared with the contents of the reactor. Therefore, a laboratory-scale reactor was designed to produce adiabatic operations and provide a basis for understanding the thermal behavior of such reactors.

The purpose of this experimental study was to develop data for providing a basis for understanding the thermal behavior of an SRC-II reactor. A laboratory-scale reactor which operates sufficiently close to adiabatic conditions was used. Heat losses from the reactor were minimized through the use of automatically controlled heaters which drive the radial temperature gradients across the reactor wall to zero.

This study was supported by the Department of Energy under Contract No. DE-FG22-80PC30243. The principal contractor was the University of Pittsburgh with Gulf Science and Technology Company being a subcontractor. The GS&TC role was two-fold. Firstly, we designed and constructed the adiabatic reactor system as a part of a cost-sharing program with the University of Pittsburgh. Secondly, we executed an experimental program plan approved by the University of Pittsburgh designed to meet the objectives of the contract.

The experimental plan centered around a strategy for exploring the existence of possible multiple steady states in the open-loop reactor operating at typical SRC-II conditions. However, because of the likelihood that high conversion states lie only in regions where significant coke deposition may occur, at unsafe conditions, the plan was necessarily limited to investigate the occurrence of reactor ignition. In addition, the effect of ash level, pressure, and nominal slurry residence time (SRT) on reactor ignition were examined. An Ireland coal was used for all experiments with a 30 wt% concentration in the feed slurry.

DESCRIPTION OF THE EXPERIMENTAL SYSTEM

An adiabatic reactor system was designed and fabricated at Harmarville for integration with the A-1 prepilot coal liquefaction unit for operation in the simulated SRC-II recycle mode. This simulated mode of recycle operation has been described elsewhere (see Reference 1). A schematic of the adiabatic reactor assembly is shown in Figure 1 with a detailed description of the reactor illustrated in Figure 2. The A-1 unit flow sheet is shown in Figure 3. Briefly, the focal point of the adiabatic system was a two-zone heater arrangement which was designed to compensate for heat losses from the reactor and stirrer shaft through feedback control of radial temperature gradients. A top view of the adiabatic reactor assembly is shown in Figure 4 while the details of the thermocouple placements for control of adiabaticity are shown in Figure 5. Each zone consisted of four adiabatic heaters with a thermocouple in the vicinity of each heater plus a thermocouple on the wall of the stirrer shaft (Zone 1) and on the wall of the reactor (Zone 2). A Calrod heater (manual control) was used to heat the reactor to the desired initial temperature level before switching to the adiabatic mode of operation. Slurry pumping and metering, gas metering, and reactor effluent separation were carried out in exactly the same manner as in previous studies and will not be detailed here (see Reference 1). No data were obtained which reflected the level of conversion in the reactor.

EXPERIMENTAL PROCEDURE

The experimental procedure employed in this study paralleled that of other studies carried out on the A-1 unit for prepilot development studies. These are described in (1). The major difference, however, centered around exploring combinations of reactor feed temperature and internal reactor temperature which may result in a stable high conversion steady state or such that an increase in feed temperature results in a reactor ignition evidenced by a rapid dynamic change in the reactor temperature. Changes in feed temperature were effected by varying the wall heat flux along the segmentally wrapped preheater. Wall temperatures along the preheater were recorded and the preheater residence time fixed independently of the reactor residence time. This preheater design allows for the possibility that for a given feed temperature, the temperature profile along the preheater may differ. This phenomenon may lead to some interesting reactor thermal behavior effects which are alluded to below.

The Calrod heater was used to bring the reactor up to a desired temperature level before switching to adiabatic control. The adiabatic mode of operation was maintained by the automatic on-off cycling of the adiabatic heater. The circuitry of the control system was such that the Calrod heater and the adiabatic heaters were not on simultaneously. Furthermore, the feedback control of the two zones was independent with a single control variable within each zone.

The temperature window of operation was set to be 420-470°C, with the upper limit being critical. If the reactor temperature fell to ~420°C, the Calrod heater was turned on. If the reactor temperature began to rapidly approach 470°C, a point where it was thought that significant coke deposition and plugging may occur, an emergency operation procedure was initiated which consisted of the following steps. First the external preheater settings were reduced. If this was effective in reducing the reactor temperature quickly, operation continued. If the internal reactor temperature continued to rise, the adiabatic heater system was turned off momentarily with a check to make sure the Calrod heater was also turned off. If this did not resolve the problem, the reactor jacket was quenched with gaseous N_2 in two different locations. Slurry flow was maintained at all times to prevent plugging. If none of these steps caused the reactor temperature to decrease, a system blowdown was to be initiated. However, during the entire experimental study, a system blowdown was not required.

RESULTS AND DISCUSSION

Five experimental tasks were carried out in this study. A task is defined as a period of continuous slurry operation of approximately 60-75 h where a specific experimental objective was sought. Table I gives a brief description of task objectives. Specific operating conditions for various periods within each task are discussed along with the corresponding results presented with the figure of results which follow.

The results of Task 1 are illustrated in Figure 6 which contains a time trace of both reactor temperature and feed temperature and also indicates the period of operation which is in the adiabatic mode. The run procedures for Task 1 as well as the other tasks consisted of operating the A-1 unit in the same fashion as that described in other prepilot coal liquefaction studies (see Reference 1) with the following exception. The heat fluxes to the preheater differed from the baseline case so that various feed temperatures could be obtained. Note that this can result in more than one preheater skin temperature profile for a given inlet feed temperature. The Calrod heater was used to raise the reactor temperature to some initial value, at which time the Calrod heater was turned off, and the adiabatic heater control system was turned on. As indicated in the key of the figures that follow, the reactor temperature-time trace in the adiabatic mode is represented by a solid line whereas the nonadiabatic period is indicated by a dotted line.

The results from Task 1 indicate that for feed temperatures in the range of approximately 415-425°C and initial reactor temperature in the range of approximately 430-450°C, there is no evidence of an ignition occurring. In fact, for a given feed temperature, the reactor temperature decreases from the initial value and approaches the feed temperature in every case. Thus, these data support the case that for an SRC-I type of feed slurry in the operating range investigated, the steady states that result are stable low (or no) conversion states. Furthermore, it is interesting to note that during the adiabatic period of operation from approximately 28-35 h, the reactor temperature and feed temperature approach each other very closely. This is supportive of a high degree of adiabaticity in the reactor since the extent of reaction at these conditions is known to be very low.

