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Thermal Behaviour of a Gas-Phase Ethylene Polymerization Reactor

BY

Krishnakant N. Shanbhag ©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

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EDMONTON, ALBERTA
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **Thermal Behaviour of a Gas-Phase Ethylene Polymerization Reactor** submitted by **Krishnakant N. Shanbhag** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering**.

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Date: 24 November, 1992

To
my parents

ABSTRACT

The thermal behaviour of gas-phase polymerization of ethylene was studied using a semibatch stirred-bed reactor. The reactor displayed thermal runaway for a wide range of operating conditions. The effect of the important operating variables on the onset of thermal runaway was studied in detail.

It was observed that the reactor displayed parametric sensitivity to ethylene pressure (i.e., small changes in ethylene pressure caused large changes in reactor temperature). The effect of seed-bed and prepolymer was also studied. It was observed that increasing the amount of seeds delayed the onset of thermal runaway of the reactor. However, increasing the amount of prepolymerization caused the reactor to reach thermal runaway conditions faster.

The experimentally observed temperature profiles frequently showed sharp discontinuities indicating local "hot spots", which can be attributed to build-up and subsequent dislodging of polymer product on the thermocouple tip. It was observed that these localised temperature surges can induce the reactor to reach thermal runaway conditions even when the temperatures at other locations inside the reactor are much lower than the melting point of the polymer.

The simplified two-phase heterogeneous model proposed for this system was shown to agree qualitatively with the general experimentally observed results. There was a lack of agreement of the model-experiment results at higher prepolymerization levels. Errors in the estimation of the soli-gas, bed-wall and oil bath heat transfer rates can be a possible cause for lack of agreement. A more detailed meso or micro model is required to model such behaviour.

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Nomenclature

A_i - Internal surface area of the reactor (cm^2)
A_p - Surface area of the growing polymer particle (cm^2)
A_w - External surface area of the reactor (cm^2)
$A_{w,m}$ - Mean heat transfer area (cm^2)
$[C_2H_4]$ - ethylene concentration (mol/m^3)
$C_{p,o}$ - Ideal gas ethylene heat capacity (J/(g·K))
$C_{p,ethylene}$ - Specific heat of ethylene (J/(g·K))
$C_{p,PE}$ - Specific heat of polyethylene (J/(g·K))
$C_{p,inerts}$ - Specific heat of inert gas (J/(mol·K))
$C_{v,seed}$ - Specific heat of seed bed (J/(g·K))
d_t - Diameter of fluidized bed (cm)
d_p - Average diameter of the polymer particles (μm)
F_g - Flow rate of ethylene (cm^3 at STP/s)
h_o - Oil bath heat transfer coefficient (J/(m^2·s·K))
h_{pg} - Solid-gas heat transfer coefficient (J/(cm^2·s·K))
h_w - Bed-wall heat transfer coefficient (J/(m^2·s·K))
k - First-order rate constant for disappearance of ethylene (m^3/(s·g cat))
k_f - Thermal conductivity of fluid medium (mW/(cm·K))
$k_{ethylene}$ - Thermal conductivity of ethylene (mW/(cm·K)
k_{helium} - Thermal conductivity of helium (mW/(cm·K))
$k_{nitrogen}$ - Thermal conductivity of nitrogen (mW/(cm·K))
k_w - Thermal conductivity of SS 316 (W/(m·K))
L_f - Length of fluidized bed (cm)
m_{cat} - Mass of catalyst (g)
m_p - Mass of one catalyst particle (g)
m_{PE} - Mass of polyethylene (g)
m_{seed} - Mass of seed bed (g)
MW - Molecular weight (g/mol)
MW_{ethy} - Molecular weight of ethylene (g/mol)

N_p - Number of growing particles
N_{Pr} - Prandtl number
N_{Re} - Reynolds number
N_u - Nusselt number
N_u^w - Nusselt number for wall
P - Pressure (MPa)
P_t - Total reactor pressure (MPa)
R - Universal gas constant (J/(gmol·K))
R_p - Radius of solid particles (cm)
r_p - Polymerization rate (mol C_2H_4/s)
T - Temperature (K)
T_g - Gas phase temperature (K)
T_p - Solid phase temperature (K)
T_{bath} - Oil bath temperature (K)
T_{in} - Inlet temperature (K)
T_R - Reference temperature (K)
U_w - Overall heat transfer coefficient ($J/(m^2 \cdot s \cdot K)$)
u - Relative velocity (cm/s)
V - Volume of reactor (cm^3)
V_g - Volume of gas phase (cm^3)
x - Thickness of the reactor wall (cm)

Greek symbols

β - Shape factor of the particles
$\Delta H(T_R)$ - Heat of reaction at 298 K ($J/g \cdot C_2H_4$)
ΔU_R - Internal energy change due to reaction ($J/g \cdot C_2H_4$)
ϵ_f - Voidage
ρ_{PE} - Density of polyethylene (g/cm^3)
ρ_g - Density of ethylene gas (g/cm^3)
μ - Viscosity of ethylene ($g/(cm \cdot s)$)

1 INTRODUCTION

Polyolefins are a group of bulk commodity polymers consisting of polyethylenes, polypropylenes, poly (butene-1) and various copolymers of ethylene, propylene and higher α-olefins. By volume used, polyolefins are the leading polymers for many applications such as plastics, fibres, films and elastomers. Indeed the world of polyethylene itself is very large and undergoing a major revolution. Table 1.1 (Karol, 1986) gives the annual production rates of the leading polyethylenes.

Table 1.1

Annual World Production Rates of Polyethylenes (10^6 Tons/yr.)

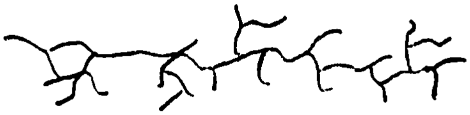
YEAR	LDPE/LLDPE	HDPE
1982	16.26	8.70
1983	16.83	9.40
1984	18.41	9.80
1985	19.27	10.07
1988	21.0	17.0

Polyethylene (PE) of density ranging from 0.91 to 0.94 g/cm^3 is classified broadly as low density polyethylene (LDPE). Before the advent of the low pressure LDPE process, LDPE was manufactured mainly by homopolymerization of ethylene with free radical initiators such as peroxide or oxygen at very severe conditions of 300°C and 250 MPa, in tubular or stirred autoclave reactors. In mid-1970, Union Carbide announced the gas-phase process technology capable of operating at less than 2 MPa and near 100°C. This low pressure LDPE technology has rapidly established itself as a low-cost route to produce polyethylene for many applications.

A key to the new low pressure LDPE technology is the family of transition metal catalysts that catalyzed polymerization reactions at very low pressures and temperatures. Moreover, most of these new low pressure processes utilize higher α-olefins such as butene-1 or hexene-1 as a comonomer to regulate the density of polyethylene. The α-olefin comonomers add side groups which disrupt the regular crystallization of the chains sufficiently to reduce the density of polyethylene to 0.92 g/cm^3 or even lower. Many of the properties of polyethylene depend largely on its crystallinity, which in turn depends upon the number of branches along the polymer chain. As the number of branches introduced increases, crystallinity decreases rapidly. The observable differences in polymer properties between high pressure LDPEs and low pressure LDPEs are due to the linearity of the main polymer chains, the molecular weight distribution, and the type of chain branching. Figure 1.1 illustrates schematically the polymer chain structures of HDPE (low pressure) and LDPE (high pressure and low pressure).

HDPE (by low pressure process)

LLDPE (by low pressure process)



LDPE (by high pressure process)

Figure 1.1 Schematic chain structure of various polyethylenes

Because of its unique structure, low pressure LDPE is called "linear low density polyethylene" (LLDPE). LLDPE has many properties distinguished from those of HDPE and conventional LDPE. LLDPE is claimed to be particularly useful for trash bags, stretch wrap, heavy wall bags, frozen food bags, telephone jacketing, houseware, container overlids, and rotational molding.

The commercial production of linear-low and high density polyethylenes is carried out by three distinct process technologies, namely, liquid slurry polymerization, solution polymerization and gas-phase polymerization.

The liquid slurry polymerization process encompasses by far the largest group of HDPE technologies. The use of a light hydrocarbon diluent, such as i-butane or n-hexane, in the process creates a major problem of swelling of the polymer in the liquid slurry medium. The swelling limits the polymer density to a minimum of about 0.925 to 0.935 g/cm^3 (Choi and Ray, 1985a). In addition, production rates at lower densities are severely restrained due to the enhanced tendency for reactor and pipework fouling. Currently, long jacketed loop reactors and continuous stirred tank reactors (CSTR) are widely used in slurry polymerization. In most cases, this process utilizes a catalyst of high activity so as to obviate the necessity of de-ashing. Excellent temperature control is a major attraction of the liquid slurry process.

Solution polymerization processes have some unique advantages over slurry processes in that the molecular weight distribution (MWD) can be easily controlled, and the process operating parameters are also more easily controlled because polymerization occurs in a homogeneous phase. The high temperature of polymerization (>130°C) also leads to high reaction rates and high polymer throughput from the reactor. However, the process is efficient only for the production of low molecular weight resins because of excessive viscosity in the reactor at high molecular weights. In some processes, precooled solvent (-40°C) is utilized for absorbing the heat of polymerization. This eliminates the problem of polymer fouling on the cooling surface; however, the large energy requirement of the solution process is a serious economic disadvantage (Choi and Ray, 1985a).

The development of a unique and versatile low-pressure, gas-phase process, the UNIPOL process, by Union Carbide Corporation has been recognized by the scientific community and industrial organizations as a major technological accomplishment. The process couples innovative reactor design and process concepts with special catalyst compositions to achieve a simpler, more versatile and much more economical route to LLDPEs and HDPEs. Sumitomo, BASF, BP and many other companies have also developed commercial gas-phase processes for PE.

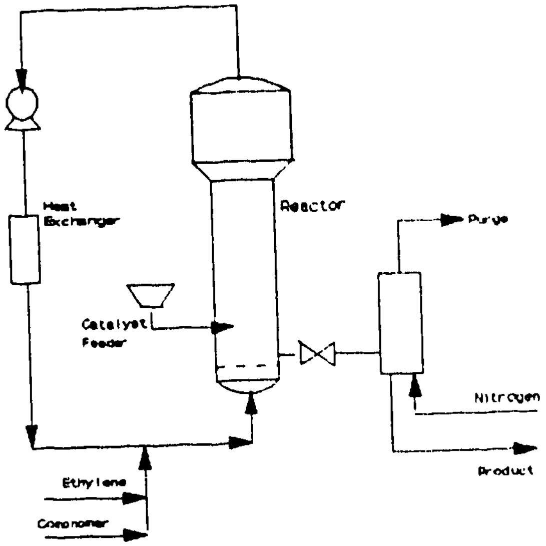


Figure 1.2 Low-pressure, fluidized bed process for LLDPE/HDPE

In the UNIPOL PE process, shown in Figure 1.2, gaseous ethylene monomer and a catalyst, in the presence of a chain transfer agent and a comonomer, are fed continuously into the fluidized bed reactor at low temperatures and pressures to produce a polyethylene product that is removed directly from the reactor as a granular solid material. This process offers significant commercial benefits. Because of the low temperatures and low pressures involved. less space is required for its operation than for high-pressure processes. Equipment costs are also substantially lower. Diluents are not required in the UNIPOL process. It eliminates the need for elaborate and costly diluent storage, recovery and purification. The simplicity of the process and the low operating pressures minimize the risk of explosion and considerably reduce the level of hydrocarbon emission. This makes the process environmentally superior. The size, shape and bulk density of the polymer product granules are suitable for subsequent customer handling without any need for further processing. All these advantages add up to savings of more than 75% in energy consumption and as much as 50% in capital costs compared to a high pressure facility (Karol, 1986).

While gas-phase polymerization has several distinct advantages over slurry or solution processes, control of reaction temperature is one of the concerns with the process. The reactor is operated at a temperature close to the softening temperature of the polymer. If the heat of reaction is not efficiently removed from the reaction zone, local hot spots may result. There is a possibility of agglomeration of the polymer and sintering of the catalyst in the bed due to the poor heat transfer rates in the gas phase and due to possibly poor fluidization. The melting point of the polymer would be reached resulting in the formation of a stationary polymer mass which, in turn causes problems in operating the reactor. Also, a suitable mode of injection of high activity catalyst is important for avoiding the formation of polymer lumps near the inlet manifold.

BASF/ICI/Norchem and Amoco/Chisso gas-phase polypropylene processes involve using stirred tank reactors and mechanical agitation for improving the heat removal capability. Nevertheless, adequate heat transfer is still a major concern in their processes (Haggin, 1992).

The purpose of this work was to observe the effects of various operating variables on the temperature of a gas-phase polymerization reactor. The phenomenon of uncontrolled increase of reactor temperature, resulting from inadequate removal of thermal energy, commonly known as "thermal runaway", was studied in detail. The work also involved developing a suitable macroscopic reactor model which could be used to predict the thermal behaviour of the reactor for different operating parameters. The goal was also to evaluate the efficacy of the various correlations available in the literature in their ability to predict the heat transfer rates of the growing polymer phase in the gas-phase polymerization process.

It was decided to study gas-phase homopolymerization of ethylene because homopolymerization kinetics are easier to model and control than copolymerization processes. The insight gained into the thermal behaviour of reactors during homopolymerization can be the starting point for subsequent studies of more complex polymerization processes.

2 TRANSITION METAL CATALYZED ETHYLENE POLYMERIZATION - A LITERATURE SURVEY

The polymerization of α-olefins with transition metal catalysts is one of the most complex physico-chemical processes found in the chemical industry. Around 1955, Ziegler and his colleagues discovered a revolutionary new chemistry which enabled polymerization of ethylene at very low pressures and temperatures (Ziegler et al., 1955). The polyethylene produced under these conditions had different properties from that of low density polyethylene produced by the original high pressure process. The "Ziegler" polyethylene had a linear structure with very little chain branching. In 1957, the Ziegler process for polyethylene was extended to the polymerization of propylene by Natta. In the early 1970s, the catalysts underwent revolutionary modifications, whereby high activity catalysts permitting no catalyst removal from the product polymer appeared on the scene. Rapid development in the ethylene/propylene catalysts further improved catalyst performance.

Inspite of about four decades of existence, transition metal catalysts and processes for olefin polymerization continue to be the object of many studies both in industrial and academic laboratories. The mode of action of the catalyst has been the subject of intense investigation, but the complex phenomena involving multiple phases, complex catalysis, catalyst deactivation and dramatic morphological changes complicate the understanding of the process. The progress made in understanding the process and the catalyst system will be reviewed, with emphasis on the kinetics and mechanisms of the high activity transition metal catalysts. In addition, recent results in modelling all the stages of olefin polymerization, from the catalyst particle to the full scale reactor, will be reviewed.

2.1 Kinetics and Mechanism of Ethylene Polymerization

The kinetic behaviour of Ziegler-Natta polymerization provides important information regarding the process. The elucidation of the basic kinetic parameters helps in understanding the nature of the polymers that are formed in the presence of these catalysts. The kinetic phenomena are the result of a delicate interplay between a number of operational factors that can be controlled during the synthesis of the catalyst and its use in polymerization. Such factors include the choice of catalyst components, catalyst physical state, their absolute and relative concentrations, and temperature of catalyst preparation. The nature and magnitude of the basic parameters such as the rate law, activation energy, concentration of active centres and average l[illegible] of the growing polymer chain, are dependent on these operational factors. The effect of operational factors are well understood but the evaluation of basic parameters has been subject to considerable interpretation, mostly due to experimental difficulties in measuring the value or contribution of individual parameters.

The problem is compounded by the fact that there are many different types of Ziegler-Natta catalysts. What is learned from a study of one catalyst may not necessarily be applicable to the understanding of another.

2.1.1 Ziegler-Natta catalysts

In the broadest sense, Ziegler-Natta catalysts are a mixture of a base metal alkyl of the groups 1 to 3 and 11 to 13; and a transitional metal salt of groups 4 to 9 and 14 to 17. In practice, only a few metal alkyls are effective. Organometallic compounds of aluminium have been overwhelmingly preferred. The most commonly used transition metal salts are halides and alkoxides of Ti, V, Cr, Co and Ni metals (Boor, 1979).

$TiCl_4$ with diethylaluminium alkyl chloride (DEAC) or triethylaluminium alkyl (TEA) as cocatalyst were among the first to be used for polymerization of ethylene. These unsupported Ziegler-Natta catalysts gave a yield of about 10-15 kg of polyethylene per gram of Ti. These catalysts were found to be very unstable. Also their behaviour was found to be very sensitive to a number of experimental factors, such as ratio of Al/Ti, temperature and time of mixing of the components, absolute and relative concentration of reactants, the time elapsed between mixing and use in polymerization, aging temperature and duration of polymerization. However, a number of important titanium metal salts have been prepared by reduction of $TiCl_4$ with metal alkyl ($Al(C_2H_5)_3$ (TEA), $Al(C_2H_5)_2Cl$ or $Al(C_2H_5)Cl_2$ and related compounds) to obtain $TiCl_3$ (Boor, 1979). It was found that $TiCl_3$ was contaminated with aluminium compounds, especially $AlCl_3$. The compositions are indicated as $TiCl_3.xAlCl_3$ where the value of x usually varies from 0.2 to 0.4. $TiCl_3$ exists in four crystalline modifications, the α, β, γ and δ forms and can have complex structures whereby a second metal is co-crystallized as an alloy in the $TiCl_3$ crystal. The particular method of reduction determines both the composition and crystalline modification. Early investigations of ethylene polymerization were done with α-$TiCl_3$ modifications combined with TEA. The α-$TiCl_3$ was synthesized by reduction of $TiCl_4$ with H_2 at temperatures between 500 to 800°C. $TiCl_4$ can also be reduced with aluminium powder at 250°C to obtain the α form. In later polymerization processes, the α-$TiCl_3$ was replaced by more active modifications, namely the γ and δ forms. The γ modification is formed by heating the β modification at 100 to 200°C (Boor, 1979).

Wilchinsky et al. (1973) showed that a large increase in polymerizing activity resulted if $TiCl_3$ was ball-milled under dry conditions. They presented direct evidence that the activating effect resulting from extensive dry ball-milling of the layer-lattice of $TiCl_3.\frac{1}{3}AlCl_3$ was due to the capability of these salts to undergo extensive crystallite size reduction. This large reduction in crystallite size was probably due to the layer structure of the salt and the porous nature of the catalyst particles.

The development of very high activity modified Ziegler-type catalysts such as titanium supported on magnesium chloride represents the next generation of Ziegler-Natta catalysts, useful for liquid slurry and gas-phase polymerizations. By 1970, the yields had improved to 250 kg of polyethylene per gram of Ti (Chandrasekhar et al., 1988). The mode of preparation of these catalysts determines the activity achieved and the properties of the polymer product. Magnesium chloride and silica copulverized with a $TiCl_4$-tetrahydrofuran complex and activated by aluminium alkyl compound showed high copolymerization activity (>500 kg of PE per gram of Ti) and yielded polyethylene of low density when used in a gas-phase fluidized bed reactor at 85°C and 2.0 MPa (Choi and Ray, 1985a). When reaction products of aluminium halides, alkoxy magnesium, TiCl4, organic compounds and an oxide carrier are mixed with organoaluminium compounds, a high activity catalyst useful for making linear low density polyethylene (LLDPE) was obtained.

Crystalline similarity of magnesium chloride (ionic radius of Mg^{2+} =0.066 nm) and titanium chloride (ionic radii of Ti^{4+} =0.068 nm and Ti^{3+} =0.076 nm), and the ability of the support to maximize the reactive sites by packing Ti at the edge of the carrier results in the very high activity of the magnesium chloride supported Ziegler-Natta catalysts (Chandrasekhar et al., 1988). Anhydrous magnesium chloride can be activated by prolonged milling which results in an increase in surface area. However, it has been found that grinding for more than 20 h led to loss of activity, caused by site agglomeration. Treatment of magnesium chloride with ethyl benzoate (EB) resulted in formation of a new crystalline phase which could be milled for as long as a hundred hours without any adverse effect on catalyst activity. The crystallite size of magnesium chloride was found to decrease with increasing ethyl benzoate, reaching a minimum at $EB/MgCl_2 = 0.17$ beyond which crystallite sizes increase, even to sizes larger than the original sizes for pure magnesium chloride (Chandrasekhar et al., 1988). A molar ratio of ethyl benzoate to magnesium chloride of 0.17 represents the support possessing the most favourable polymerization properties.