As a test for adiabaticity and the effectiveness of the adiabatic control system, temperature profiles within the two zones of the adiabatic system were recorded and examined so that the thermal gradient in the radial direction could be evaluated. These data are illustrated for all tasks in Table II for the time intervals within the overall period of operation which correspond to adiabatic conditions. The feedback control of the adiabatic heaters in Zone 2 was governed by the difference in the temperature measurement between Thermocouple 1 and the wall (reactor) thermocouple (see Figure 5). For Zone 1, the corresponding temperature difference was that for Thermocouple 7 and the wall (shaft) thermocouple. Inspection of these radial temperature differences, which correspond to points several hours into a period of adiabatic operation, indicate that typical temperature differences were in the range of 0-6°C in the reactor Zone 2 and were in the 0-16°C in the shaft Zone 1. However, temperature differences for the other radial thermocouples in the zone were observed to be somewhat higher. These uncontrolled gradients could be reduced significantly in future studies by implementing a multiple feedback control system where the four adiabatic heaters within a given zone are independently controlled.

In addition to radial heat losses from the reactor zone and the stirrer shaft zone, several other sources for heat loss are possible. These include axial heat conduction losses along the stirrer shaft and heat losses through the bottom of the reactor. The latter includes both heat losses through the Marinite insulation and the bolt heads fixing the reactor to the outer casing of the adiabatic system. The estimate of the axial heat conduction losses along the stirrer shaft are based on actual shaft wall temperature readings taken at measured distances along the shaft. Estimates of the other conduction heat losses are based on the difference between the reactor temperature and the ambient temperature. The summation of these three additional heat losses indicate a relatively insignificant total heat loss compared with the heat release for typical extents of coal liquefaction (~4000-8000 cal/h). For a typical coal liquefaction reaction, consuming approximately 5% hydrogen per gram of MAF coal, this heat loss is approximately 5-11% of the heat generated upon reaction.

The results of Task 2 are displayed in Figure 7 in the same fashion as those of Task 1. In this run sequence, the feed slurry corresponded to that of a typical SRC-II slurry with a significant quantity of recycle ash (~11 wt%). It is interesting to note that at approximately 23 h into the task, the reactor temperature begins to increase rather rapidly from an initial value of 415°C with a feed temperature of about 405°C. The reactor temperature continues to rise significantly even after the feed temperature levels off at approximately 410°C. The rise in the reactor temperature from 413°C to approximately 425°C can be attributed to a corresponding rise in feed temperature of 405°C to 410°C. However, the continued rise in reactor temperature to 437°C while the feed temperature remains constant at 410°C is attributable to the long dynamic lag of the reaction system, since the rate of reactor temperature increase is modest compared to the subsequent ignitions which occurred and are discussed below. At approximately 45 h into the task, the heat flux to the preheater was increased, resulting in an approximate step change in the feed temperature to about 418°C. At this point, the reactor temperature increased dramatically, signifying an ignition. As the reactor temperature closely approached the 470°C mark, the emergency operation procedures were initiated and the reactor was cooled to approximately 441°C. This ignition behavior was observed again after 66 h of operation when, once again, the feed temperature was increased to about 416°C with the same preheater temperature profile as that when the first ignition occurred. Thus, both ignitions occurred with approximately the same feed temperature, reactor initial temperature, and preheater temperature profile and demonstrates a reproducibility of the experiment.

Because of the success of Task 2 in locating and repeating the ignition type of phenomenon, Task 3 was designed to continue to explore other combinations of feed temperature and initial reactor temperature for typical SRC-II operating conditions which may result in an ignition type of behavior. These dynamics are shown in Figure 8. No ignitions were observed for feed temperature less than 415°C. At the 25 h point into the task, the feed temperature was increased gradually from about 415°C to 420°C. The reactor temperature remained relatively constant at 430°C until approximately the 40 h mark where the preheater temperature profile was increased, resulting in an increase in the feed temperature and a significant increase in reactor temperature. However, the feed temperature during the ensuing period was unexplainedly erratic and the slope of the reactor temperature-time trace was not as pronounced as that in the two ignitions that occurred in Task 2. One possible explanation for this difference in behavior between Task 2 and Task 3 is due to the differences in the heat fluxes to the preheater in each case. As discussed previously, the same inlet feed temperature can be obtained for a variety of heat fluxes to the preheater. This suggests that there may be an important preheater effect which results in significantly different thermal behavior within the reactor. Preheater effects, of course, are known to be very important in coal liquefaction performance and is a subject which warrants extensive additional study.

The results of Task 4 are displayed in Figure 9. The pertinent run conditions at the beginning of this task were changed to 2 wt% recycle ash, 1500 psig pressure, and a 1.0 h SRT. At approximately 15 h into the task, the system was switched to the adiabatic mode of operation which resulted in a rapid decrease in the reactor temperature from approximately 430°C. Concurrently, the feed temperature was increased rapidly from 390°C to 418°C, which resulted in only a modest decline in the rate of temperature decrease in the reactor. In fact, for the transient time period from approximately 20-26 h, the feed temperature exceeded the reactor temperature, with no substantial evidence of an incipient ignition. Increasing the SRT to 1.5 h did not alter the decreasing trend of reactor temperature. It is interesting to note that during the period of 30-40 h, the reactor temperature and feed temperature-time traces were almost identical, again providing experimental evidence in support of a high degree of reactor adiabaticity in this region of operating conditions.

To continue the exploration for ignition points, the recycle ash in the feed slurry formation was increased to ~5 wt% and both the reactor temperature and feed temperature were increased significantly. At approximately 44 h, the system was switched to the adiabatic mode at a point where the reactor temperature was 447°C and the feed temperature was 406°C. The SRT at this point was 1 h. Although the feed temperature continued to rise during the ensuing period, the reactor temperature decreased and, hence, there was no evidence of an ignition. However, when the reactor temperature was brought up to 460°C with the Calrod heater; with a subsequent switch to the adiabatic mode of operation, the reactor temperature leveled off at 460°C for a period of about 7 h. During this time, the feed temperature remained relatively constant at about 415°C. This particular run period does provide some evidence for the possibility that there may be a stable steady state for the open-loop reactor, operating at most likely a middle steady state, and should be explored more extensively. A further increase in the feed temperature via an approximate 1.4°C/h ramp caused the reactor temperature to increase from 460°C to above 470°C and, hence, the emergency operation procedure ensued. Although the reactor temperature rise is significant, it does not parallel the ignitions observed in Task 2 and is attributed to the fact that the feed temperature is rising at a commensurate rate. It is interesting to note that after the reactor was cooled and brought back up to approximately 460°C, and the feed slurry composition was again reduced to 2 wt%, the reactor temperature decreased steadily while the feed temperature remained relatively constant in the range of 411-414°C. These observations support the important role of recycle ash content in the thermal behavior of a coal liquefaction reactor.

The Task 5 results, which are illustrated in Figure 10, contain experimental results exploring the effects of higher pressure (3000 psig) and various nominal slurry residence times (0.5-1.5 h) with a feed slurry containing ~11 wt% recycle ash at typical SRC-II operating conditions. During the 10-20 hr period, which corresponded to a 1.0 h SRT, the reactor temperature remained relatively constant within the 462-467°C range, despite the fact that the feed temperature was decreasing and increasing significantly during this period. However, unlike other periods of operation, these feed temperature variations were at a low level (380-395°C). At the 20 h point, the feed temperature is increased from 390°C to 398°C with the result that the reactor temperature increases from 462°C to above 470°C, at which time emergency operating procedures were initiated. In fact, the reactor temperature overshot to 475°C before cooling took place. Because both the reactor temperature and feed temperature rates of increase were similar, the conclusion that an ignition occurred here is not warranted. The nitrogen quench reduced the reactor temperature quickly and during this period the feed thermocouple temperature indications were erratic. During the remaining period of the task, no evidence of ignition behavior occurred at 3000 psig and 1.5 h SRT for reactor initial temperature of 457°C and feed temperatures in the range of 395-400°C.

Table III summarizes the most significant experimental observations resulting from the five tasks performed.

As a final note, it is interesting to report that the inspection of the reactor and its internals at the completion of this experimental program showed absolutely no signs of coke or cement-like solid deposition even though reactor temperature went as high as 475°C. This datum supports one of the important results achieved in our previous prepilot development program for SRC-II (see Reference 2) which verified that if the mixing power input to the reactor is high enough, higher severity levels of operation are feasible. This severity level is much higher (475°C vs 450°C) than was normally used in the bubble column reactor in various PDUs.

CONCLUSIONS

The adiabatic reactor system developed to study the thermal behavior of coal liquefaction was successful. For the first time, data were obtained on the ignition/quench behavior of an adiabatic coal liquefaction reactor operated in an open-loop fashion.

The data obtained form the basis for further analysis and study. The results of this work are important to the design, scale-up, and control of large-scale coal liquefaction reactors, including the SRC-II process.

WEK:dae
WPC (3597)

REFERENCES

1. "Prepilot SRC-II Development Project: Hydrogen Consumption Kinetics," N. L. Carr, W. E. King, Jr., and W. G. Moon, Report No. 627RM096.

2. "Prepilot SRC-II Development Project: Hydrogen Mass Transfer Study," N. L. Carr, W. E. King, Jr., and W. G. Moon, Report No. 627RM085.

Table I

TASK OBJECTIVES

Task 1:	Search for ignition points (or stable steady state points) for coal liquefaction of feed with no recycle slurry (SRC-I mode) 30 wt% Ireland coal 70 wt% Ireland process solvent 0 wt% recycle ash 2000 psig 1 h SRT 4 g of H_2/100 g of feed slurry treat rate
Tasks 2 & 3:	Search for ignition points (or stable steady state points) for coal liquefaction of feed with recycle slurry (SRC-II mode) 30 wt% Ireland coal 33 wt% Ireland recycle slurry 37 wt% Ireland process solvent 11 wt% recycle ash 2000 psig 1 h SRT 4 g of H_2/100 g of feed slurry treat rate
Tasks 4 & 5:	Investigate the effects of recycle ash, nominal slurry residence time, and pressure on ignition behavior 30 wt% Ireland coal 11-33 wt% Ireland recycle slurry 37-59 wt% Ireland process solvent 2-11 wt% recycle ash 1500, 3000 psig 0.5, 1.0, 1.5 h SRT 4 g of H_2/100 g of feed slurry treat rate

Table II

ADIABATIC SYSTEM TEMPERATURE-TIME DATA

Task	Time Period, h	Radial Gradient ΔT, °C (Zone 2)	Reactor Zone Temperature, °C					Radial Gradient ΔT, °C (Zone 1)	Magnadrive Zone Temperature, °C				
			1	2	3	4	Wall		5	6	7	8	Wall
1	30	4	425	448	439	463	429	0	282	287	299	291	299
	47	4	432	456	445	470	436	3	289	293	305	296	302
	49	5	438	462	453	478	443	0	289	294	305	297	305
	53	4	442	466	455	482	446	0	289	293	305	296	305
2	20	2	429	439	428	432	431	8	329	316	323	325	331
	25	2	429	440	429	433	431	7	322	309	316	317	323
	42	2	449	460	449	453	451	12	338	323	329	332	341
	50	3	468	480	470	472	471						
	63	3	447	458	445	452	450	16	318	309	317	317	333
	70	3	461	472	461	465	464	8	343	335	343	343	351
	73	3	472	485	472	477	475	8	353	345	354	354	362
3	8	5	445	454	441	454	440	15	358	359	353	357	368
	13	5	437	444	433	445	432						
	25	3	444	454	439	452	441	12	366	267	360	363	372
	35	3	443	452	437	450	440	13	365	265	358	363	371
	45	1	447	457	441	454	446	11	373	271	365	369	376
	55	3	464	474	458	471	461	12	385	280	377	381	389
	58	3	472	482	467	480	469	11	390	283	384	386	395
4	20	5	428	436	420	433	423	1	369	242	366	384	365
	35	6	412	421	404	416	406	3	357	234	355	372	352
	46	6	458	467	450	464	452	1	387	258	386	402	387
	53	5	475	484	467	481	470	3	402	266	400	418	403
	56	5	476	485	468	481	471	3	403	265	401	420	404
	60	6	480	488	471	484	474	3	404	266	403	421	406
	63	1	478	490	472	484	477	3	407	267	406	424	409
	70	4	471	480	463	474	467	4	404	267	401	420	405
	80	4	465	474	456	461	461	5	399	261	393	414	398
5	15	0	470	481	468	456	470	5	416	260	409	430	414
	20	1	466	477	460	455	467	4	411	258	405	425	409
	23	2	472	484	467	480	474	5	416	262	409	429	414

----- Control Thermocouple Pair

Table III

SUMMARY OF IMPORTANT EXPERIMENTAL OBSERVATIONS FOR TYPICAL SRC OPERATING CONDITIONS

Task	Comments
1	● No reactor ignitions occurred in the absence of recycle ash in the feed slurry for feed temperature below 425°C. ● During the 33-35 h period of operation, almost identical feed and reactor temperatures support a high degree of adiabaticity in the experimental system.
2	● Repeatable ignition behavior occurred for approximately the same combination of feed temperature and reactor initial temperature (416°C, 437°C, 418°C, and 441°C) when the recycle ash level was ~11 wt%. ● Stable open-loop operation of an SRC-II reactor at the operating conditions of Task 2 does not appear to be realistic.
3	● No reactor ignitions were observed for feed temperatures below 415°C and initial reactor temperatures below 430°C (low conversion steady states). ● The effect of the heat flux along the preheater appeared to have an effect on reactor thermal behavior. This effect was not systematically studied.
4	● No ignitions occurred at a low ash level (2 wt%) and low pressure (1500 psig) for feed temperatures in the range of 390°C to 422°C with initial reactor temperatures in the 410°C to 430°C range. ● Preliminary evidence of a possible steady state was observed at the operating conditions of Task 4 during the 48-55 h period, but needs to be explored further. ● During the 30-40 h period, system behavior substantiated a high degree of adiabaticity, even under transient conditions. ● The importance of recycle ash was substantiated as to its influence on thermal behavior.
5	● No definitive ignitions were observed when the feed temperature was below 400°C. ● The effect of pressure was not shown to be significant in affecting reactor ignition over the range studied. ● Feed temperatures below 400°C prevent reactor ignition even at relatively high initial reactor temperatures.