Compared with conventional high pressure low density polyethylene (LDPE), low pressure LLDPE has had poor shrink properties and poor film clarity (Choi and Ray, 1985a). As the film market is the largest for LDPE, current industrial research on LLDPE seems to be strongly oriented toward modifying or developing copolymerization catalysts which can produce LLDPE copolymer having good optical properties. In addition, improvements in tear strength, dart impact and processibilty are also sought. The current generation of Ziegler-Natta catalysts include the bi-supported Union Carbide catalyst having $MgCl_2$ and silica support. This catalyst, $TiCl_3/TEA/THF/MgCl_2/SiO_2$ is claimed to be capable of producing copolymers having improved haze and gloss properties (Choi and Ray, 1985a).

In the following section, the kinetics and mechanism of some of the Ziegler-

Natta catalysts described in the previous section will be reviewed. Since many of the later generation catalysts have been discussed mainly in the patent literature, the understanding of these catalysts is not comprehensive.

2.1.2 Formation of active centres

The kinetics and mechanism of organotransition metal catalysts and Ziegler-Natta catalysts can be better understood in terms of the nature and number of active centres. Though the composition of these catalysts, which are extensively used for gas-phase proccsses, differ significantly, the mechanism of chain propagation in ethylene polymerization over these catalysts is thought to be similar.

(a) Unsupported Ziegler-Natta catalysts (Chandrasekhar et al., 1988):

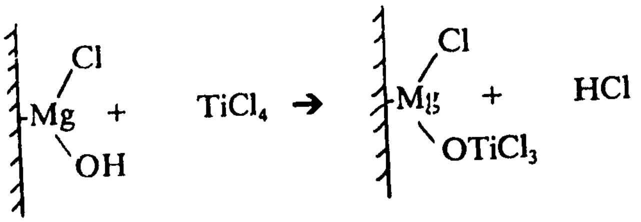
The formation of the active site on the surface of the titanium trichloride occurs due to alkylation by metal alkyl. This is shown by the following equation:

$$\underset{\text{(catalyst)}}{\mathrm{Cl_2\text{-}Ti\text{-}Cl}} + \underset{\text{(co-catalyst)}}{\mathrm{Al(C_2H_5)_3}} \rightarrow \underset{\text{(active centre)}}{\mathrm{Cl_2\ Ti\text{-}C_2H_5}} + \mathrm{Al(C_2H_5)_2Cl} \qquad (2.1)$$

The active centre is considered to be the titanium centre with both an alkyl substituted and a chlorine vacancy located on the edge of a titanium trichloride crystal. The chain growth occurs by two steps, (i) the complexation of the monomers on the active site, and (ii) further insertion of monomer between transition metal-carbon bond.

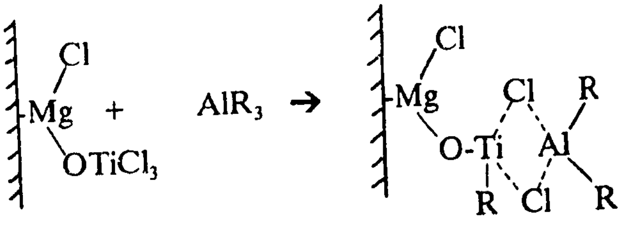
(b) Supported Ziegler-Natta catalysts:

Karol (1978) reported the mechanism of active centre formation, chain propagation and chain transfer for supported Ziegler-Natta catalyst systems. In catalysts prepared from surface hydroxyl containing supports, such as $Mg(OH)Cl$, the first step for the formation of an active surface complex of $TiCl_4/Mg(OH)Cl$ is chemisorption taking place by reaction of a halogen atom from $TiCl_4$ with hydroxyl groups at the surface of $Mg(OH)Cl$, which results in Ti-O bonds:



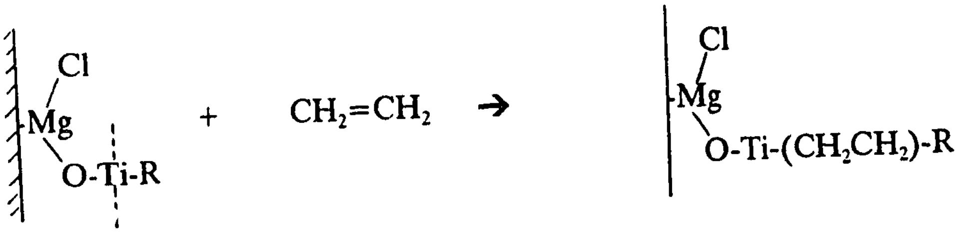
(2.2)

This supported titanium compound is then activated by addition of an aluminium alkyl to provide an active catalyst site with a structure of the type shown below:



(2.3)

Propagation takes place subsequently by repeated insertion of coordinated monomer into the Ti-C bond:



(2.4)

Yashima and Doi (1982) suggested that the following reaction occurs when $TiCl_4$ is supported on $MgCl_2$.

$$2MgCl_2 \quad + \quad TiCl_4 \rightarrow \quad MgCl_2.Mg(TiCl_6) \qquad (2.5)$$

2.1.3 Kinetics using unsupported Ziegler-Natta catalysts

A kinetic study of ethylene homopolymerization with $TiCl_3$ (AA-grade, surface area 40 m^2/g)/triethylaluminium alkyl (TEA) system by Keii (1972) revealed that the rate was almost constant during the initial stages ($t<15$ minutes) after which it decreased gradually with time until a stationary value was attained. Nitrogen had no apparent effect on the rate though hydrogen depressed the rate considerably. Earlier work by Schindler (1963) using $TiCl_4/Al(C_2H_5)_2Cl$ had shown some depression of rate in the presence of nitrogen. The gradual decrease of the polymerization rate with time has been examined at various pressures and temperatures. Smith and Zelmer (1963) proposed a second-order deactivation law to express the rate behaviour. The catalyst system $TiCl_3/Al(C_2H_5)_2Cl$ gave acceleration type kinetic curves with ethylene. Berger and Grieveson (1965) examined the kinetics of γ-$TiCl_3$ and diethylaluminium chloride (DEAC) and found a rather curious temperature dependence of the stationary rate. The activation energy below 50°C was 56.5 kJ/mole, while above 50°C the apparent value of the activation energy was negative. They attributed this to the "diffusion control" of the polymerization rate. The rate law obtained by Schnecko et al. (1963) gave an activation energy of 40.6 kJ/mole for ethylene polymerization with $TiCl_3$/triethylaluminium alkyl (TEA) and 36.4 kJ/mole with $TiCl_3$/DEAC which was similar to that obtained by Keii (1972).

The kinetics of $TiCl_4$/DEAC system was investigated by Schindler (1963) who represented the rate curve by a linear relation between the reciprocals of the polymerization rate and time which he accounted to bimolecular deactivation of the propagation centres. From experimental results using [Al]/[Ti] =0.5 and 4.0 at 30°C, Keii (1972) concluded that the higher the catalyst concentration, the shorter the time required to reach the stable state. The deactivation of catalyst was considered to be due to excess DEAC based on the observation that deactivation could be minimized by dilution of the catalyst system with solvent.

2.1.4 Kinetics using supported Ziegler-Natta catalysts

The polymerization activity of supported Ziegler-Natta catalysts have shown some interesting features. Bohm (1978) found that a high activity catalyst proposed for ethylene showed little activity for propylene. He also observed more generally that the rate of ethylene polymerization was much higher than the rate of propylene polymerization. Zakharov et al. (1975) carried out kinetic studies on various supported catalysts. They reported the activities and kinetic parameters of the following catalysts: $TiCl_4/MgCl_2$ + TEA and δ-$TiCl_3.\frac{1}{3}AlCl_3$ + TEA. They reported that the supported catalysts had a higher concentration of active transition metal sites than conventional unsupported Ziegler-Natta catalysts. Zakharov et al. (1975) and Baulin et al. (1975) attributed the significant enhancement of polymerization activity in supported Ziegler-Natta catalysts solely to an increase in the total number of propagation centres. However, when Doi et al. (1982) carried out gas-phase olefin polymerization on $TiCl_4/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$, they found that the rate of polymerization depended on both the titanium concentration and surface area of $MgCl_2$-supported catalysts. They estimated the number of active centres and the propagation rate constants by quenching the polymerization system with radioactive carbon monoxide. Their study indicated that the high activity olefin polymerization catalysts showed an increase in both propagation rate constant and number of active centres. Zakharov and co-workers (1975) also determined the number of propagation centres and the propagation rate constant for ethylene polymerization over a supported titanium catalyst. Based on their study, they suggested that the increase in the number of active centres in Mg-supported Ziegler catalysts is due to the formation of isolated titanium ions stabilized on the surface of $MgCl_2$ and the formation of finely dispersed $TiCl_3$ clusters (<5 nm) on the support surface.

The first-order dependence of reaction rate on the monomer concentration for highly active supported titanium-magnesium catalysts was observed by Zakharov et al. (1975). They prepared two catalysts; one was prepared by supporting $TiCl_4$ on anhydrous magnesium chloride and the other was prepared by reducing $TiCl_4$ with butylmagnesium chloride. The polymerization rate at 80°C was first order with respect to the catalyst concentration ($3x10^{-6}$ to $20x10^{-6}$ mmol Ti/cm^3) and monomer concentration (120 to 600 mol of C_2H_5/m^3. They also observed that the polymerization rate depended not only on the nature of the organoaluminium cocatalyst but also on the relative concentration of the cocatalyst in the catalyst mixture. They also obtained first-order reaction rate dependence on monomer concentration for $Zr(C_3H_5)_4/SiO_2$ and $Zr(CH_2C_6H_5)_4/Al_2O_3$ catalyst. The optimum [Al]/[Ti] ratios for the $TiCl_3/SiO_2$ and $TiCl_4/SiO_2$ systems were considerably higher than those for conventional Ziegler-Natta systems. The activation energy for many organotransition metal catalysts was observed to be about 40-60 kJ/mole. It is interesting to note for the [$TiCl_4$+DEAC] SiO_2/TEA catalyst system, Zakharov et al. (1974) observed that the apparent activation energy decreased with increasing temperature. They reported E_a= 42.0 kJ/mole at 30-50°C and E_a= 13 kJ/mole at 50-95°C.

Carrick et al. (1972) observed that the pore size of the support was an important factor in designing organotransition metal catalysts. The pores of the support had to be large enough for the catalyst components to penetrate and react effectively therein during catalyst preparation. When using silica as a support, they observed that it had to have a pore diameter larger than 6 nm and a particle diameter less than 250 μm. The activities of supported Ziegler-Natta catalysts are not in simple proportion to the surface area of the support material. For instance, yields for a $TiCl_3$ catalyst supported on $MgCl_2$ have been reported to be about 10-40 times higher than for catalysts possessing much larger surface area (Choi and Ray, 1985a). The activity of a $MgCl_2$ supported catalyst was highly dependent on the pretreatment of anhydrous $MgCl_2$ in the presence of certain electron donor compounds. Makhtarulin et al. (1978) conducted x-ray measurements of $TiCl_4$ supported on anhydrous magnesium chloride, to elucidate the role of support materials in ethylene polymerization. An increase in catalyst activity was observed when $TiCl_4$ was deposited on magnesium chloride prepared with a high degree of disorder into its crystalline structure. The amount of absorbed $TiCl_4$ tends to decrease with increasing crystallinity of the support. They believed that upon interaction with the support, $TiCl_4$ was inserted into the defect regions of $MgCl_2$ crystallites, which resulted in the ordering of their structure, and a more stable surface. For amorphous $MgCl_2$, they discovered that the interaction of $TiCl_4$ with $MgCl_2$ resulted in the formation of surface complexes. These type of active complexes were different from those in other supported catalysts in which covalent bonding of the transition metal compound with surface hydroxyl groups occurred.

The above literature review has summarized ethylene polymerization kinetics and mechanisms for complex catalyst systems. Use of state-of-the-art catalyst systems have resulted in dramatic improvements in process economics as well as product quality; however, understanding of the various phenomena is still incomplete.

2.2 Modelling of Olefin Polymerization Reactors

Ziegler-Natta olefin polymerization is both *catalytic*, involving chemistry of solid surfaces, adsorption and morphology of porous solids, and *addition polymerization* involving the familiar kinetic steps of chain propagation and transfer. The combination of these two arenas of reaction engineering makes it one of the most complex physio-chemical processes found in industry.

In heterogeneous systems, polymer, monomer and active sites are partitioned between different phases at all stages of polymerization. Monomer is solubilized in a 3-dimensional polymer phase and adsorbed on a 2-dimensional surface phase. The active site is on a 2-D solid surface. Polymer is in a 2-D adsorbed surface phase and a 3-D bulk solid. When all these processes are coupled, it is virtually impossible to come to a detailed understanding of the polymerization process without the use of mathematical models. The combined effect of all the important phenomena can be predicted by a detailed model.

The application of process modelling to the transition metal catalyzed polymerization of α-olefins has not advanced as far as in other areas of polymerization. However, recent work has been directed towards developing useful models for this class of polymerization.

2.2.1 Model structure

Similar to other types of models, polymer reactor models have a definite hierarchial structure based on the principal size scales which are considered. The three scales of interest for transition metal catalyzed polymerization over solid catalysts, microscale, mesoscale and macroscale, are shown in Figure 2.1 (Ray, 1986).

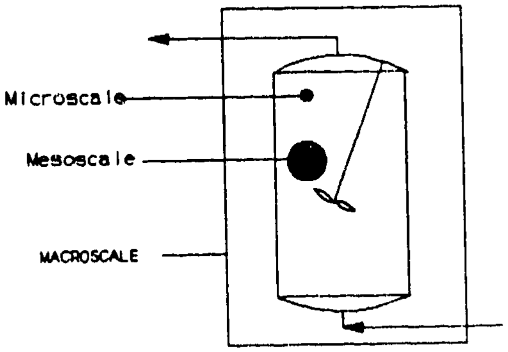


Figure 2.1 Levels of modelling

The phenomena which have to be considered at each scale of modelling and the modelling efforts of these scales are discussed below.

2.2.2 Microscale kinetic phenomena

At the microscale, the phenomena occurring at the active site level on the catalyst are modelled and their effects are studied. Natta and co-workers (Boor, 1979) proposed a coordination mechanism typically involving the steps of initiation of chain growth at active sites on the catalyst, propagation by coordination and insertion of monomer at the active sites, and chain termination by chain transfer reactions (e.g. with monomer, cocatalyst or agents such as H_2). Although the precise nature of the mechanism is still under discussion, there is strong evidence that there are several types of active sites present which vary both in activity and in their ability to produce completely stereoregular polymer (Boor, 1979). They considered that the active metal could be transition metal (later accepted by most workers to be the case) or a base metal (previously considered valid by many workers but later by only few).

Eirich and Mark (1956) first suggested that adsorption kinetics probably played a significant role in Ziegler-Natta polymerizations. Subsequently Keii (1972) applied the Langmuir-Hinshelwood type rate law and also the Rideal model to describe the observed polymerization rate behaviour. In the Rideal model, the rate determining step is the surface reaction as shown in the following equation;

$$[(C_2H_5)_3Al\ \text{dimer}]_{ads} + (C_2H_4)_{sol} \xrightarrow{k_s} \text{polymer} \qquad (2.6)$$

Rate = $k_s.P_B.\theta_A$

k_s = rate constant describing the reaction of adsorbed metal alkyl.

P_B = concentration of monomer.

θ_A = degree of coverage of metal alkyl on the surface.

In the Langmuir-Hinshelwood model, the rate determining step is the surface reaction between triethylaluminium alkyl dimer (A) and an adsorbed olefin monomer (M). Both the species are said to be adsorbed at identical sites; i.e., they competed for the same sites:

$$(\text{TEA dimer}) + M \xrightarrow{k_s} \text{polymer} \qquad (2.7)$$

The surface reaction rate is given by

Rate = $k_s.\theta_A.\theta_B$

θ_A and θ_B are degree of coverage of surface sites by molecules A and M respectively.

Webb et al. (1989) measured adsorption rates of ethylene on chromium-silica at 50°C and 101 kPa using reactive chromatography. They showed that adsorption was very fast relative to chain insertion and was not rate determining relative to intrinsic insertion and/or transport times.

There is often significant catalyst deactivation over the lifetime of a growing polymer particle. Doi et al. (1982) studied gas-phase propylene polymerization with the highly active supported catalyst $TiCl_4/MgCl_2/C_6H_5COOC_2H_5/Al(C_2H_5)_3$ and observed that the rate decreased gradually during the course of polymerization. The rate of decay of polymerization was represented by a second-order decay law, which was attributed to the second-order deactivation (disproportionation) of active centres resulting in the reduction of Ti^{3+} to Ti^{2+}. Yoon and Ray (1987) proposed a model for the observed decay in the polymerization rate of propylene over δ-$TiCl_3.\frac{1}{3}AlCl_3$ (DEAC) catalyst based on the consumption of cocatalyst through chain transfer and accumulation of a byproduct inhibitor competing for active sites.

2.2.3 Mesoscale particle phenomena

The growth of the polymer particle on the catalyst has aroused much interest. The initial motivation stemmed from the observation that the morphology of the progeny polymer particles could be controlled by proper choice of the morphology of the heterogeneous Ziegler-Natta catalysts (Boor, 1979). This discovery enabled workers to control the polymer particle morphology by controlling the morphology of the transition metal component. Figure 2.2 shows the schematic of the growth of the polymer particle during polymerization.

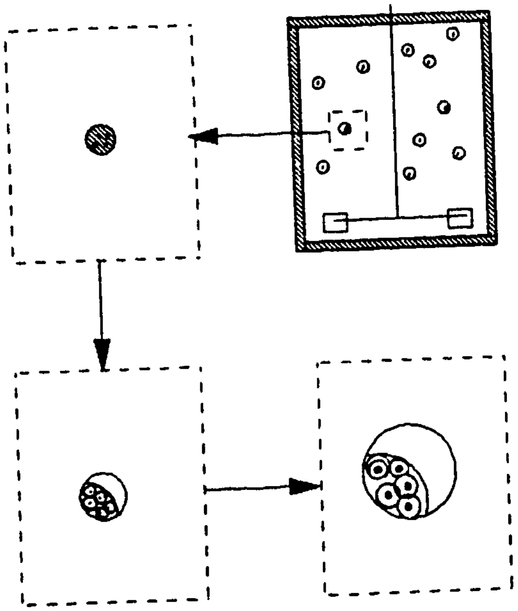


Figure 2.2 Schematic of the growth of polymer particles in the bulk of the polymerization reactor

As shown in Figure 2.2, the original catalyst particle quickly fractures into tiny micrograins of catalyst which are encapsulated by polymer to form microparticles. These microparticles then grow by continued polymerization at the surface of the catalyst grain. Under normal conditions, these microparticles remain agglomerated to form a macroparticle of polymer which can grow to 10-40 times the size of the original catalyst particle. In solid catalyzed olefin polymerization, these mesoscale phenomena are very important because the fragmentation process and the physical processes of heat and mass transfer on the particle level can play very important roles in limiting the polymerization rate as well as introducing severe operational problems in the gas-phase process.