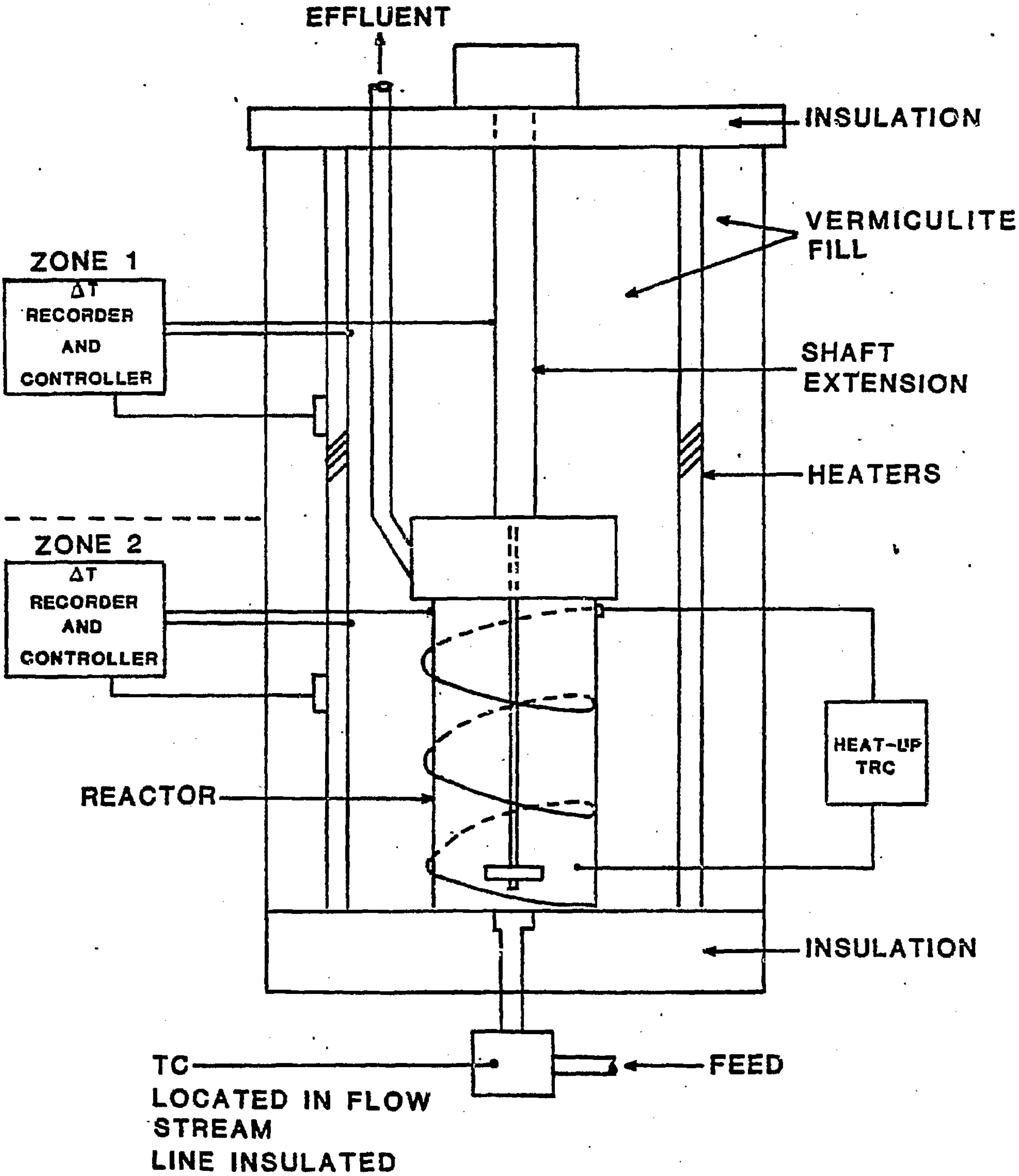

Figure 1 ADIABATIC REACTOR ASSEMBLY SCHEMATIC

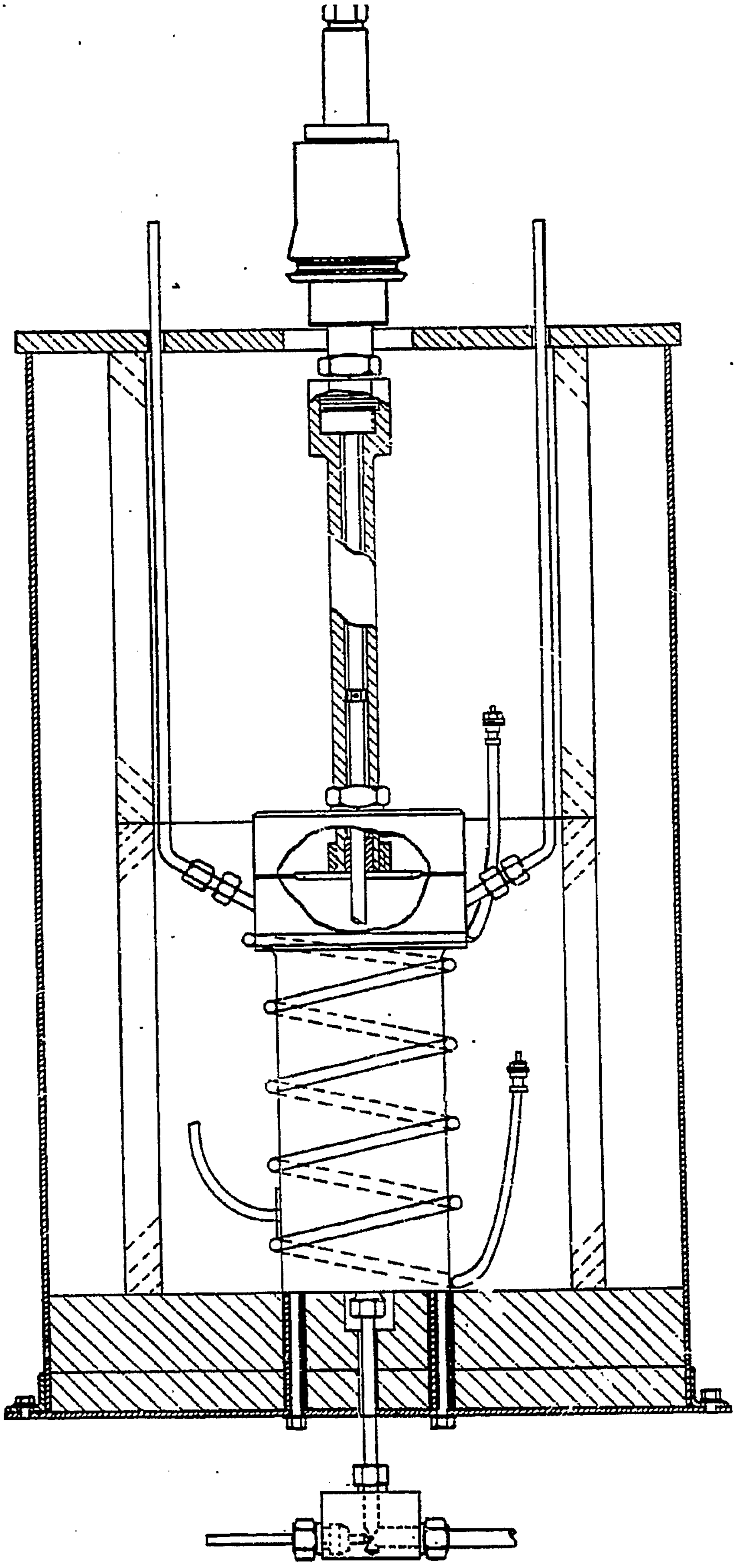

Figure 2 ADIABATIC REACTOR DETAIL

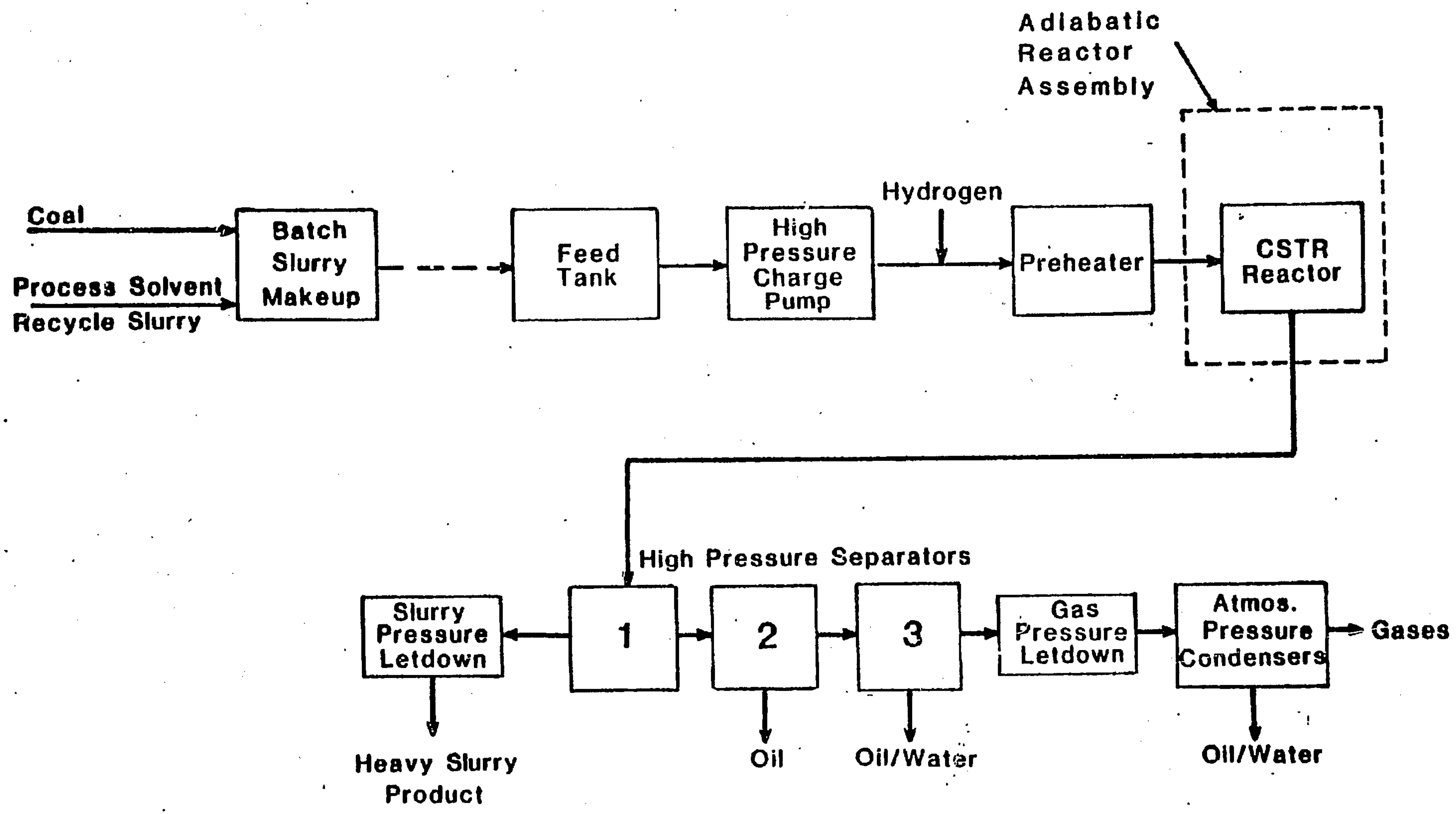

FIGURE 3 A-1 Prepilot Coal Liquefaction Unit Simulated Recycle Mode