In the early "hard-core" model proposed by Schmeal and Street (1971) and Singh and Merrill (1971), it was assumed that polymerization occurred around a centre catalyst particle which was non-friable. Since the model assumed no disintegration, it predicted a slowly decreasing rate of polymerization with polymer accumulation due to increasing transport resistance of monomer through the growing polymer shell. This model is perhaps applicable to non-friable catalysts. They also reported a "uniform" site model and "expanding-core" model for the friable catalysts. The uniform and expanding-core models both assumed friability but recognised different growth mechanisms. The uniform model assumed that fragmentation of catalyst was completed early in the polymerization. Polymer grew around each catalyst crystallite at equal rates resulting in uniform dispersion within the polymer particles. In the "expanding-core" model, the fragments were convected to the exterior particle surface by internal expansion. Lawrence and Chiovetta (1983) proposed the multigrain, multilayer approach in which the original catalyst particle quickly fractured into tiny micrograins of catalyst which were encapsulated by polymer to form microparticles. These microparticles then grew by continued polymerization at the surface of the catalyst. Under normal conditions, these microparticles remain agglomerated to form a macroparticle. They modelled the nascent exotherm and fragmentation processes in gas-phase polymerization of propylene by magnesium chloride supported titanium catalysts at industrial conditions. Their model predicted that the nascent polymerization is inherently unstable. A minimum gas-phase Nusselt number is necessary to overcome the thermal instability. They employed a simple fragmentation model, based on particle attrition and a constant fracture-yield criteria. They ignored particle agglomeration and melting and assumed uniformity in the bed and in the particles, i.e., a single particle analysis. Their model predicted that fragmentation and the exotherm were over within one pore volume of the polymer yield (0.1-5.0s). The influence of the nascent period on observable kinetics would be minimal, for such systems, provided external heat transfer conditions were capable of dissipating the short lived surge of thermal energy and preventing agglomeration during that period. For systems having magnesium chloride supported catalysts which are known to be highly friable, the experimental data qualitatively followed the trends predicted in the model.

Floyd et al. (1986) used the multigrain model as the basis of their mesoscale particle model. The model has two levels of heat and mass transfer, one at the gas-microparticle level and the other at the macroparticle level. Both slurry and gas-phase systems predicted significant monomer concentration gradients at the microparticle level for high activity catalysts and those yielding large catalyst fragments after breakup. The model did not predict any serious thermal gradients across the microparticles for either the gas or the liquid slurry process.

Significant concentration gradients were predicted in the macroparticle for slurry phase systems. Only very large particles of very high activity catalyst showed macroparticle gradients in gas-phase systems. Investigating the boundary mass and heat transfer effects, Floyd et al. (1986) reported that interphase mass transfer resistance was negligible for the gas-phase process and could be significant only during the early growth of high activity catalysts in slurry process. Thermal gradients across the boundary were negligible in slurry phase reactors, but were very significant for particles formed from large, highly active catalyst particles in gas-phase polymerization. Also, the polymer particle overheating due to heat transfer resistance was seen only for very short times after which the gradients declined to a value close to that of the reaction medium. But the consequence of thermal gradients in the gas-phase reactors is the potential for catastrophic particle temperature increases beyond the melting point of the polymer. The polymer could agglomerate or stick to the reactor internals, thus causing chunks of polymer and fouling of the reactor. For catalyst particles which are attracted to the wall of the reactor (smaller particles), a even more serious situation was predicted. The heat removal rate of these particles is low because of the stagnant fluid boundary layer near the wall, consequently they would overheat under a wide range of conditions. Thus, while large catalyst particles are more susceptible to overheating when freely circulating, smaller catalyst particles are more likely to be attracted to the wall and cause wall fouling.

Floyd et al. (1987) reported that these mass transport limitations could confound the interpretation of reaction rate data. Depending on the value of macroparticle diffusivity, their simulation gave rate curves which were of the decay type, acceleration type and of the hybrid type. Detailed mathematical modelling allowed interpretation of rate data in terms of both catalyst deactivation and mass transfer limitation.

The above model completely ignored the nascent period, fragmentation, agglomeration and particle morphological influences. They assumed a set of parameter values describing kinetics, heat and mass transport for polymer particles at high yields and assumed bed and intraparticle active site uniformity. Because this model ignored the nascent period, it is limited to well-behaved reactors (isothermal, well-mixed) and friable catalysts. However, Webb et al. (1991) maintained that the model could not predict behaviour of silica supported catalysts which are more durable than the magnesium chloride catalyst. They observed that silica catalyst did not fragment in the way described by Floyd et al. (1986) and the "multigrain" picture was not appropriate. According to them, a more complex model of catalyst morphology and fragmentation process was needed which requires a representative model of the void and solid network of amorphous mesoporous silica. The model must incorporate monomer mass transfer, heat transfer and also predict pore strengths and stresses developed by polymer accumulation. They showed that thermal instability during the nascent period and limited friability could compromise the activity of the catalyst. They observed that transport and morphological influences were controlling during the nascent period. Webb et al. (1991) proposed a rate model for use in heterogeneous polymerization (slurry or gas phase) in catalysts of limited friability. They based their rate evaluation on a lumped, overall characterization of catalyst performance. The kinetic model presented by them did not involve the effects of catalyst or polymer particle void morphology. Morphology is important since it determines the transport rate of mass and heat thereby influencing the intrinsic kinetics. Also, morphology affects the degree of catalyst fragmentation. They developed criteria for significant mass transport influences.

2.2.4 Macroscale reactor phenomena

Macroscale reactor phenomena determine the reaction environment of the growing polymer particles. Material and energy balances (for each phase), particle size distributions and flow patterns are important parts of the macroscale reactor model. Issues such as limited heat removal capabilities affecting reactor dynamics and control, process monitoring, optimization and control rely on the macroscale reactor model. The effect of choice of the reactor type (gas or slurry, CSTR or fluidized bed, etc.) on the reactor performance is crucial.

Brockmeier (1979) carried out modelling of a semibatch stirred-bed reactor and a continuous backmix reactor for propylene gas-phase polymerization with $TiCl_3$ catalysts. The model generated yields and production rates for a variety of catalyst parameters such as activity, stability and particle size, and operating conditions such as temperature, pressure, reaction time and gas composition. Their model postulated two significant resistances in series: diffusion through the growing shell (R_{DF}) and polymerization at the catalyst surface (R_{CAT}). The heat transfer resistance between the polymerizing solids and gas was neglected, so that both solids and gas were at the same temperature. Their model indicated that propylene gas-phase polymerization with highly active $TiCl_3$ catalyst shifted from kinetic control at short residence times to diffusion control at longer times when the catalyst yield exceeded about 4000 g of polypropylene per gram of $TiCl_3$. The effect of diffusion and catalyst decay caused yields from the continuous backmix reactor to be 25 to 30% lower than from a semibatch reactor at the same residence time.

Choi and Ray (1985b,1988) studied the steady-state and dynamic behaviour of gas-phase polymerization reactors. They developed detailed mathematical models for fluidized bed and continuous stirred-bed reactors and carried out simulations for gas-phase ethylene and propylene polymerization over unsupported Ziegler-Natta type catalysts. Their study showed that the fluidized bed has unstable steady states for a wide range of operating conditions. This meant that the reactor was prone to temperature runaway and meltdown if there was any serious disturbance to the operating conditions. Most of the reactor design and control problems are associated with inadequate heat removal from the reactor. Normal operating temperature of gas-phase reactors is about 30 to 40°C below the melting point of the polymer. Therefore, the continuous operation of the reactor cannot tolerate any significant temperature excursions. The work of Choi and Ray (1988) showed that the continuous stirred-bed reactor also had instability associated with inadequate heat removal. Detailed analysis showed that the gas-phase propylene polymerization was open-loop unstable for most operating conditions and required feed-back control strategies on bed level, temperature and pressure to stabilize the system.

Most of the previous macroscale modelling efforts (Choi and Ray, 1985a, 1985b; Hutchinson and Ray, 1987) for gas-phase ethylene polymerization have dealt with operation of the fluidized bed or the stirred-bed reactor. The models were presented to investigate temperature control problems and to predict reactor stability. However, recently, McAuley et al. (1990) presented a kinetic model for industrial gas-phase copolymerization of ethylene and α-olefins. This model was developed to predict copolymer composition and molecular weight properties in an industrial scale fluidized bed reactor under good temperature regulation. The model considers the existence of multiple types of active sites on the heterogeneous Ziegler-Natta catalyst. The two-site model can predict the changes in production rate, weight average molecular weight and copolymer composition which occur in response to gas-phase composition and catalyst grade changes in the industrial reactor.

It would seem from prior discussion that modelling should form an integral part of experimental studies of olefin polymerization. A detailed model validated by experiments would give a powerful tool, which could form the basis of process design, optimization and control.

In reviewing the previous studies on the macroscale reactor level phenomena, it is necessary to note that the investigations reported so far on the operation of the fluidized bed and stirred-bed reactors for gas-phase polymerization of α-olefins have been almost exclusively theoretical. The simulation results on the temperature control problem and reactor stability indicate the very critical need to investigate experimentally the thermal behaviour of the gas-phase reactors giving special attention to the various operating parameters which result in undesirable temperature excursions. It is also very desirable to express as quantitatively as possible with the help of a suitable macroscale model, the effect of various operating conditions on the temperature control of the reactor.

3 MATERIALS, EQUIPMENT AND EXPERIMENTAL PROCEDURES

The main objective of this work was to investigate the thermal behaviour of gas-phase ethylene polymerization reactors giving special attention to operating conditions which can result in undesirable temperature excursions. Heat transfer from the catalytically active site in the core of the growing polymer is dependent on how effectively the surrounding gas phase, which is a poor heat transfer agent, can remove heat to the reactor heat exchange surface. As a result, the temperature of the growing polymer particle can be much higher than that measured by the temperature probes in the reactor. These temperatures can reach the melting point of the polymer, resulting in large scale agglomeration of the product. Also, physical encapsulation of the catalyst by the molten polymer can result in rapid catalyst deactivation. Reproducible introduction of the catalyst and co-catalyst into gas-phase reactors is another problem. However, these problems can be largely alleviated by using proper operating procedures and conditions.

3.1 Catalyst Selection

Catalyst selection is very crucial in the study of the reactor behaviour. The Ziegler-Natta catalyst to be used for the study had to have a high activity approaching that used in industrial gas-phase reactors so that the results obtained from experiments could be utilized for similar large scale reactors. In addition, it was desired that the catalyst exhibit a high rate of ethylene polymerization, comparable to those achieved in industrial operations so that the consequence of the heat generation rate on the solid polymer product could be observed. Various supported and unsupported titanium catalysts prepared in the laboratory, were tested using different co-catalysts (diethylaluminium chloride, triethylaluminium, tri-n-octyl aluminium, etc.). The commercially available Stauffer AA Type 2.1 (δ-$TiCl_3.\frac{1}{3}AlCl_3$), an unsupported Ziegler-Natta catalyst, was also studied for activity in gas-phase polymerization of ethylene.

In Table 3.1, activity of some of the catalysts tested for the current study of gas-phase ethylene polymerization are reported.

Table 3.1

Prior Laboratory Study of Some Ziegler-Natta Catalysts

Reference condition: $P_{ethylene}$=0.5 MPa, $T_{reaction}$=60°C

Catalyst/co-catalyst	Pseudo steady-state activity g_{PE}/gcat h	Remarks	References
δ-$TiCl_3$.⅓$AlCl_3$ / diethylaluminium chloride	200	Time invariant. No deactivation for at least 12 hours.	Lynch and Wanke (1991)
High activity supported $TiCl_4$ / triethylaluminium	975	Time dependent activity profile. Deactivates fast.	Jejelowo et al. (1991)
TTMTS.3 (3.5 wt% Ti) / tri-n-octyl aluminium	1320	Complicated kinetics. Not first order.	
TTMTS.8 (1.1 wt% Ti) / tri-n-octyl aluminium	340	"	

A key consideration was that the catalyst should exhibit a time invariant activity profile, i.e., no significant catalyst deactivation should occur. Since the main objective was to study the physico-chemical phenomena occurring in the macroscale reactor environment, a varying rate profile would create an added undesirable complexity in determining the thermal energy generation rate which would now vary with time This would greatly complicate the investigation of the thermal behaviour of the gas-phase reactor. Many industrial Ziegler-Natta catalysts are high activity titanium catalysts which are supported on various supports such as silica and magnesium chloride. Table 3.2 gives the composition of some of the catalysts claimed to have utility for gas-phase polyethylene production.

Table 3.2

Commercial Catalysts for Gas-Phase Polymerization

CATALYST	COMPANY
$TiCl_4 + MgCl_2 + THF + SiO_2 / (C_2H_5)_3Al$	UNION CARBIDE CO.
$TiCl_4/Mg$ based support$/(C_2H_5)_3Al$	AMOCO CO.
$[MgCl_2+TiCl_4+ClCH_2CH_2Cl]_{milled} / (C_2H_5)_3Al$	NIPPON OIL CO.
$[\alpha\text{-}TiCl_3+Al(C_2H_5)_2Cl]+ (C_4H_9)_2Mg.1/6Al(C_2H_5)_3$	DOW CHEMICAL CO.

High activity supported titanium catalysts usually have time dependent activities. Initial catalyst activity is high with no induction period and catalyst deactivation becomes measurable fairly early in the polymerization process. Karol (1985) observed the rate profiles for several high activity magnesium-titanium catalysts of the type described in Table 3.2. The rate of polymerization of $MgCl_2/TiCl_4/THF$ (tetrahydrofuran) catalyst showed a very high catalytic activity during the first hour of polymerization after which there is a rapid deactivation with very little polymerization after two hours. The decaying polymerization rate behaviour shown by the industrial catalysts was unsuitable for the present study. However, the Stauffer catalyst showed a constant rate profile as shown in Figure 3.1. As seen in the Figure 3.1, the $\delta\text{-}TiCl_3.\frac{1}{3}AlCl_3$ shows a slowly accelerating polymerization rate profile initially. Following the stabilizing period, the rate

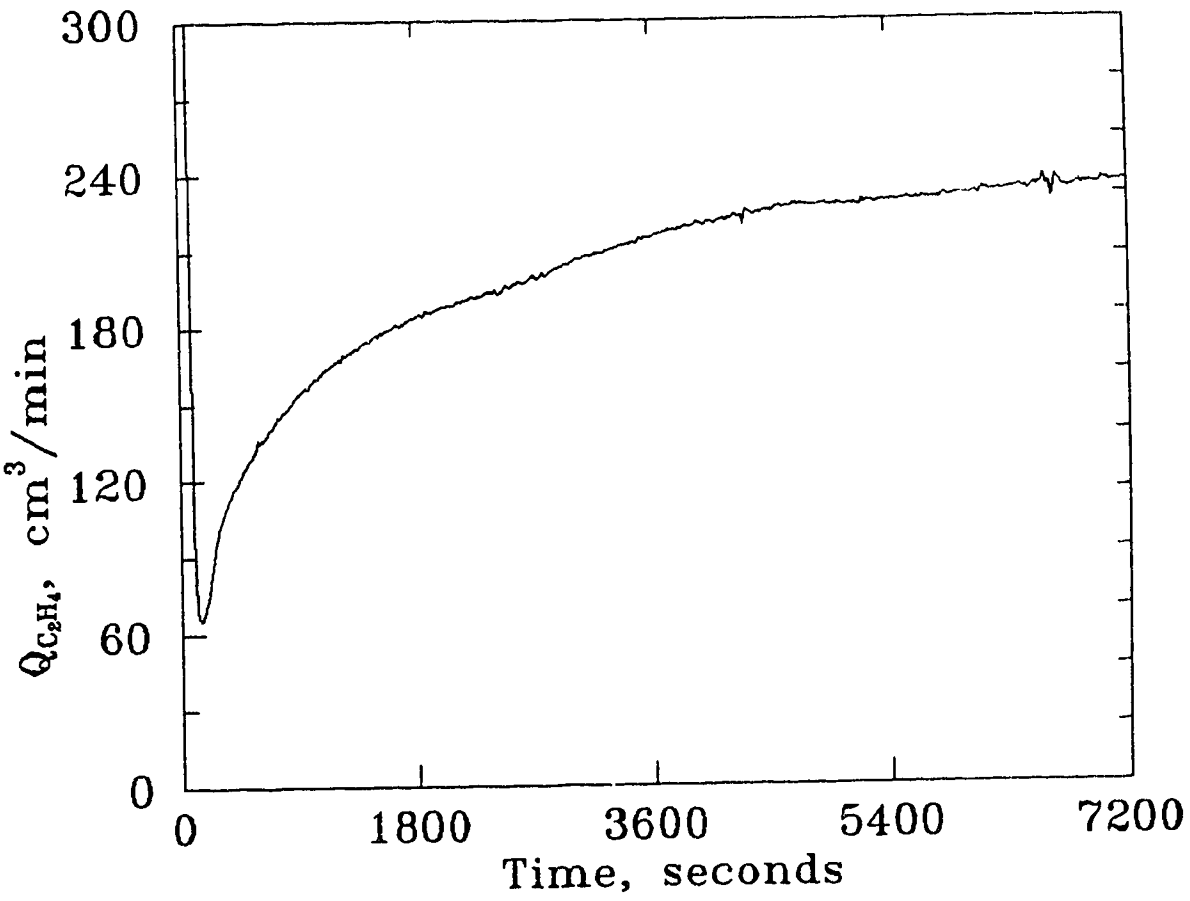


Figure 3.1 Polymerization rate behaviour after initial exposure to ethylene (0.1 g Stauffer AA Type 2.1 catalyst, 0.5 cm^3 DEAC co-catalyst, $P_{ethylene}$ = 0.55 MPa)

becomes approximately constant after 2 h. Long term experiments have shown that a very slow increase in activity can occur for up to 12 h after initial exposure to ethylene. This increase was very minimal for the duration of the experiments; hence, the activity profile of the δ-$TiCl_3.\frac{1}{3}AlCl_3$ is essentially constant. Finally, the δ-$TiCl_3.\frac{1}{3}AlCl_3$ catalyst is very "well-understood", i.e., the reaction order, kinetic parameters and rate behaviour are known to a very high degree of accuracy. Previous study on gas-phase ethylene polymerization carried out by Lynch and Wanke (1991), had described the operating conditions which resulted in precise and reproducible kinetic measurements for a δ-$TiCl_3.\frac{1}{3}AlCl_3$ catalyst (Stauffer AA Type 2.1) with diethylaluminium chloride (DEAC) as the co-catalyst. They found that the system displayed first order kinetic behaviour over the temperature range of 20 to 90°C, with an activation energy of 32.6 kJ/mol.

The overall rate of disappearance of ethylene was described by

$$-r_p = m_{cat}\ k\ [C_2H_4] \tag{3.1}$$

where

$$k = 1.42 e^{(-3920/T)} \tag{3.2}$$

The final choice, therefore was to use δ-$TiCl_3.\frac{1}{3}AlCl_3$ (Stauffer AA Type 2.1) with diethylaluminium chloride (DEAC) as co-catalyst for studying the thermal behaviour of the reactor during ethylene polymerization.

3.2 Reactor Design

The choice of an appropriate reactor design involved the following requirements to be fulfilled. The main operational problems for gas-phase polymerization reactors are proper suspension of the solid polymer and catalyst particles (stirring) and temperature control. Uniform mixing of the reactor contents was essential to eliminate temperature gradients within the reactor. Also, proper agitation of the heated polymer particles with cooler surrounding gas (ethylene and inert (He or N_2)) was required to facilitate heat transfer to the reactor heat exchange surface. Unsupported Ziegler-Natta catalyst δ-$TiCl_3.\frac{1}{3}AlCl_3$ (Stauffer AA Type 2.1), which was used for the polymerization experiments, is very sensitive to impurities, especially oxygen and moisture. In presence of impurities from atmosphere, the catalyst deactivates rapidly. Therefore, it was important for the reactor to be designed leak tight so that the catalyst could be placed inside the reactor under an inert atmosphere. Also, the co-catalyst diethylaluminium chloride (DEAC) is highly pyrophoric. Proper handling facility for catalyst and co-catalyst was necessary along with arrangements for safe transfer from storage to the reactor. Reproducible injection of the catalyst and co-catalyst was also a major requirement because it has been observed that the manner of addition of the catalyst components plays an important role in the resulting thermal behaviour of the gas-phase reactor at a later stage. In addition, the design had to be such that the operating parameters such as pressure of ethylene gas, operating temperature and flow rate of gases could be measured with a high degree of accuracy and also be easily manipulated. Therefore, good instrumentation and computer control of the reactor was imperative. The main objective of the experiments was to observe the thermal behaviour of the reactor and to obtain the effect of the various operating parameters on the temperature within the reactor. Hence, it was necessary to measure the temperature at various radial and axial locations within the reactor during the course of the polymerization run. A good data acquisition system was a must for the study.

The earliest published work on developing a laboratory reactor capable of gas-phase operation at pressure and temperature conditions used commercially was carried out by Choi and Ray (1985c). They designed a 1000 cm^3 autoclave reactor for propylene polymerization. The reactor was provided with a specially designed U-shaped stirrer for uniform mixing of the solids. After heating to the required temperature, a mixture of catalyst and co-catalyst in n-heptane could be injected into the reactor. The polymerization rate was then determined by the propylene feed rate required to maintain constant pressure in the reactor. A small volume of glass beads was placed in the reactor to act as a support. There are two potential problems with this type of operation: firstly, premixing of catalyst and co-catalyst prior to injection into the reactor can result in catalyst deactivation due to over-reduction of the catalyst. Also, during the reactor operation, before monomer feed was started, the reactor was evacuated for approximately one hour to remove n-heptane to prevent the possibility of having a small slurry mixture in the reactor. This evacuation removes some of the co-catalyst; hence, it is not possible to accurately determine the ratio of co-catalyst to catalyst (Al:Ti molar ratio) under reaction condition.

In the other study concerned with gas-phase ethylene polymerization at industrial conditions (Spitz et al., 1988), a 675 cm^3 stainless steel reactor was used. Catalyst, mixed with potassium chloride or polyethylene to ensure initial stirring, was introduced separately from the co-catalyst (isoprenylaluminium in hexane solution). To avoid the possibility of grinding by stirring, the entire reactor was made to oscillate vertically (6 cm stroke, 7 Hz). The effectiveness of this method of stirring is not well understood. Stirring is a very important factor in such reactors given the tendency of growing polymer particles to agglomerate. Also large static charges are developed when the particles are rubbed together. The maintenance of the well-mixed state would be particularly difficult as the reactor fills with polyethylene.

The laboratory reactor designed in the Department of Chemical Engineering, University of Alberta for studying gas-phase polymerization processes overcame the limitations of the earlier designs. The reactor was well instrumented making it appropriate for carrying out studies on the effect of various operating parameters. Special attention was paid to impurity levels in the reactor prior to catalyst injection, state of mixing in the reactor and temperature distribution within the reactor. The reactor system consisted of the following main sections: the stirred reactor, feed streams along with the purifiers and the oil bath for temperature control of the reactor. The schematic diagram of the reactor system along with the allied instrumentation is shown in Figure 3.2.

As seen in Figure 3.2, the reactor vessel was cylindrical in shape with a capacity of approximately 1000 cm^3. It was constructed from Type 316 stainless steel with wall thickness of 1.5 cm, an inside diameter of 11.4 cm and a depth of 10.2 cm. The top flange of the reactor was rigidly fixed to a support stand and the removable bottom section of the reactor was bolted to the flange with a leak-proof seal

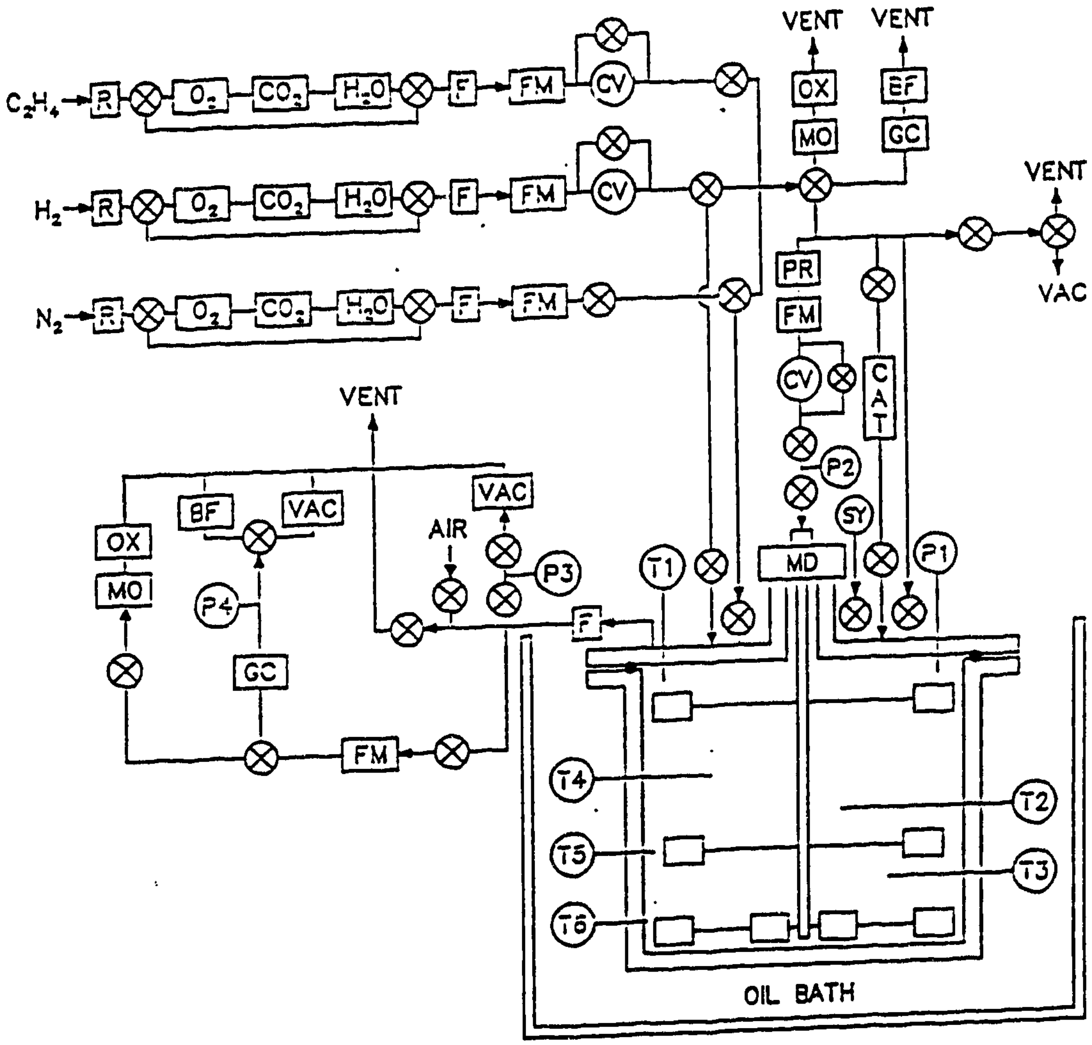


Figure 3.2 Schematic diagram of the reactor system. (BF - bubble flow meter; CAT - injection port for solid catalyst; CV - control valve for flow controller; F - filter; FM - flow transducer; GC - gas chromatograph; MD - magnetically coupled stirrer; MO -moisture analyzer; $O_2/CO_2/H_2O$ - gas purifiers; P1-4 - pressure gauges; PR - pressure regulator; R - gas cylinder regulator; T1-6 - thermocouples; SY - syringe injection port for liquid co-catalyst; VAC - vacuum pump).

provided by a Viton o-ring. All valves, fittings and tubing connected to the reactor were made of either 316 or 304 stainless steel.

A low pressure load cell pressure transducer was directly attached to the reactor to monitor the pressure. Reactor pressure was held constant by means of a pressure regulator (Tescom Model 26, 0 to 3.4 MPa range). A higher precision pressure transducer (Omega Model PX621) was connected between the pressure regulator and the feed entry port. A mechanical pump and diffusion pump were used to remove impurities during reactor pretreatment. The reactor contents were stirred by using an Autoclave Engineers Ltd. model 1.5-1-5 K magnetic stirrer driven by a variable speed motor. Variable-angle paddle-type stirring vanes were attached to the stirrer shaft. They were fitted at various heights from the bottom of the shaft as shown in Figure 3.2. The vanes at the bottom were normally angled upwards and the vanes at the top angled downwards, in order to promote axial mixing.

For temperature control, the reactor was immersed in a 26 litre bath filled with a medium viscosity silicon oil (Dow Corning 200 fluid). The temperature of the oil was maintained to within ±0.1°C by a Lauda, Model MS constant temperature immersion circulator, which when used in combination with a cooling coil, enabled the bath to be operated over the range of 5 to 120°C. The oil bath could be physically raised or lowered and during operation the surface of the oil was about 2 cm above the top surface of the flange. To promote agitation in the oil bath, a stirrer driven by a constant speed DC motor was immersed in the oil. Uniformity of temperature across the bath was monitored by noting the temperature on the constant immersion circulator and the reading of a type J thermocouple located at the far end of the oil bath. During operation, the temperature across the bath was observed to be uniform. The temperature in the reactor vessel was monitored by means of six, sheathed, type J thermocouples situated at various radii and axial locations as shown in Figure 3.2 (TC's 2 and 3 are in a vertical row; there is a 2.5 cm vertical separation between pairs of thermocouples, with TC 6 and TC [illegible] located 1.3 cm and 3.8 cm, respectively, above the bottom of the vessel).

Ethylene and nitrogen feed gases were obtained from Matheson or Linde and had a minimum purity of 99.998% with less than a combined total of 10 ppm of oxygen containing compounds (H_2O, O_2, CO_2 and CO). Each of these gases was further purified by passing through individual trains consisting of Altech high pressure gas purifiers located on each feed line for the removal of oxygen, carbon dioxide and water. Matheson mass flow meters were used to monitor the flow rates of these streams. Any of the feed streams could be routed to the oxygen and moisture analyzers to verify operation of the purifiers. Both the feed streams could be individually regulated and directly routed to the reactor through individual ports on the top flange. However, during normal operation of the reactor, the feed streams were passed under pressure control to a port on the top of the magnetic stirrer before entering the reactor. The use of this port helped to prevent fouling of the stirrer during reactor operation.

The mass flow controllers, mass flow meters, thermocouples, and pressure transducers were interfaced with OPTO 22 input/output subsystem to a PC for data acquisition and control. Figure 3.3 shows the block diagram of the experimental set-up. Values of all monitored quantities were normally recorded every 10 s.

3.3 Catalyst and Co-catalyst Handling

Most of the titanium metal salts used as Ziegler-Natta catalysts are prepared by reduction of titanium tetrachloride ($TiCl_4$) with metal alkyls such as triethylaluminium alkyl (TEA) or diethylaluminium chloride (DEAC) and related compounds. Hence, these compounds usually are contaminated by aluminium trichloride ($AlCl_3$) which plays a very important role in the activity of the catalyst. In the presence of trace quantities of oxygen impurities, oxidation can result in substantial reduction in the activity of the catalyst. The δ-$TiCl_3 \cdot \frac{1}{3}AlCl_3$ (Stauffer AA Type 2.1) which was used for the experimental investigation of ethylene homopolymerization, is also extremely sensitive to oxygen and moisture impurities. In addition, the co-catalyst diethylaluminium chloride is extremely pyrophoric. Therefore the handling and storage of the catalyst and co-catalyst was performed in a glove box (Model HE-493 from Vacuum Atmospheres Ltd.) equipped with a

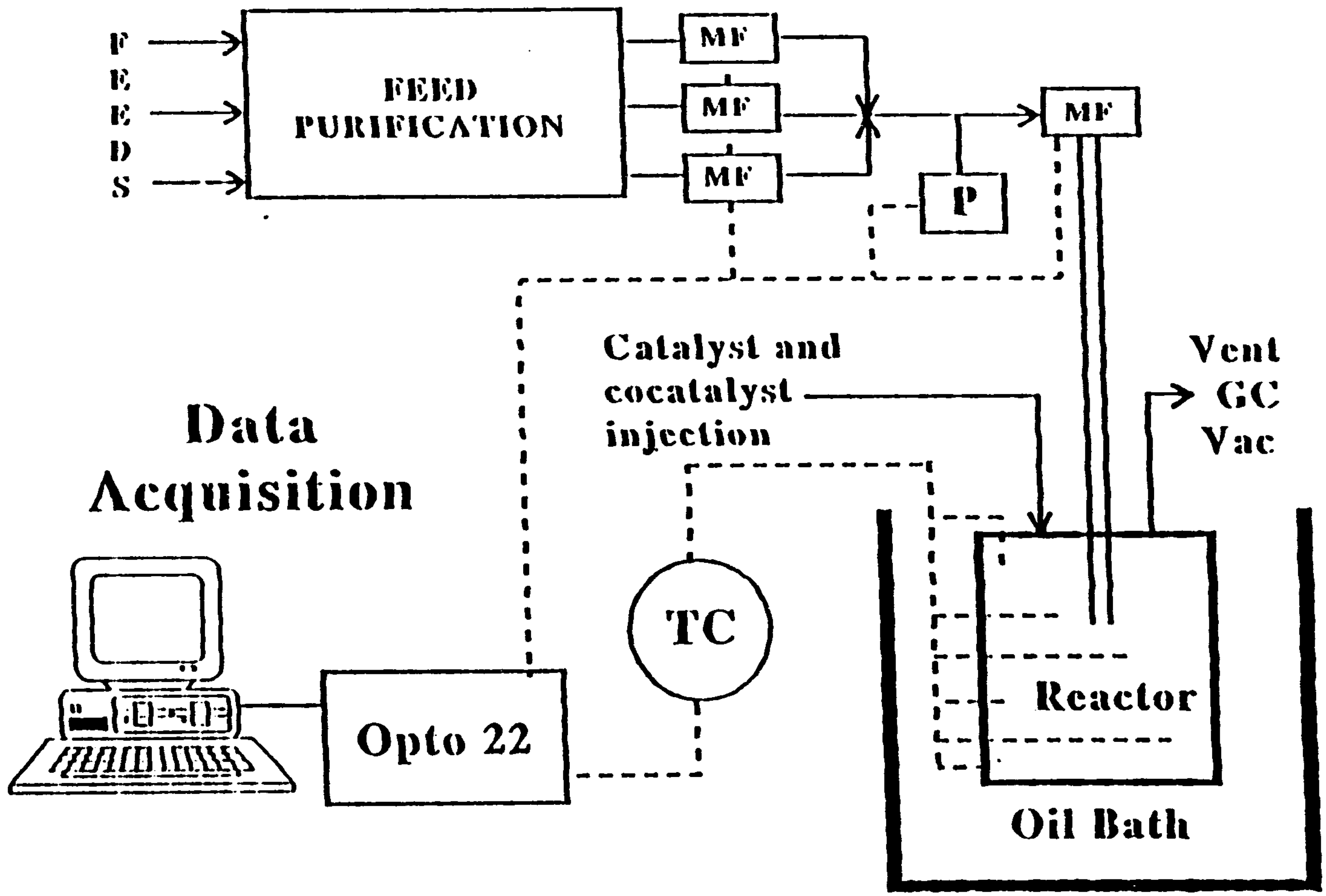


Figure 3.3 Block diagram of the experimental set-up

purifier for removing oxygen and water impurities from the nitrogen atmosphere. The HE-493 (shown in Figure 3.4) provided an oxygen-free and moisture-free environment in the sealed glove box. This was done by replacing all the air from the box with dry, inert nitrogen gas. Nitrogen gas was then continuously cycled through the chemical purifier which contained two chemical purification agents. One was a layer of molecular sieve in the purifier canister which removed moisture from the gas flowing through it by a process of molecular adsorption. The other agent was an oxygen reducing agent (Q1), a material consisting of finely divided copper on an alumina matrix, developed by the Dow Chemicals company. The Q1 combined chemically with oxygen thereby removing it from the nitrogen gas.

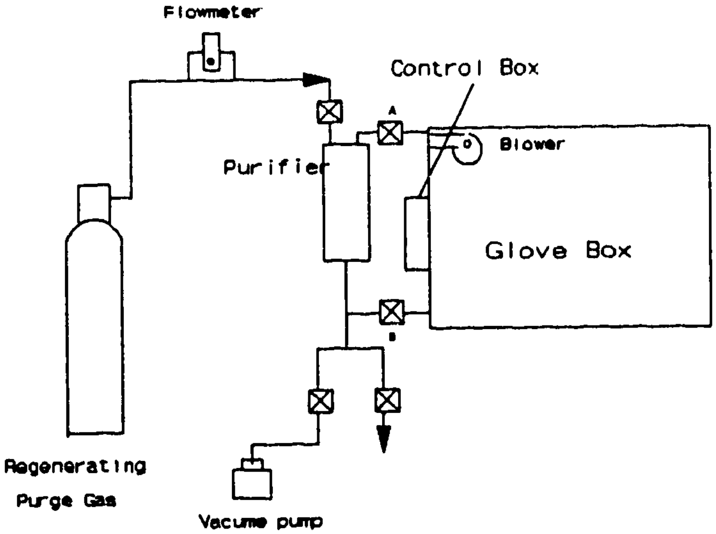


Figure 3.4 Schematic diagram of catalyst and co-catalyst handling system

Online moisture (MCM Dewmatic Model 600 Hygrometer) and oxygen analyzers (Custom Sensors & technology Model 8205) were utilised for continuously monitoring the impurity levels in the glove box. Oxygen levels of less than 1 ppm and moisture levels of less than 4 ppm were normally maintained in the glove box.

As an added precaution against any accidental contamination, all the catalyst samples were stored in sealed hypovials or double containers. The liquid co-catalyst used in all experiments, diethylaluminium chloride (DEAC), was obtained in pure form from Aldrich. DEAC is highly flammable and therefore was also stored in the glove box. DEAC was transferred to the reactor by means of a gas tight syringe which was filled in the glove box. The end of this syringe was sealed prior to removal from the glove box. The catalyst was transferred from the glove box to the reactor by means of a catalyst holder. The catalyst holder was constructed from a stainless steel quick-connect with plug valves attached at each end. The quick-connect and plug valves have essentially no internal constrictions permitting a free flow of sample through the holder. Catalyst samples (typically 0.05 to 0.25 g ± 0.001 g) were placed into the male half of the quick-connect with approximately 0.15 g of Teflon powder (450 μm particle size) on either side of the catalyst sample. When the female half of the quick-connect was attached with the plug valves closed, the sample holder could be removed from the glove box and connected to the top flange of the reactor without contaminating the catalyst.

To avoid exposure to atmospheric impurities during transfer of material through the glove box, every time the outer chamber was exposed to atmosphere, the following procedure was used before opening the inside door of the glove box:

1. Both chamber doors were closed.
2. Refill valves were closed.
3. Chamber was evacuated to at least 50 μm Hg and then refilled with inert nitrogen gas.

Regeneration of the purifier was done when the purifier agents were saturated by moisture and oxygen impurities, and were no longer maintaining the required purity in the glove box. The regeneration process involved removal of moisture from the molecular sieve and oxygen from the oxygen reducing agent (Q1). Once the regeneration was completed, the copper was returned to its reduced form. The process was accomplished by isolating the purifier from the glove box, by closing the inlet and outlet circulation valves, A and B, shown in Figure 3.4. The purifier was heated to approximately 200°C, desorbing most of the adsorbed moisture. After a period of three hours, the purifier was purged and vented with 8% H_2 in nitrogen mixture to reduce the oxidized copper. This regenerated the oxygen reducing agent. Then the purifier was evacuated overnight to complete the removal of the moisture. The entire regeneration process takes about twelve hours and the whole process is done automatically. Regeneration of the purifier was done on three month intervals.

3.4 Reactor Operating Procedure

The reactor operating procedure was developed after much experimentation by Lynch and Wanke (1991). The following steps, largely based on their observations, were performed for each gas-phase ethylene polymerization run.