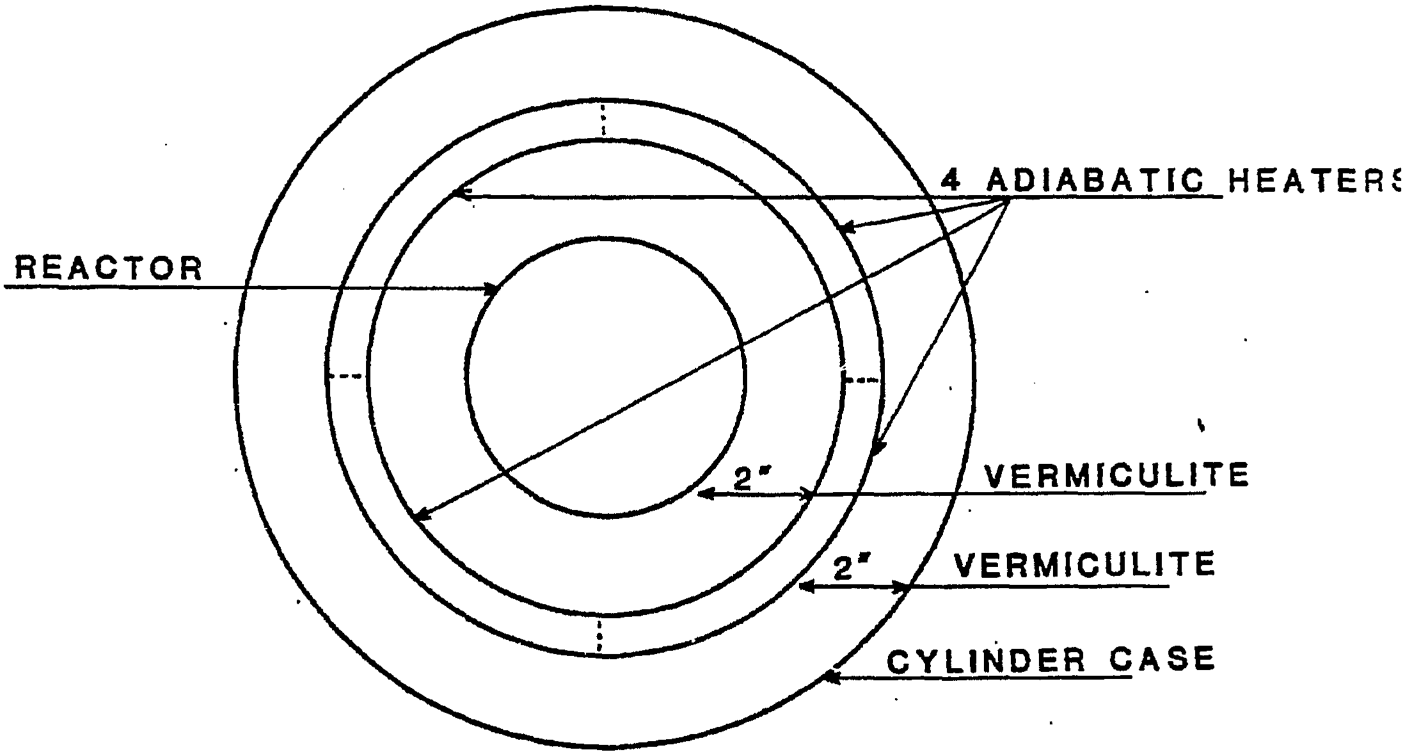

Figure 4 TOP VIEW OF REACTOR ZONE

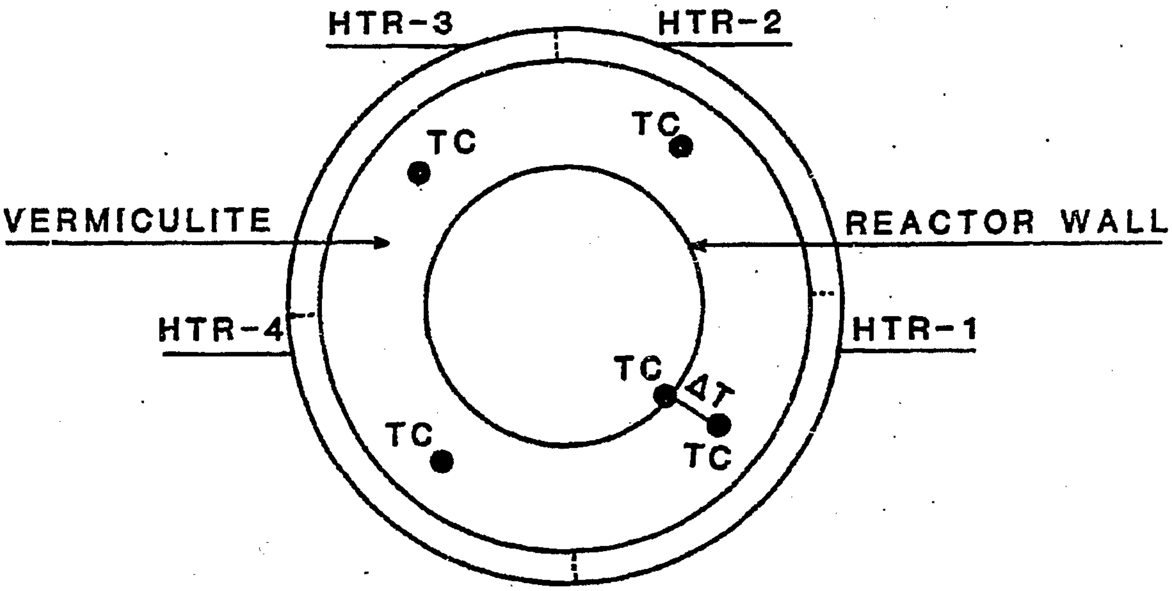

Figure 5 TOP VIEW ADIABATIC CONTROL OF REACTOR ZONE