1. The reactor was cleaned thoroughly to remove any polyethylene product formed in the previous run. In almost every polymerization run, the temperature within the reactor reached the melting point of polyethylene (≈133°C) resulting in substantial agglomeration of the product. This polymer product usually adhered to the stirrer blades and the temperature probes inside the reactor vessel. It was necessary to clean the thermocouples to ensure that the correct temperature was measured during the subsequent experiment. In some runs, a thin polyethylene film covered the walls of the vessel. This film could act as a significant resistance for heat transfer and had to be removed completely before the reactor could be utilized for the next experiment.
2. A known amount of polyethylene powder (18 to 80 g) was added to the reactor. The polymer powder was placed to act as a support (seed) bed for the catalyst (not yet injected), because it was observed that, without the seed bed, a hard layer of polyethylene would usually build up at the bottom of the vessel immediately on addition of ethylene gas. Also, since the amount of catalyst was very small (0.1 to 0.2 g), catalyst loss by entrapment in crevices in the reactor (stirrer blades, various entry and exit ports, and 'dead' spots in the reactor corners and under the top flange) was found to be minimized when it was distributed on the seed bed. Polyethylene (600 μm diameter) was chosen as the support bed because in industrial reactors the product

polyethylene acts as a support bed for the injected catalyst.

3. The reactor was then sealed and leak-tested (up to 2 MPa) using inert gas (nitrogen or helium). It is imperative for the reactor to be leak tested; even a small leak would immediately deactivate the catalyst upon injection inside the reactor during the run.
4. The reactor was heated to about 90°C by placing it inside the oil bath. Simultaneously, the reactor was evacuated for a minimum of 12 h to ensure removal of oxygen and moisture from the inside walls of the reactor.
5. At the end of the evacuation period, the reactor was filled with inert gas (N_2 or He) to a pressure of 0.125 MPa. The reactor pressure was kept higher than atmospheric pressure and the catalyst holder was removed from the glove box and connected to the flange of the reactor. The higher pressure inside the reactor prevented air from entering through the opening before the catalyst holder could be placed in its position.
6. The reactor was then again leak tested (1.5 MPa) to ensure that the connection at the catalyst holder (denoted by "CAT" in Figure 3.2) was sealed completely. The sealed leak-free reactor was evacuated twice to less than 0.005 MPa pressure to remove any traces of impurities which could have entered while attaching the catalyst holder.
7. The reactor was then filled with nitrogen or helium to approximately 0.125 MPa pressure and co-catalyst DEAC (0.5 cm^3) was injected by a syringe through the syringe port shown in the Figure 3.2. Even after a prolonged period of evacuation at 90°C, there is still a significant amount of water adsorbed on the walls of the reactor. It is known that one molecule of water can produce two molecules of ethane when contacted with aluminium alkyls (Kissin, 1985). Previous studies (Lynch and Wanke, 1991) indicated that at least 30 minutes should be allowed following DEAC injection to ensure a moisture-free environment.
8. After about 30 minutes, the reactor was again evacuated to remove the traces of ethane formed by reaction with DEAC. The temperature of the reactor

was then adjusted to the operating temperature of the polymerization experiment (typically 70°C) and the reactor was filled with nitrogen or helium gas (0.125 MPa). This mode of operation ensured that a known amount of inert was present while conducting the experiment.

9. Since some DEAC was utilized in removing moisture in the reactor, a fixed amount of co-catalyst DEAC (usually 0.5 cm^3) was again injected into the nitrogen or helium filled (0.125 MPa) reactor. This DEAC then acted as the co-catalyst for ethylene polymerization. Stirring (600 rpm) of the reactor contents was started immediately upon addition of the co-catalyst to distribute the liquid uniformly on the surface of the seed bed.
10. Upon addition of the co-catalyst, some time (5 to 10 minutes) was given for the liquid to wet the surface of the powder bed. Later, the catalyst sample in the holder was pushed into the reactor by applying nitrogen or helium pressure on the upstream side of the catalyst holder which was much higher than the pressure in the reactor. The catalyst sample was introduced inside the reactor by quickly opening and closing the valves on either side of the catalyst holder. The inert atmosphere inside the reactor helped in preventing the formation of large polyethylene agglomerates which could occur if the catalyst was introduced into an ethylene containing environment. Catalyst injection into an evacuated reactor could result in fouling problems with the stirrer and with severe plugging in the flange ports. Therefore, catalyst was always injected into a nitrogen or helium reactor environment (approximately 0.125 MPa) with the support bed present and stirred at approximately 600 rpm.
11. Following catalyst injection, the total pressure in the reactor would typically be 0.25 to 0.3 MPa. During normal operation, ethylene was added directly to the nitrogen or helium in the reactor, with the ethylene partial pressure determined by difference. This mode of operation ensured that no DEAC or catalyst was lost from the reactor. Following catalyst injection, a minimum of 5 to 10 minutes was allowed to pass (with the reactor being stirred) before

starting the flow of ethylene under pressure control (0.85 to 1.0 MPa) to the reactor, in order to ensure adequate contacting of DEAC with the catalyst.

12. The reactor temperature was kept constant at the operating temperature by using the temperature controller on the oil bath. The ethylene flow rate indicating the polymerization rate, reaches a pseudo-steady state in approximately 2 h. A known amount of polymer was produced under this operating condition which is known as the "prepolymerization period". The polymer produced in the prepolymerization period is termed as "prepolymer".
13. Once the desired amount of prepolymer was produced, the ethylene pressure was raised (3.0 MPa) and the thermal behaviour of the reactor was studied. The temperatures measured by the six thermocouples placed at various radial and axial locations were used to study the temperature control problems associated with the gas-phase reactor for ethylene polymerization.
14. Once the melting point of the polymer was reached, the ethylene flow was stopped and the reactor temperature was allowed to decrease to the original operating temperature (70°C). Ethylene flow was again started and adjusted to the "prepolymerization period" pressure. The ethylene flow rate indicates the final polymerization rate achieved by the catalyst. The catalyst may now be encapsulated by the previously molten polymer. The amount of deactivation of the catalyst could then be obtained.

4 EXPERIMENTAL RESULTS

4.1 Preliminary Experiments

Reaction rate measurements were made by admitting ethylene to the reactor under pressure control. Preliminary study of the thermal behaviour was carried out by admitting ethylene to the reactor which had been charged with DEAC (0.5 cm^3) and Stauffer catalyst (0.184 g). About 18 g of polyethylene (obtained from Novacor Chemicals Ltd.) of particle size range between 355 to 841 μm was used as the seed bed for the run. The total pressure was kept constant at 0.271 MPa and the initial partial pressure of inert nitrogen inside the reactor was 0.3 MPa. The initial rate behaviour is shown in Figure 4.1. It can be seen in this figure that the rate of polymerization increased with time-on-stream until a steady state was reached. The initial rise in the ethylene flow rate (reported in cm^3(STP)/min), followed by a rapid drop (for time less than three minutes), seen in Figure 4.1, is due to the filling of the reactor with ethylene gas and not due to reaction of ethylene. The rate became approximately constant after 40 minutes, and the temperature inside the reactor was essentially constant at 70°C. Figure 4.2 shows the temperature profiles obtained for each of the five inner thermocouples (T_2-T_6), for the above experiment. It can be seen in this figure that the temperature inside the reactor was uniform and constant during this initial period.

Following the stabilizing period, the effect of increasing ethylene concentration on the reactor behaviour (temperature control) was studied. The period from 1 to 3.15 hours of Figure 4.3 shows stepwise changes that were made to the reactor pressure (ethylene concentration) and how this affected the flow rate of ethylene to the reactor.

In Figure 4.3, it is seen that when the total pressure was raised to the final value of 1.2 MPa that no stable state was reached but instead the temperature and the flow rate (polymerization rate) increased at an accelerating rate until the maximum values shown in Figure 4.3 were reached.

The time dependence of the temperature, at two locations, 3 and 5, is shown

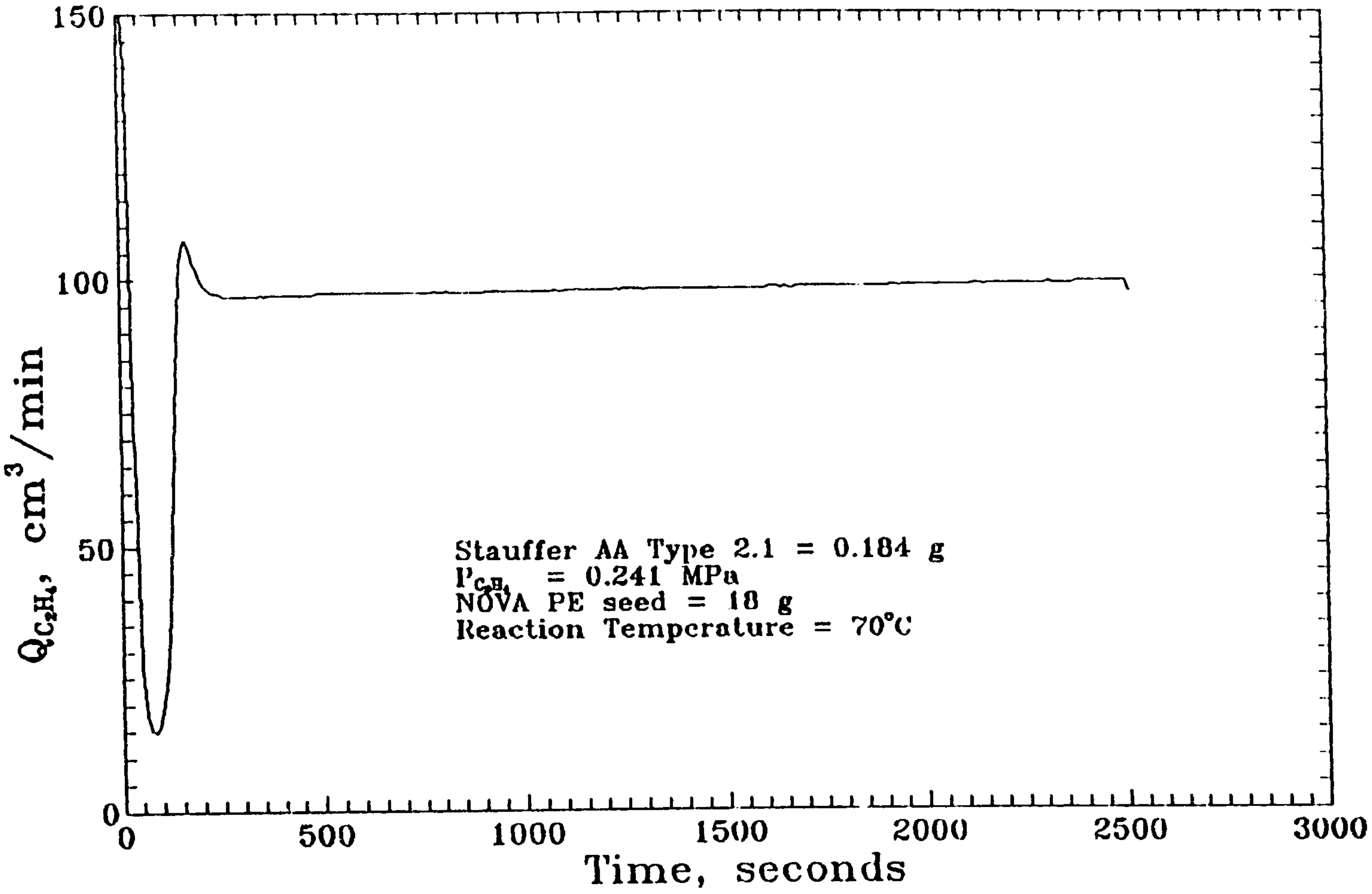


Figure 4.1 Rate behaviour after initial exposure to ethylene

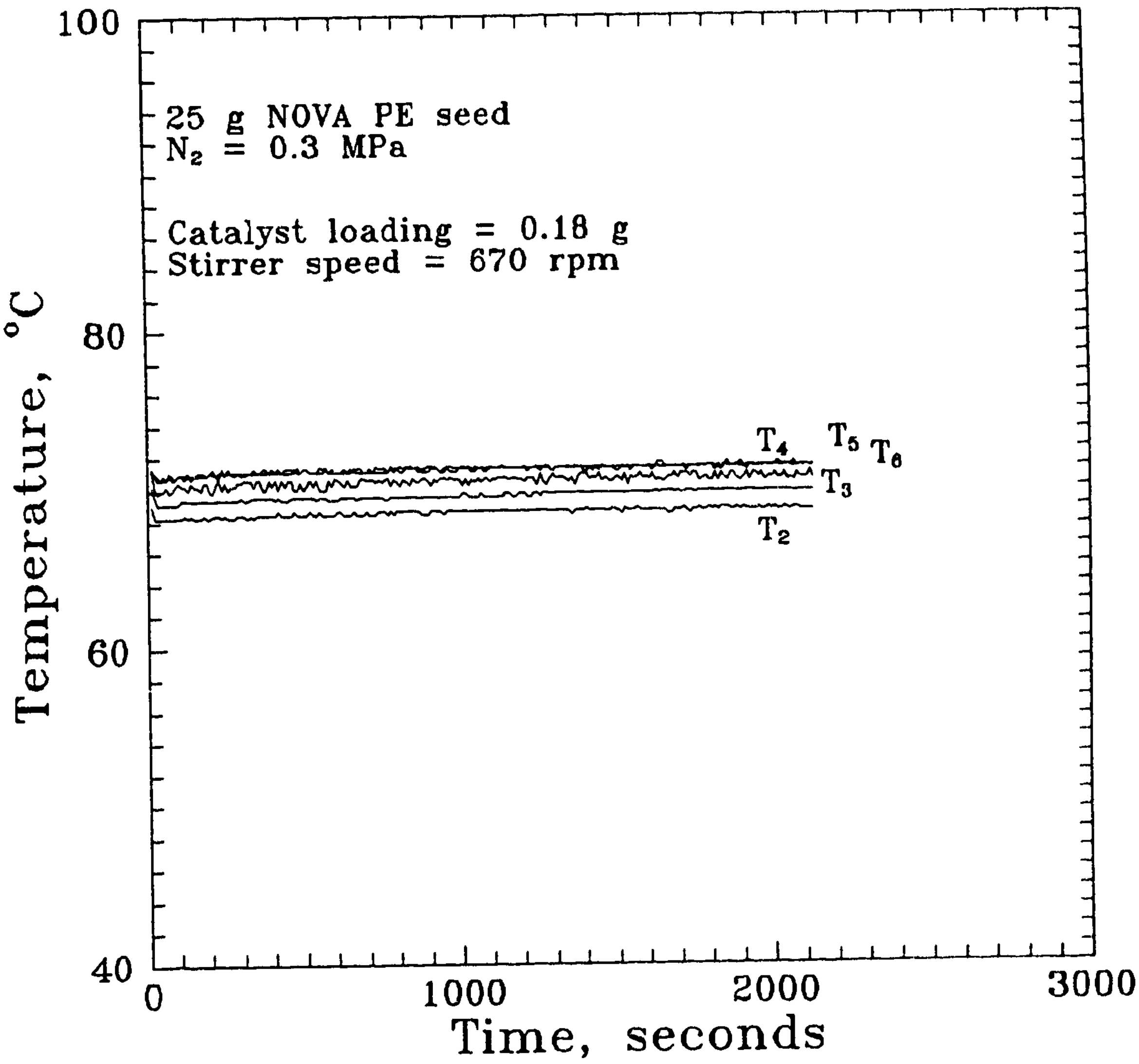


Figure 4.2 Radial temperature distribution after initial exposure to ethylene

in the lower panel of Figure 4.3. The time dependence of the temperature at five locations inside the reactor is shown in Figure 4.4. It is seen that even during the rapid temperature increase there was only a small difference among the temperatures at the three innermost thermocouple locations (3,4 and 5), indicating that the reactor contents were well-mixed. Also, the observation that the temperatures at locations 2 to 6 all reached their maximum values within 10-20 s of each other indicated that the stirring speed of 470 rpm employed for this experiment, was sufficient to maintain a uniform well-mixed state of the contents inside the reactor. The temperature at location 6 (nearest the wall) reached its maximum value approximately 200 s after the other four temperatures had peaked. Also, the temperatures indicated at locations 2 and 6 were lower than the average temperatures noted by temperature probes at locations 3, 4 and 5. Especially during the latter stages, there was approximately 50°C difference between locations 2 and 6. The observations shown in Figures 4.3 and 4.4 demonstrate that it is imperative to measure temperature at different internal locations inside the reactor. Thus, temperature control based solely on thermocouple 6 or 2 would be ineffective because its temperature increased by only 10°C while the temperatures in the interior of the reactor actually increased uncontrollably. This phenomena of uncontrollable increase in temperature of the reactor is termed "thermal runaway".

The heat transfer limitations encountered in this reactor due to the relatively low rates of heat transfer between the reactor contents and the walls of the reactor is responsible for the occurrence of the "thermal runaway" phenomena at high polymerization rates. The heat transfer limitation sets an upper bound on the feed rate of ethylene to the reactor at which the reactor operation can be controlled; if this maximum feed rate is exceeded, then thermal runaway occurs. After reaching the maximum temperature of about 200°C, at a total polymerization rate of approximately 0.1 mol of ethylene per minute, there was a spontaneous decrease in polymerization rate and temperature as shown in Figure 4.3. This drop in rate occurred without experimental intervention to control the ethylene feed rate and temperatures. The rapid decrease could be attributed to substantial deactivation of

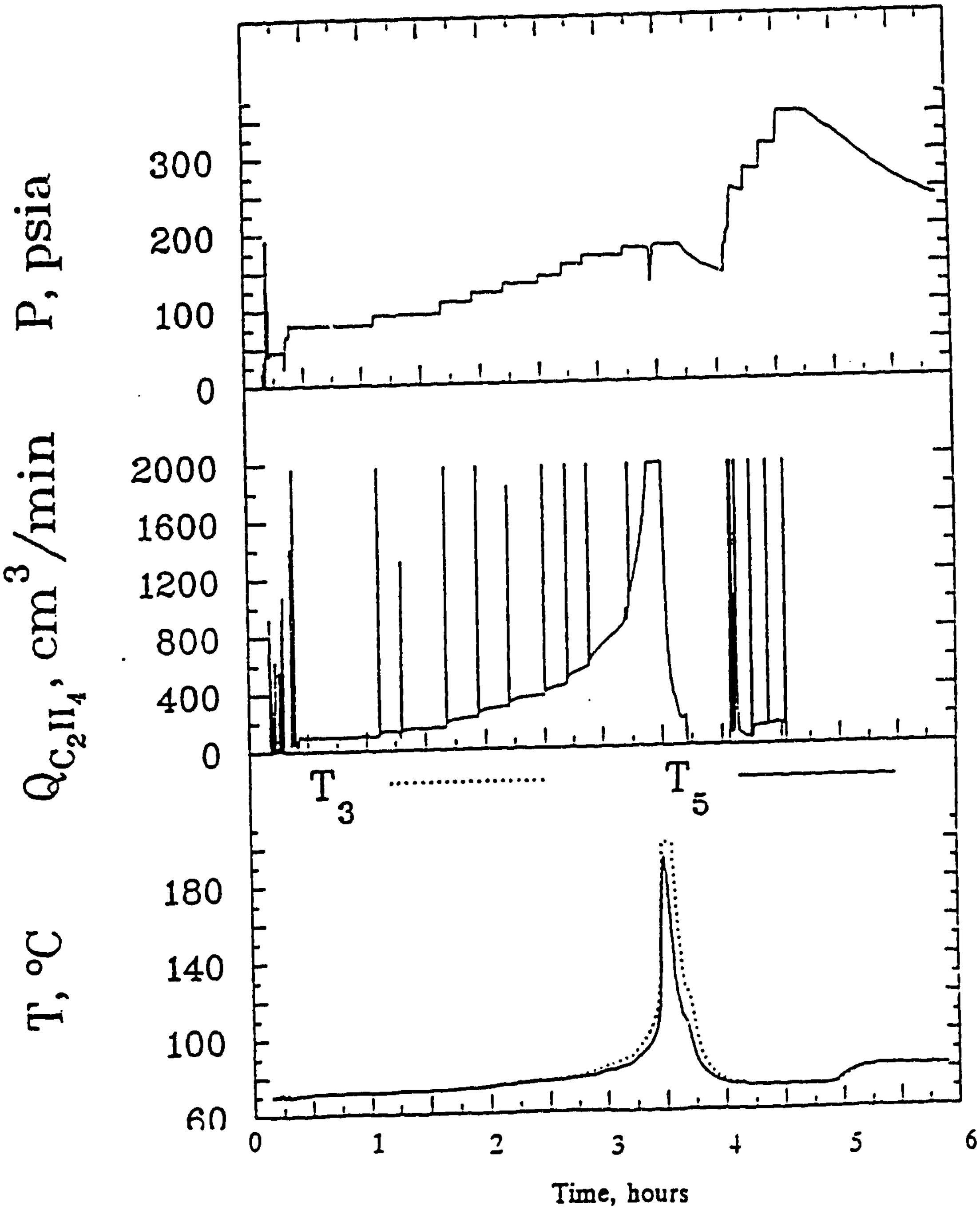


Figure 4.3 Time dependence of total pressure, ethylene feed rate and temperature for Run GAS9109

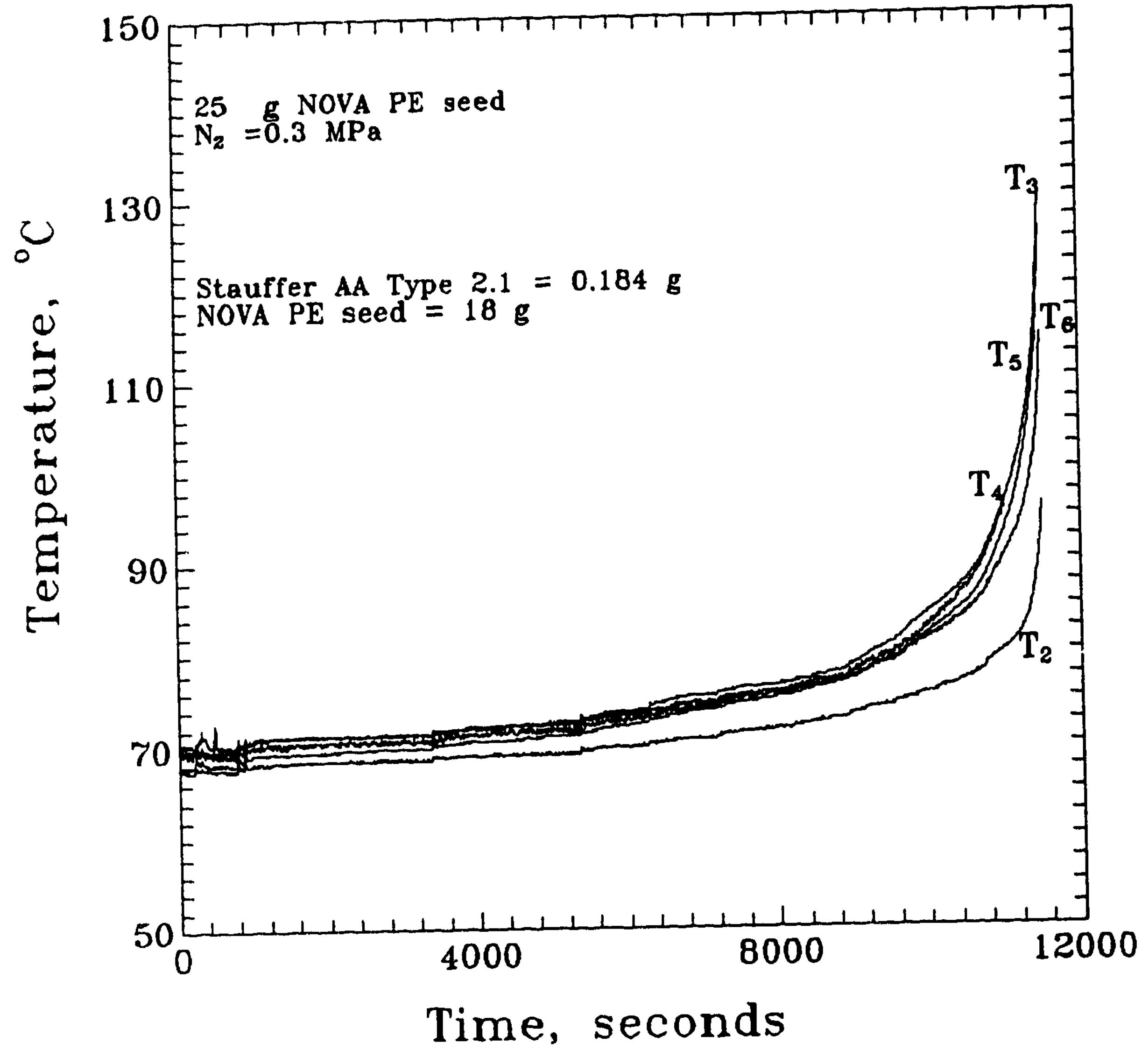


Figure 4.4 Radial temperature profile during Run GAS9109

the catalyst that had occurred near the end of the experiment when the reactor was clearly operating in a state where it was very sensitive to the operating parameters (extreme parametric sensitivity). The maximum temperature of 189°C reached by the thermocouple at location 3 is substantially higher than the known melting point of 133°C for high density polyethylene homopolymer. Thus, it is likely that the substantial deactivation of the catalyst was probably due to melting of the polymer with subsequent encapsulation of the catalyst.

After about 3.75 hours of the experiment shown in Figure 4.3, the ethylene flow to the reactor was stopped and the reactor contents were allowed to cool to 70°C. Because the reactor contents had exceeded the melting point of the polymer, agglomeration of the product had occurred. This was evidenced when mechanical agitation of the contents produced the loud noise of stirrer blades scraping against the agglomerated product. To check the final activity of the catalyst, the reactor contents were stabilized at 70°C and ethylene flow again started. It was found that the catalyst activity had decreased by about 85% which could account for such a spontaneous decrease of over 50°C followed by a concomitant decrease of about 90% in the rate of ethylene consumption. After opening the reactor, it was found that the product was one large mass of agglomerated polymer.

The observations of the preliminary experiment can be summarized as follows:

(i) Above some value of the ethylene pressure, the temperature in the reactor increased uncontrollably.

(ii) Temperatures at the interiors of the reactor exceeded the melting point of the polymer.

(iii) Spontaneous decrease in the polymerization rate and the reactor temperature occurred after the uncontrollable temperature excursion.

(iv) Polymer particle agglomeration was observed.

The preliminary results clearly indicated the need to study the thermal behaviour of gas-phase reactors. Ethylene polymerization is a moderately exothermic reaction. The heat of reaction is about 108.7 kJ/mol C_2H_4 (Sawada, 1976), but at the high rates of polymerization achieved by the Stauffer catalyst accompanied by the heat transfer limitations of the gas-phase reactor, there is a possibility of "thermal runaway" phenomena occurring in the reactor. The resultant deactivation of the catalyst and the agglomeration of the product severely compromise the efficacy of the gas-phase process. Therefore, there was a compelling necessity to examine the effect of various operating parameters on the onset of runaway conditions. The objective of such a study is to quantify the effects of various operating variables on the thermal runaway behaviour.

4.2 Operating Conditions for Examining Thermal Runaway

The first step in studying the thermal runaway phenomena exhibited by the semi-batch stirred-bed reactor for gas-phase polymerization of ethylene involved identifying the operating parameters which were important for the observed thermal runaway behaviour of the reactor. The following operating variables were identified as probable factors which could affect the thermal behaviour of the gas-phase reactors:

1. Ethylene pressure at which the reactor was operating.
2. Mass of catalyst.
3. Reactor operating temperature.
4. Mass of the seed bed.
5. Particle size of the seed bed material.
6. Length of prepolymerization, i.e., amount of prepolymer formed in reactor.
7. Presence of inert gases in the reactor, e.g., nitrogen or helium.
8. Stirring speed.

Before examining the effect of variation of each of the parameters on the thermal runaway phenomena, it was necessary to establish base conditions, i.e., reproducible initial conditions from which variation of the various parameters could be studied.

In the early gas-phase experiments (GAS9108-GAS9111 and GAS9201) described in Appendix A, a catalyst charge of about 0.2 g was used. It was found that the maximum value of temperature reached inside the reactor at locations 2,3,4 or

5 approached 200°C. The temperature profile observed by the thermocouples at the various locations (2 to 5) for all the experiments is shown in Appendix B. The large temperature rise always produced an agglomerated product with the additional problem of the build-up of a thick polymer film on the reactor surface. The fused product resulted in additional heat transfer problems because now the thermal energy transport required conduction through the agglomerate, further reducing the heat transfer rate from the solid product to the reactor wall. Also, once the chunks were formed inside the reactor, it was difficult to maintain a uniform well-mixed state of the reactor contents. Proper suspension of the growing polymer particles is very critical for maintaining thermal uniformity. Therefore, it was important for the final product to remain in the powder form after the thermal runaway occurred. In order to limit the temperature excursion to levels at which product remained in the powder form, the catalyst charge was reduced to 0.1 g. The co-catalyst and seed bed amounts were reduced by the same proportion.

Experiments (GAS9202-GAS9210), summarized in Appendix A, involved establishing the total pressure at which thermal runaway behaviour occurred so that further study could be carried out keeping the same values of operating reactor pressure. The effect of ethylene partial pressure on thermal behaviour is shown in Figure 4.5. The temperatures plotted in this figure are representative of the reactor temperature and are the average of values measured by thermocouples at locations 2, 3, 4 and 5. In some cases, due to non-uniform distribution of the catalyst on the seed particles, temperature excursions occurred on small sections inside the reactor with values reaching the melting point of the polyethylene, even though the average temperature across the rest of the reactor was close to 70°C. Near the end of the experiment when the reactor was operating in a state where it was very sensitive to the operating parameters, the temperature values shown at the various locations 2, 3, 4 and 5 differed by approximately 10 to 20°C. In such a situation, the mean values of the three locations were used to represent the overall temperature inside the reactor. The solid line in Figure 4.5 indicates the temperature inside the reactor when the ethylene partial pressure was increased from 0.55 to 2.14 MPa (Run No.

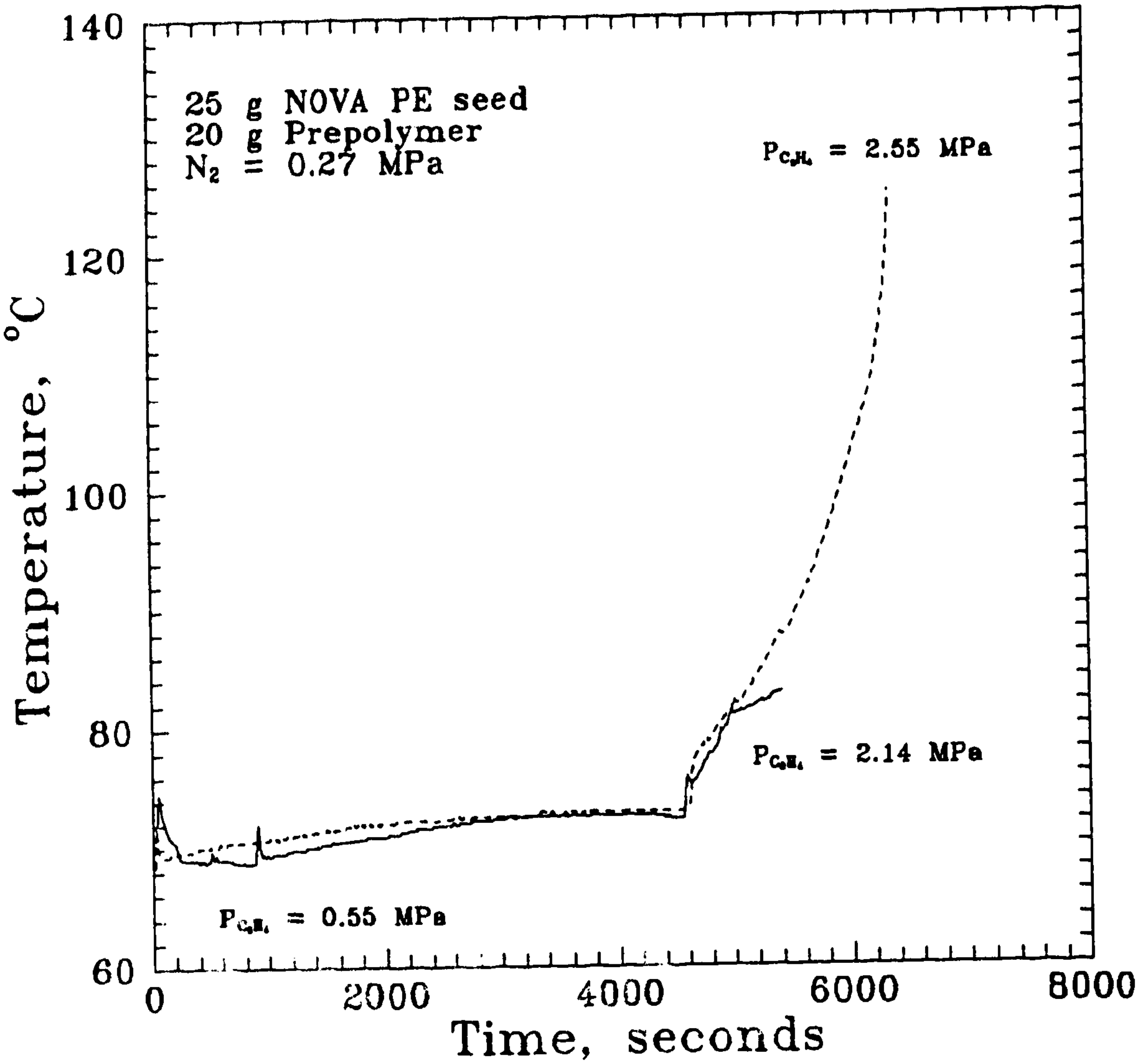


Figure 4.5 Effect of ethylene pressure

GAS9209). It can be seen in this figure that for an initial ethylene pressure of 0.55 MPa, the reactor temperature is constant at the operating temperature of 70°C. When the ethylene partial pressure was raised to 2.14 MPa, the temperature of the contents inside the reactor approached a new steady-state value (approximately 84°C). The oil bath temperature was kept constant at 70°C throughout the experiment. The thermal generation rate was compensated by the heat transfer through the reactor heat exchange surface and no thermal runaway occurred. The thermal behaviour observed for Run GAS9210 is shown by dashed lines in Figure 4.5. In this experiment, the ethylene partial pressure initially was kept fixed at the same value as in Run GAS9209 (0.55 MPa). As seen in the figures given in Appendix A, polymerization rate for both the runs at ethylene partial pressure of 0.55 MPa reached nearly the same pseudo-steady-state value after about 20 g prepolymerization. After establishing the steady-state ethylene feed rate, the ethylene partial pressure in Run GAS9210 was increased to the final value of 2.55 MPa. As seen in the Figure 4.5, the temperature inside the reactor increased slowly initially and later at an accelerating rate to reach a maximum value much greater than the melting point of polymer. Thus, it can be clearly observed, that at a certain value of the ethylene partial pressure, the thermal energy generation rate became greater than the energy dissipation capacity of the reactor; thereby triggering the onset of thermal runaway of the reactor.

In the above experiments (GAS9209 and GAS9210), about 20 g prepolymer was produced during the reaction at ethylene partial pressure of 0.55 MPa before the pressure was increased. Later experiments revealed that a minimum of 40 g had to be produced in the prepolymerization period before the polymerization rate stabilized. Figure 4.6 shows the polymerization rate profile for the gas-phase runs GAS9210 and GAS9262. The dashed line in the Figure 4.6 indicates the ethylene feed rate until 20 g prepolymer was formed during the reaction and the solid line shows the rate when the prepolymerization amount was extended to 40 g. During the course of Run GAS9262 (40 g prepolymer), the ethylene partial pressure was adjusted to achieve the same polymerization rate as Run GAS9210. This is seen by

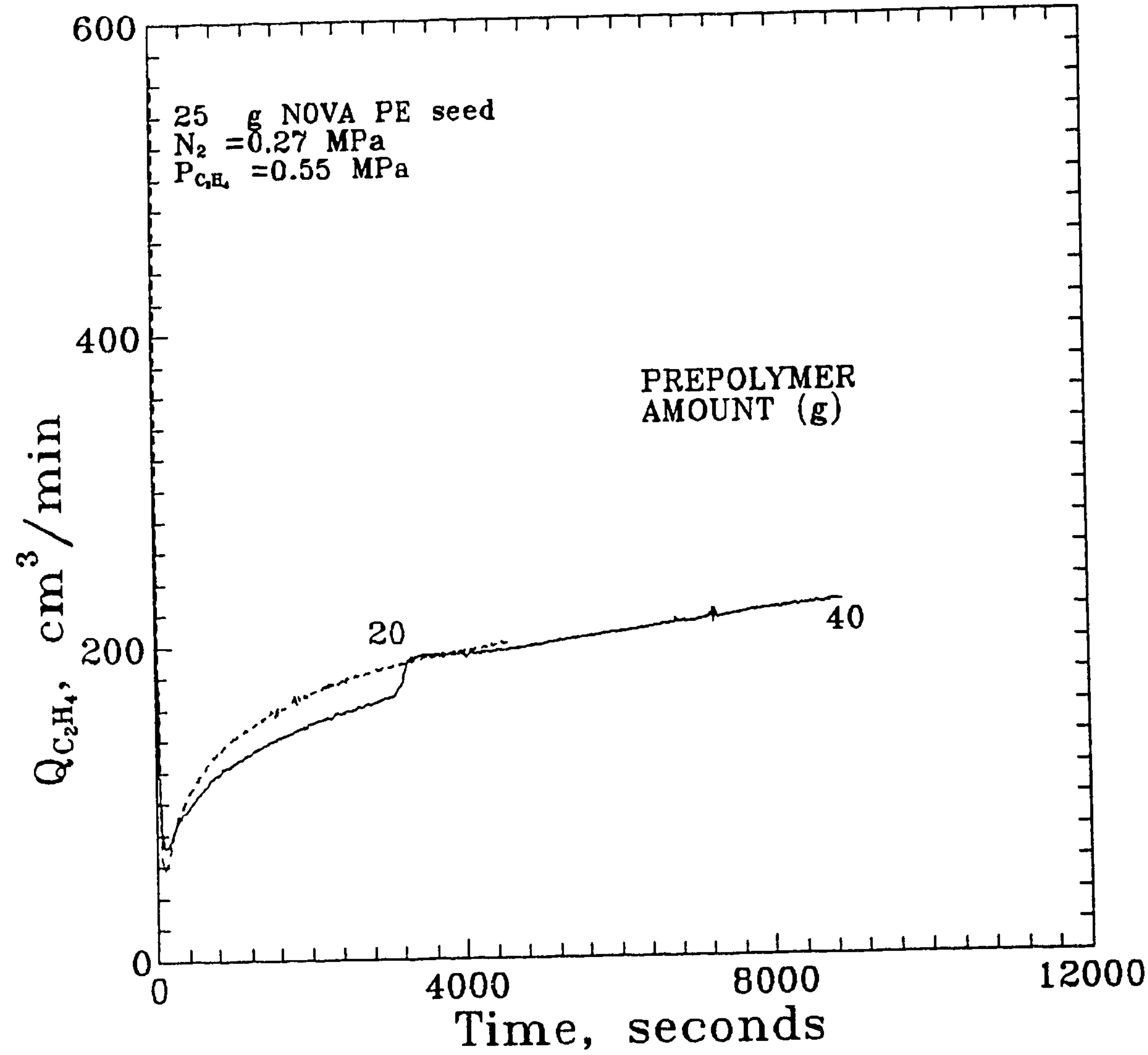


Figure 4.6 Minimum prepolymer amount required for constant activity

the abrupt rise in the ethylene feed rate after approximately 55 minutes. As seen, the polymerization rate was still increasing at a very slow rate after about 40 g prepolymer was formed in the reactor. The ethylene feed rate was fluctuating around the average mean value. The maximum fluctuations were less than 1%. Therefore, the polymerization rate was considered to have reached the pseudo-steady-state rate after 40 g prepolymer had been formed. The effects of the variation of the operating parameters were studied after allowing a minimum prepolymerization period corresponding to 40 g.