Figure 6 TASK 1 RESULTS

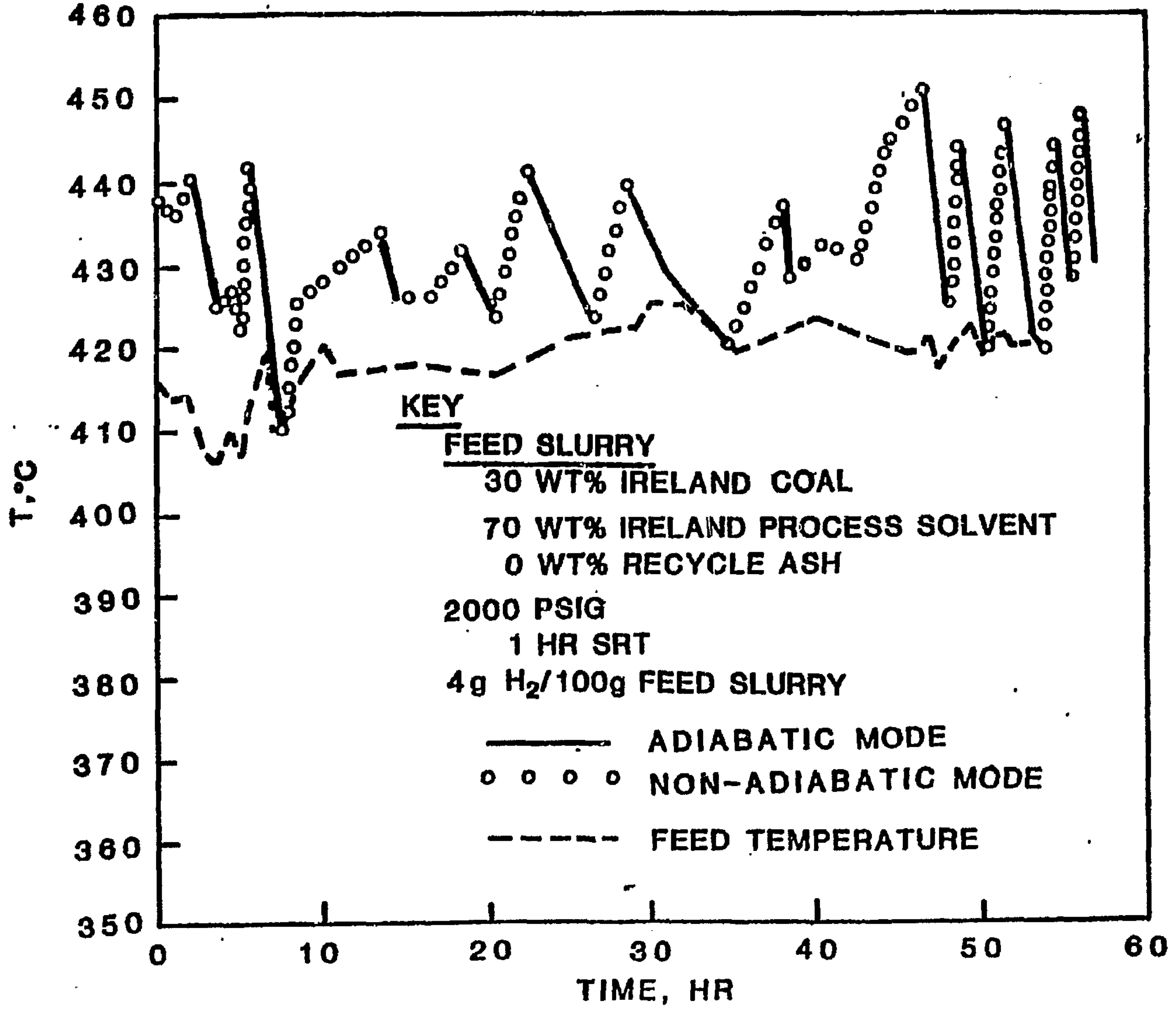

Figure 7 TASK 2 RESULTS

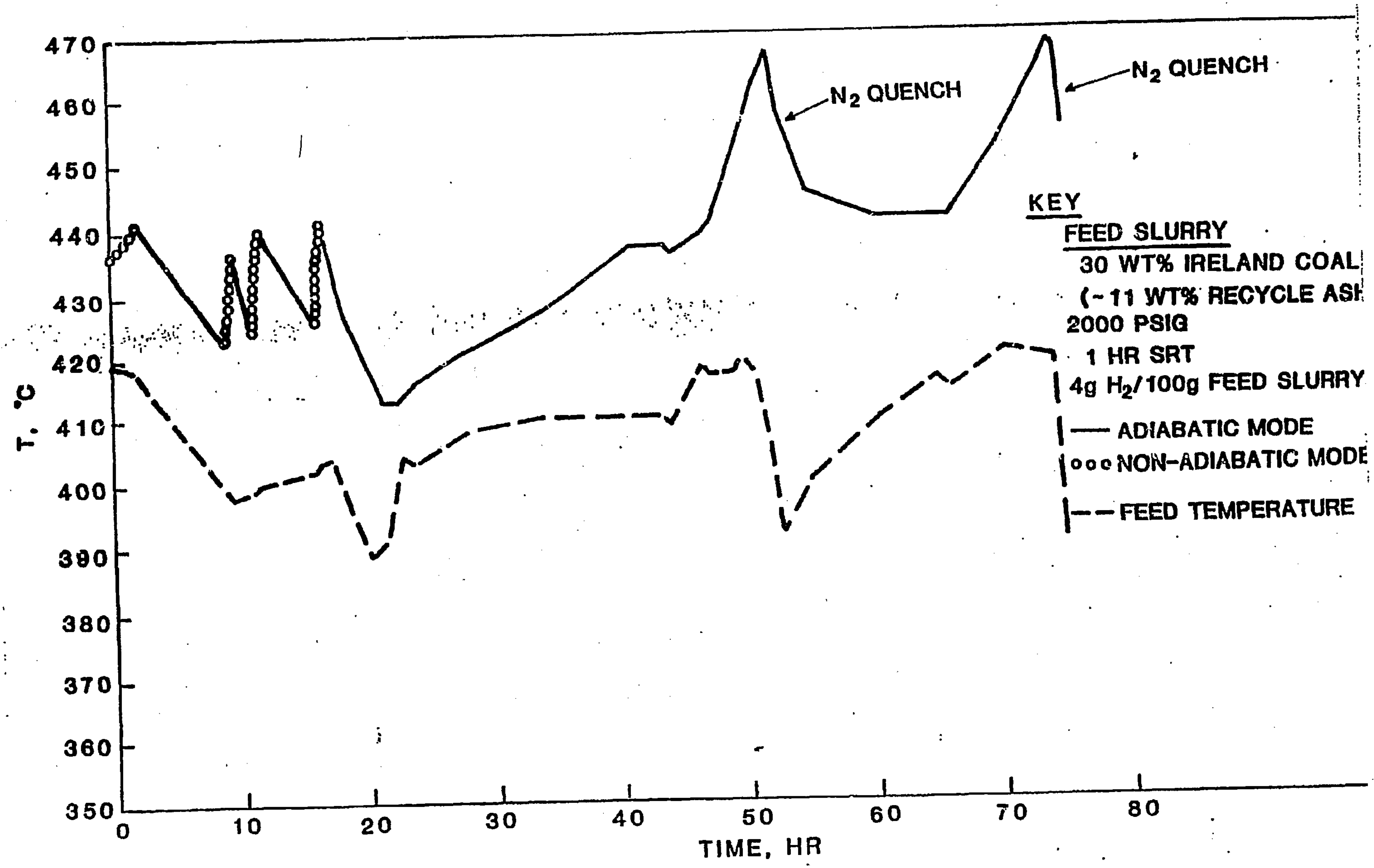