Proper stirring (uniform suspension) of the growing polymer particles is very important for maintaining temperature control in gas-phase reactors. The effect of stirring rate is dramatic, particularly in its relation to producing a powder product in contrast to a fused product. Even when a powder product is obtainable, it is important to maintain uniform temperatures inside the reactor. Figures 4.7 and 4.8 show the temperature profiles at locations 3 and 5 for gas-phase runs GAS9201 and GAS9218, respectively. The temperature-time trajectories frequently showed sharp discontinuities at lower stirring speeds, for example the temperature profile at location 3 shown in Figure 4.7 has a discontinuity at about 5000 s. These sudden increases followed by sharp decreases in temperature can be attributed to build-up and subsequent dislodging of polymer product on the thermocouple tip. In run GAS9201, the stirrer speed was initially kept constant at 470 rpm (for 30 minutes) during which time there was a build-up of solid polymer on the tip of thermocouple at location 3. As seen in Figure 4.7, this localised "hot Spot" at location 3 induced the reactor to reach thermal runaway conditions even when the temperature profile at location 5 was constant at 70°C. Subsequent increase in the stirring speed to 670 rpm could not dislodge the agglomerated product. Run GAS9218 was carried out at a stirring rate of 670 rpm. As shown in Figure 4.8, the temperature profiles at locations 3 and 5 are very close indicating the absence of "hot Spots". Typical stirring speed of 670 rpm was used for maintaining uniform temperature of the contents.

In the initial gas-phase experiments, the typical reactor operating conditions were established at which thermal runaway phenomena could be studied. It was also

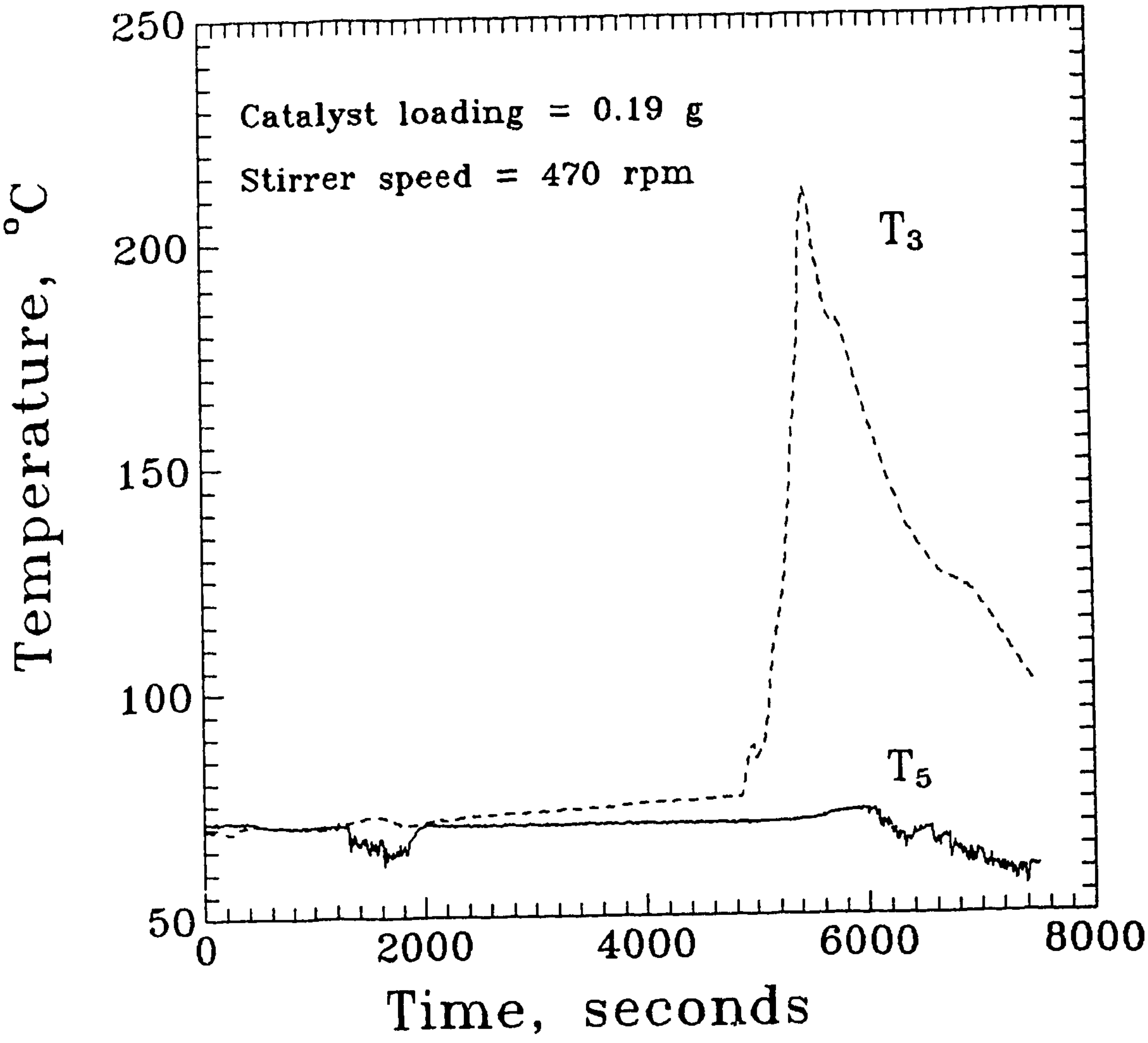


Figure 4.7 Non-uniform temperature distribution

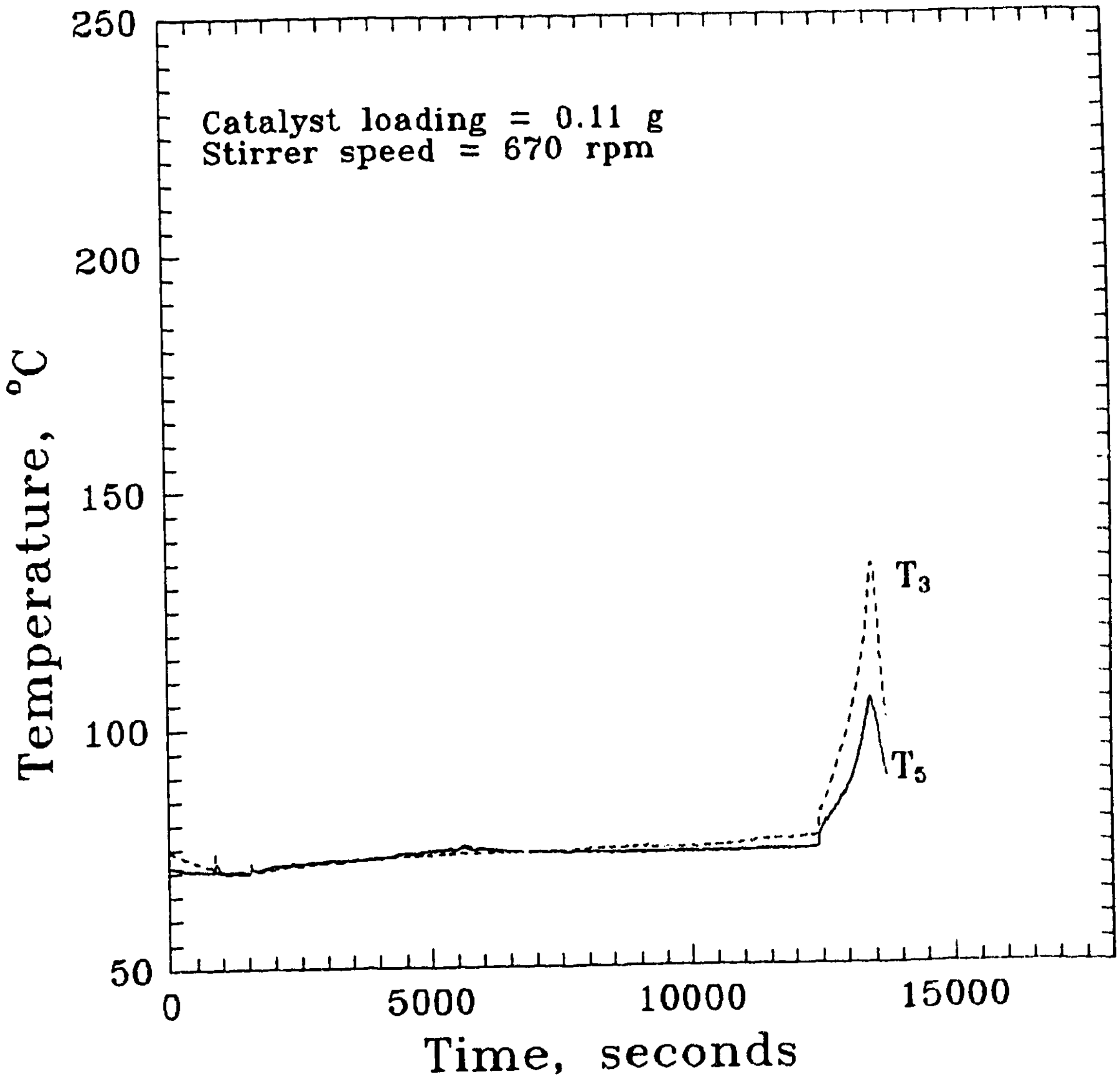


Figure 4.8 Uniform temperature distribution

observed that, after the onset of thermal runaway, it is necessary for the ethylene flow to be stopped after the temperature reached about 125°C, otherwise very high temperatures (≈ 200°C) were obtained along with agglomeration of product. Even after stopping the ethylene feed rate, temperatures above the melting point of polyethylene were obtained (GAS9218) but the product was usually in powder form. The experiments describing the temperatures obtained when ethylene feed rate was stopped at different temperatures is presented in Appendix A (GAS9203-GAS9216) and the temperature profiles are shown in Appendix B.

The base conditions for studying the thermal runaway phenomena can be summarized as follows:

1. Ethylene partial pressure: 0.55 - 2.55 MPa.
2. Amount of catalyst: 0.1 g.
3. Mass of seed: 25 g polyethylene (obtained from Novacor).
4. Prepolymerization amount: 40 g (minimum).
5. Initial Reactor temperature: 70°C.
6. Stirring speed: 670 rpm.

In all of the preceding experiments, nitrogen was used as background gas. The partial pressure of inert nitrogen was 0.27 MPa over which the ethylene gas was admitted. Once the base condition was established, the next step was to study the effect of variation of the operating parameters on the thermal behaviour of the gas-phase semi-batch stirred-bed reactor. Table 4.1, given at the end of the chapter, summarizes the gas-phase experiments conducted during the study. The results are summarized in the following sections.

4.3 Seed Bed Variations

In the initial experiments described in the previous section, it was found that a minimum support bed amount of 25 g was needed for uniform distribution of the catalyst particles and for sustained mixing of the reactor contents inside the reactor. Polyethylene homopolymer obtained from Novacor Chemicals Ltd. was used for the seed bed. The seed bed particles were of the size range between 355 to 841 μm. The catalyst particles had an average size of 55 μm.

In all the gas-phase experiments, unless otherwise stated, the ethylene partial pressure was changed from 0.55 MPa to 2.55 MPa at the conclusion of the prepolymerization period. In all the plots, the time at which the ethylene partial pressure was increased from 0.55 MPa to 2.55 MPa was arbitrarily set at 1800 s. The true time of prepolymerization varied depending on the amount of prepolymerization (~ 225 s are required per g of prepolymer). This normalization of the temperature profiles was carried out for comparison of the time required for thermal runaway at different prepolymer amounts.

Three experiments GAS9262, GAS9267 and GAS9269 were carried out using 25 g, 45 g and 65 g seed beds, respectively. The base case amount of prepolymerization was fixed at 40 g. Figure 4.9 shows the temperature profiles observed for the above three runs. The prepolymerization rates for the three runs were approximately the same. The oil bath temperature was kept uniform at 70°C during the prepolymerization period. The temperature profile as seen in Figure 4.9 indicates that the thermal runaway of the reactor was delayed by increasing the mass of the seed bed. The time required for runaway was highest for 65 g of polyethylene seed bed and was lowest for 25 g of seed bed. The presence of inert solids inside the reactor acts as thermal capacitance and increasing the mass of seed bed delayed the onset of temperature excursions.

The effect of seed bed variation at different prepolymerization levels was studied. Figure 4.10 shows the temperature profile for the Runs GAS9263 (25 g seed), GAS9273 (45 g seed) and GAS9270 (65 g seed). About 60 g prepolymer was formed during the run before the thermal runaway behaviour was studied. Similar to the earlier observations (for 40 g prepolymerization), there was an observed retardation in the rate of temperature rise in the reactor on increasing the seed bed amount. But the proximity of the temperature profiles for 25 g seed bed and 45 g seed bed runs compared with the rate of temperature rise for the 65 g seed bed is in contrast to the observed temperature profiles in the earlier runs (Figure 4.9) for 40 g prepolymerization. It is seen in Figure 4.10, that the initial average temperature

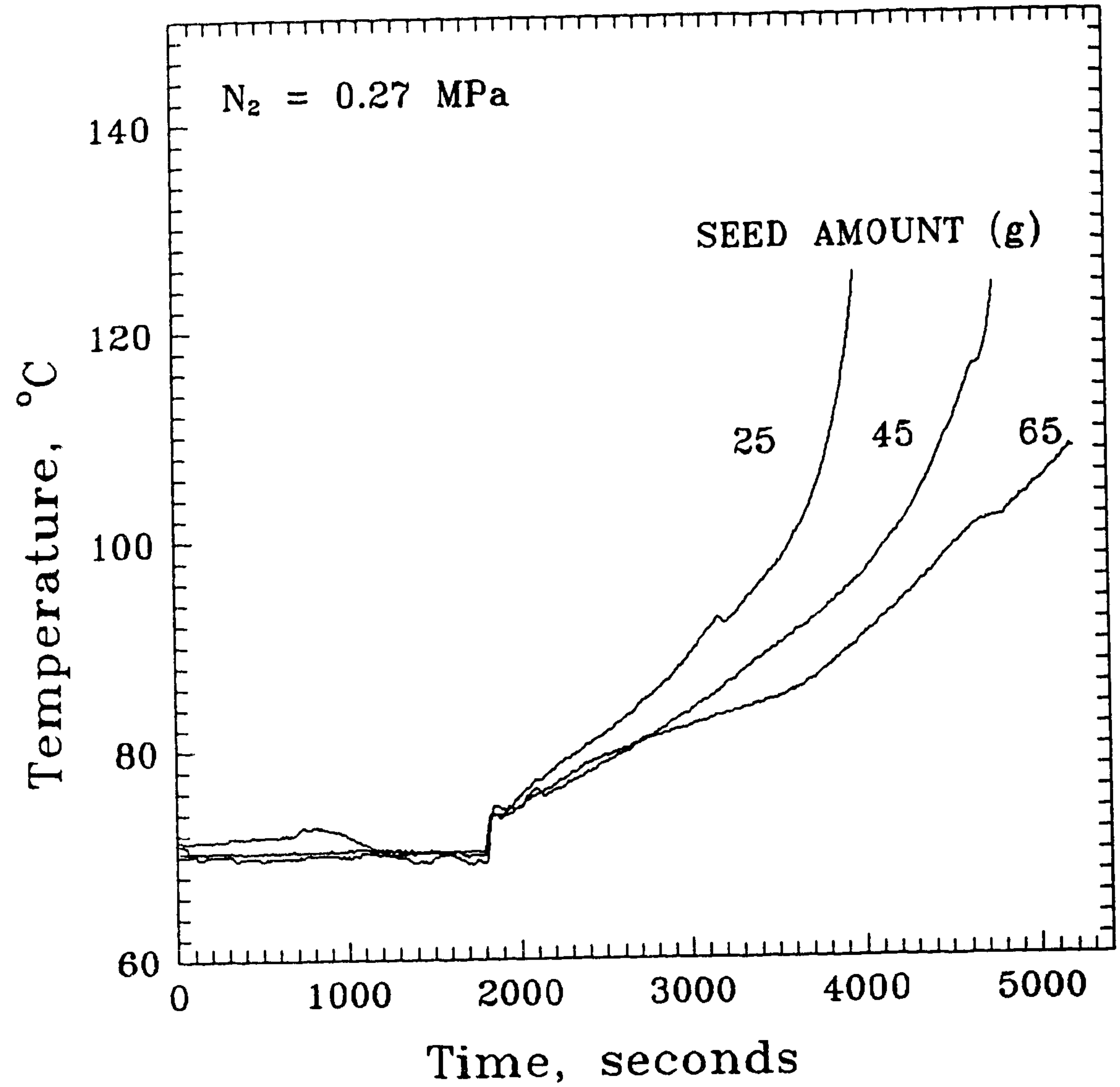


Figure 4.9 Variation of seed amount at 40 g prepolymerization

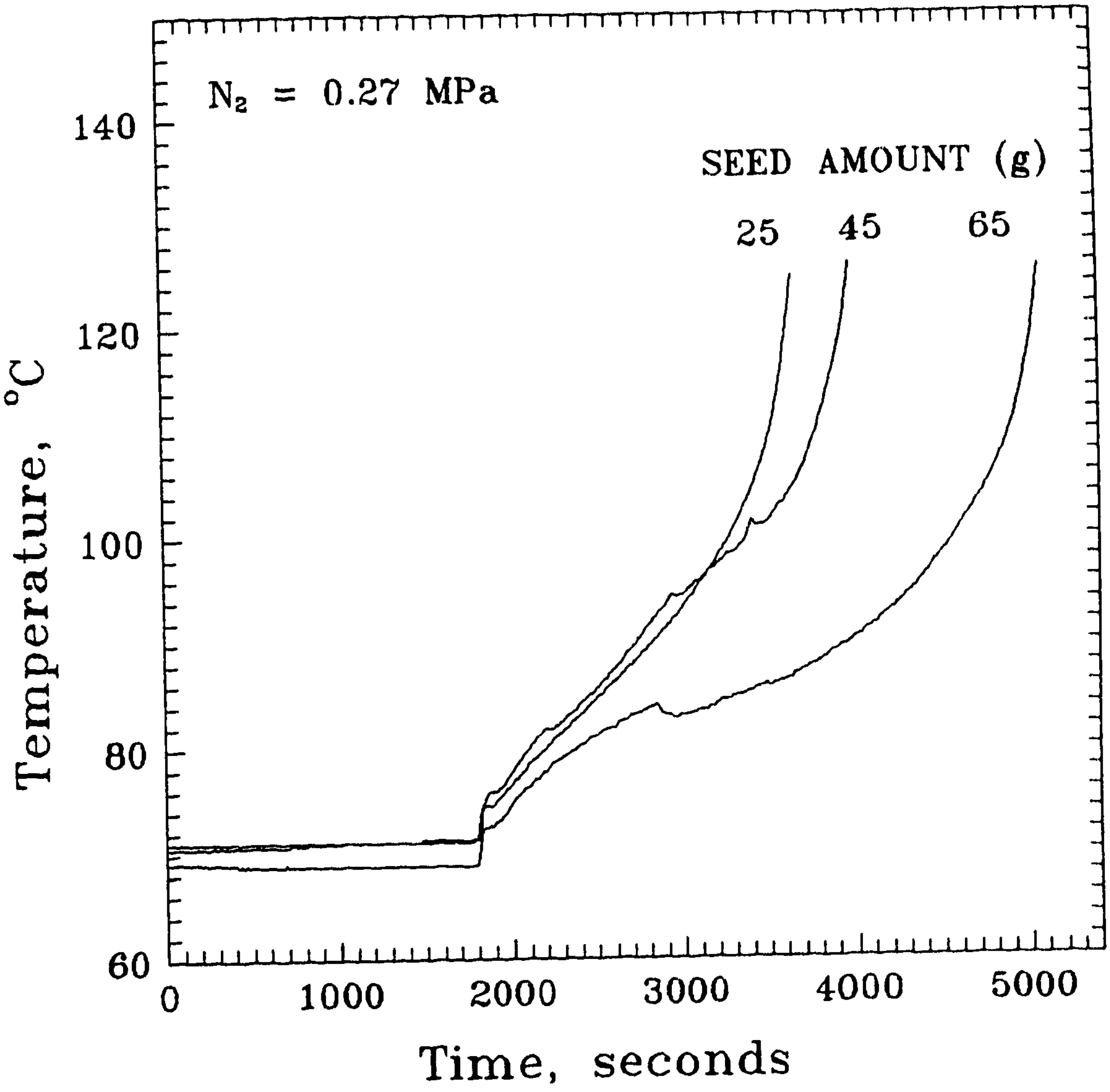


Figure 4.10 Variation of seed amount at 60 g prepolymerization

of the reactor during the prepolymerization period in the case of 65 g experiment (Run GAS9270), was about 2°C lower than the temperatures for the 25 g and 45 g experiments. The lower initial temperature delayed the onset of thermal runaway in the reactor, but it cannot account for the relatively large difference in the rate of temperature rise between the 65 g seed bed run and the two runs at lower seed bed levels. This indicates that at higher prepolymerization levels, larger amounts of seed bed are required to retard or completely control the temperature excursions observed in gas-phase reactors. The effect of seed bed was also studied at 80 g prepolymerization. The temperature profiles for the two runs, GAS9264 (25 g seed) and GAS9271 (45 g seed) are shown in Figure 4.11. As seen in Figure 4.11, the results are analogous to the earlier observations, i.e., the time for reaching the melting point of the polymer was lower when 25 g seed was used, while, increasing the amount of seed to 45 g delayed the runaway behaviour.