Figure 8 TASK 3 RESULTS

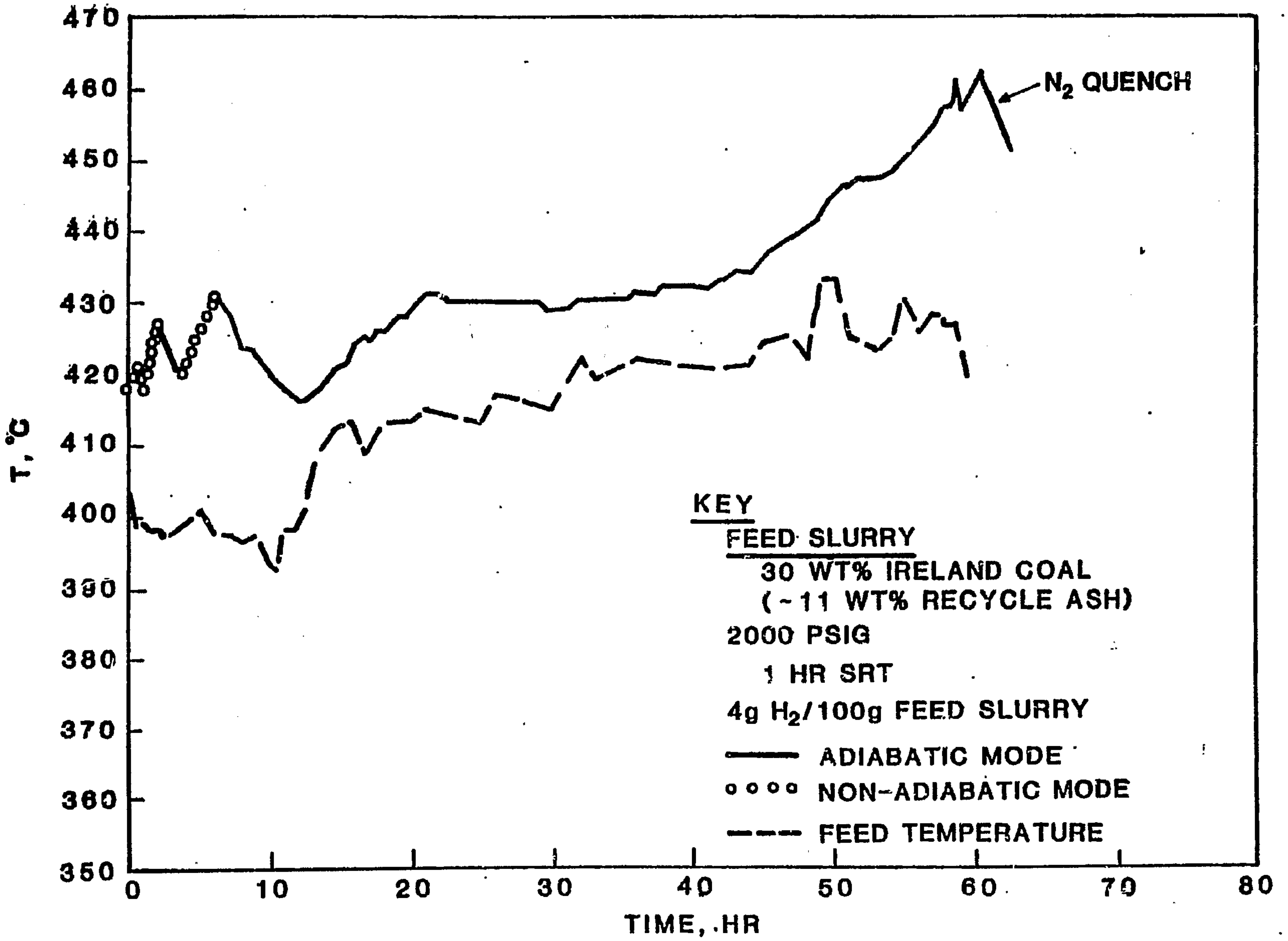

Figure 9 TASK 4 RESULTS

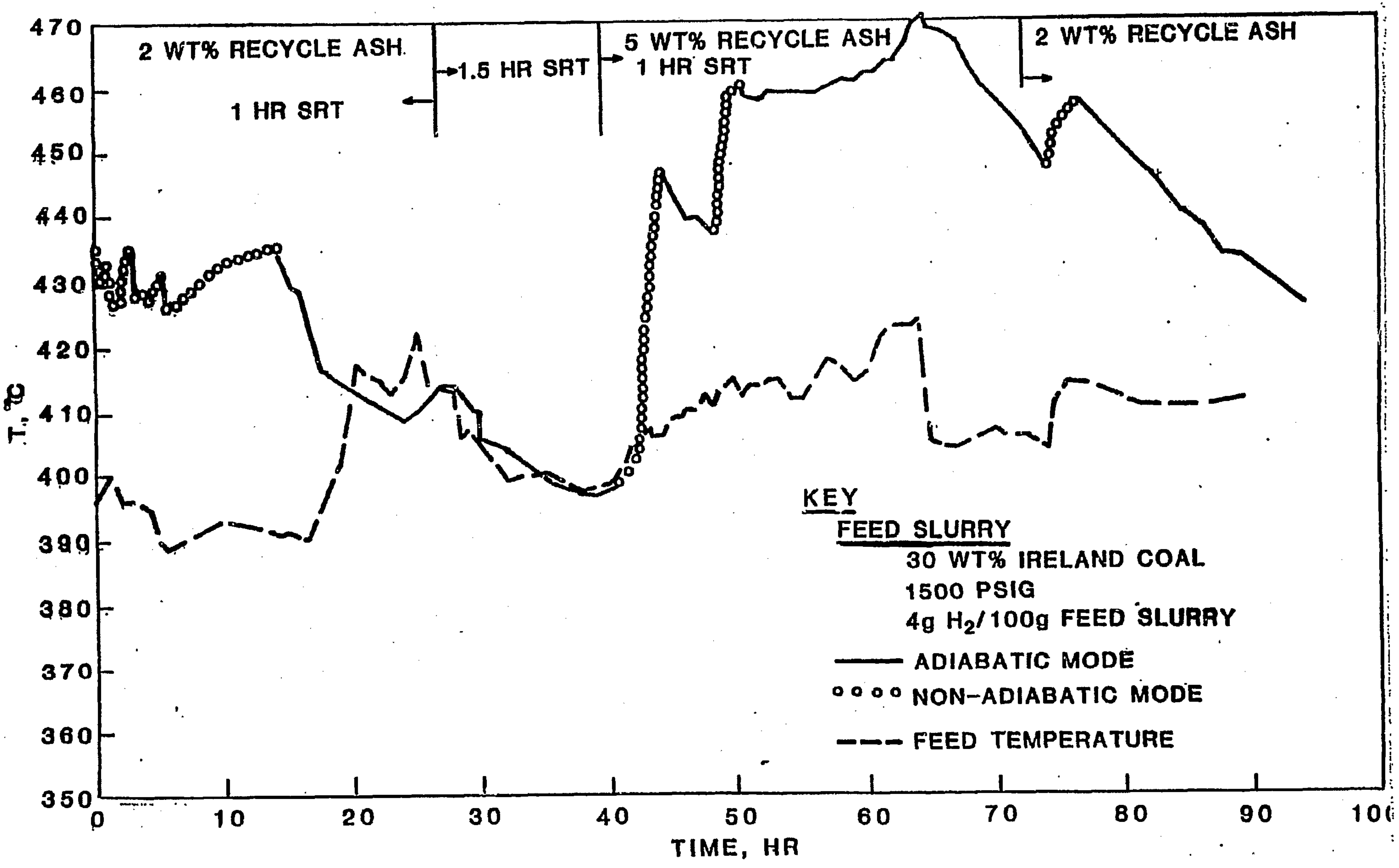

Figure 10 TASK 5 RESULTS