4.4 Variation in Prepolymer Amount

The minimum length of prepolymerization for these experiments was such that 40 g of prepolymer was formed. Experiments were carried out to study the effect of variation in the prepolymerization period on the thermal runaway rate of the gas-phase reactor. Figure 4.12 shows the effect of variation of prepolymer amount on the rate of temperature rise in the reactor. Experiments GAS9262, GAS9263 and GAS9264 having 40, 60 and 80 g of prepolymer respectively, were carried out using a 25 g seed bed. As seen in Figure 4.12, the time required for reaching the melting point of the polymer was lowest when 80 g of prepolymer formed inside the reactor and the rate of temperature rise decreased as the length of prepolymerization was reduced.

The total amount of solid polymer inside the reactor for Run GAS9262 (40 g prepolymerization), at the time of increasing the ethylene partial pressure, was 65 g. The total amount of solids inside the reactor for GAS9263 (60 g prepolymerization) and GAS9264 (80 g prepolymerization) was 85 g and 105 g, respectively. A larger amount of solids inside the reactor was expected to act as an

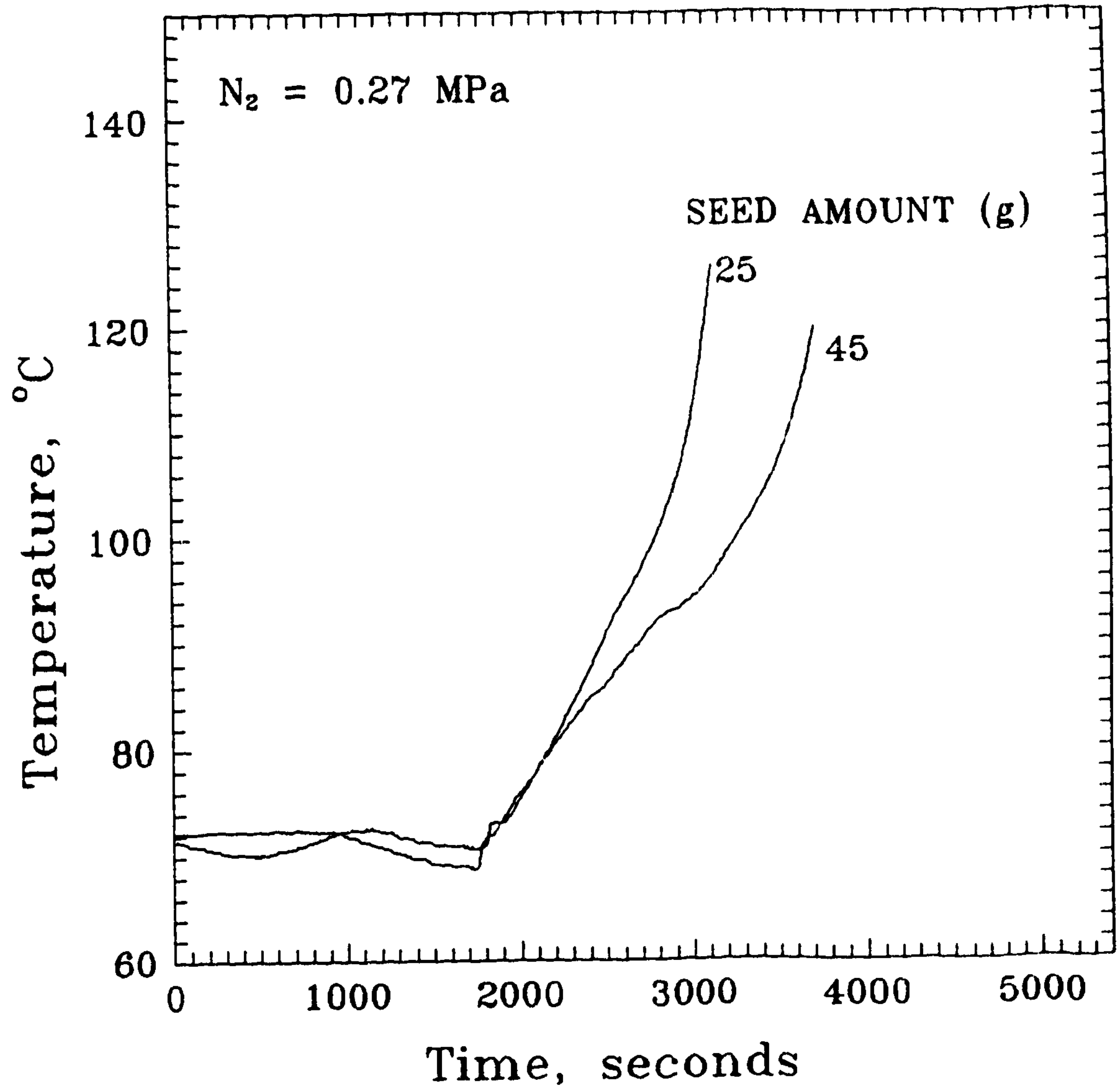


Figure 4.11 Variation of seed amount at 80 g prepolymerization

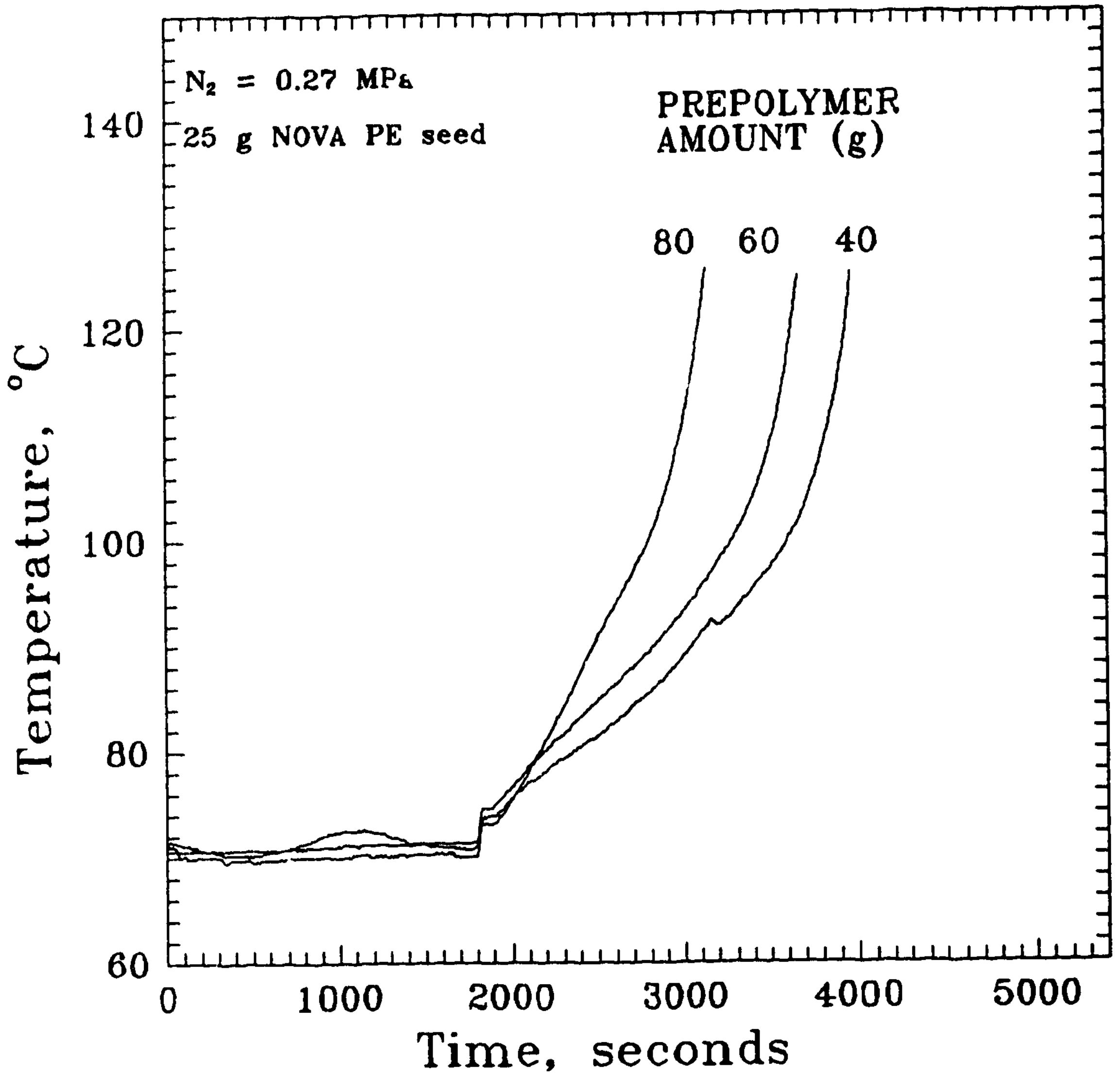


Figure 4.12 Variation in amount of prepolymerization

additional thermal capacitance in the similar manner as the greater mass of seed bed seen in Figures 4.9, 4.10 and 4.11. On the contrary, as shown by Figure 4.12, increasing the prepolymerization levels lowered the time for runaway.

The effect of prepolymerization period at different mass of seed bed was studied. Figure 4.13 and Figure 4.14 show the temperature profiles for experiments carried out at 45 g and 65 g seed bed amounts, respectively. It is seen in Figure 4.13, that the rate of temperature rise for Run GAS9267 (40 g prepolymer) was the lowest. The thermal behaviour for 60 g (GAS9273) and 80 g (GAS9271) of prepolymer was very close and the temperature increase in either run was much faster than the observed rate for 40 g (GAS9267) of prepolymer. In all the above three experiments, 45 g polyethylene seed bed was employed. Similar results were observed when 65 g seed bed was employed, where the reactor temperature reached the melting point of polymer earlier when 60 g of prepolymer was formed (GAS9270) than when 40 g of prepolymer (GAS9269) was formed. The results for these two runs are presented in Figure 4.14. The slopes of the temperature profiles for the runs shown in Figures 4.12, 4.13 and 4.14 indicate that the effect of amount of prepolymer is decreased with increase in amounts of seed bed, i.e., the effect of prepolymerization amount on the thermal runaway of the reactor was much more pronounced for 25 g seed than for 45 or 65 g of seed bed.

The combined effect of prepolymerization and seed bed mass on the thermal runaway of the reactor was studied in Runs GAS9263 and GAS9267. In Figure 4.15, temperature profiles for these runs are presented. The total solid polymer inside the reactor in both the runs at the time of the step-change in ethylene partial pressure was 85 g; but was composed of 25 g of seed bed and 40 g of prepolymer for GAS9263 and 45 g of seed bed and 40 g of prepolymer for GAS9267. As seen in Figure 4.15, the rate of temperature rise for theses two runs differ from each other considerably. The reactor temperature in the case of the 25 g seed and 60 g prepolymer combination reached the melting point of polymer much more rapidly than the 45 g seed and 40 g prepolymer combination. This indicates that the effect of solids inside the reactor on the temperature depends on whether the solid is

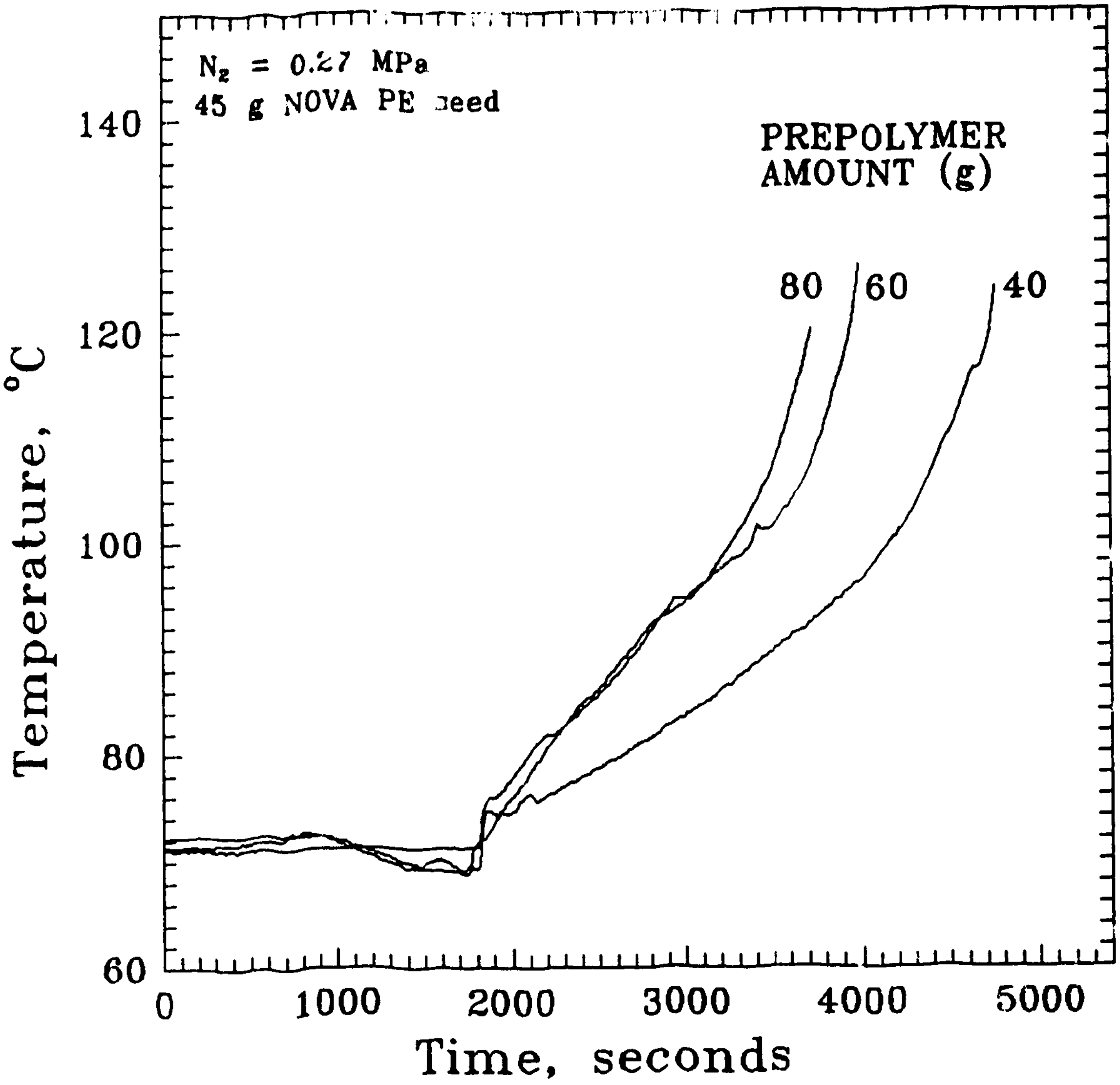


Figure 4.13 Variation in amount of prepolymerization

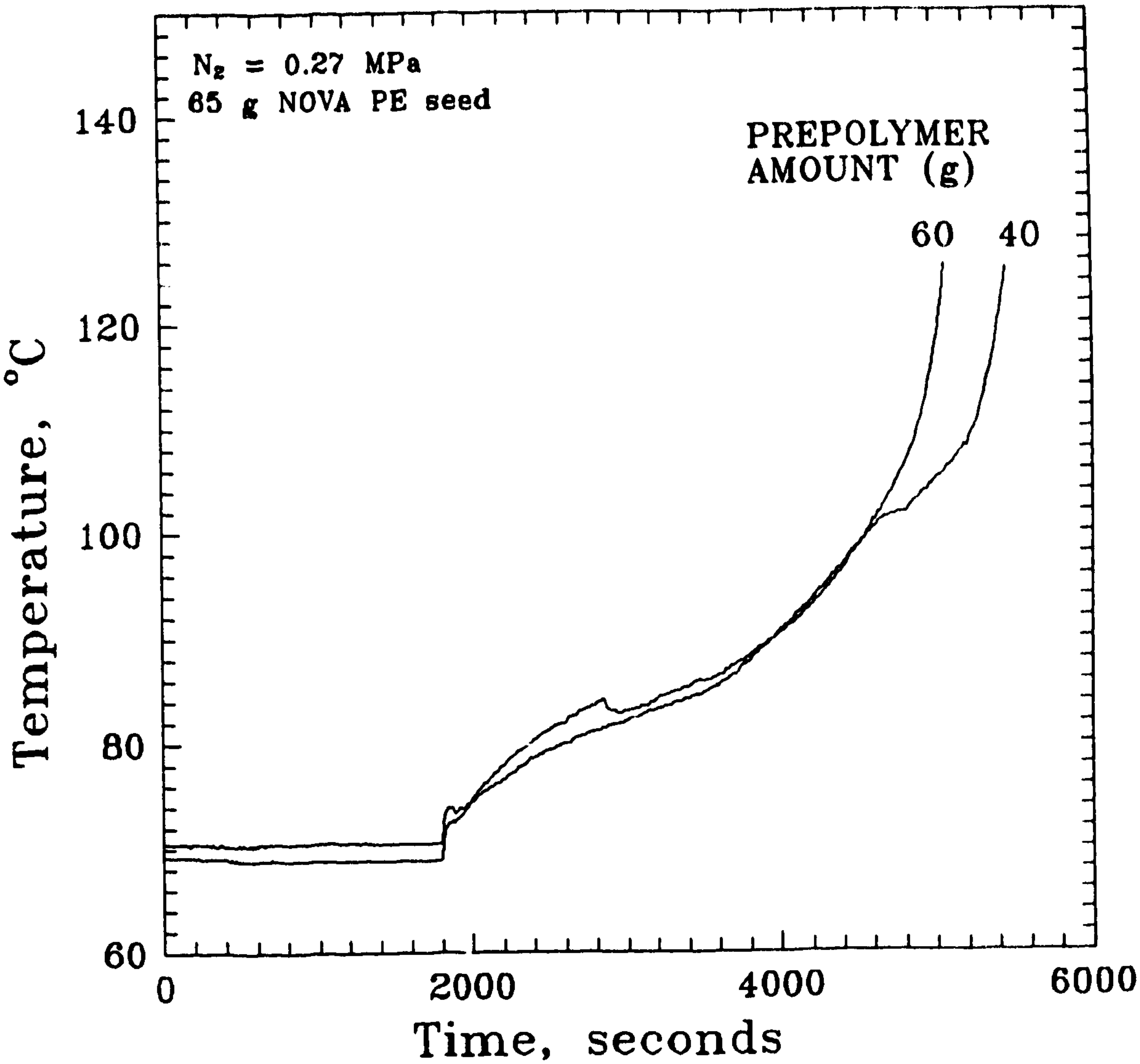


Figure 4.14 Variation in amount of prepolymerization

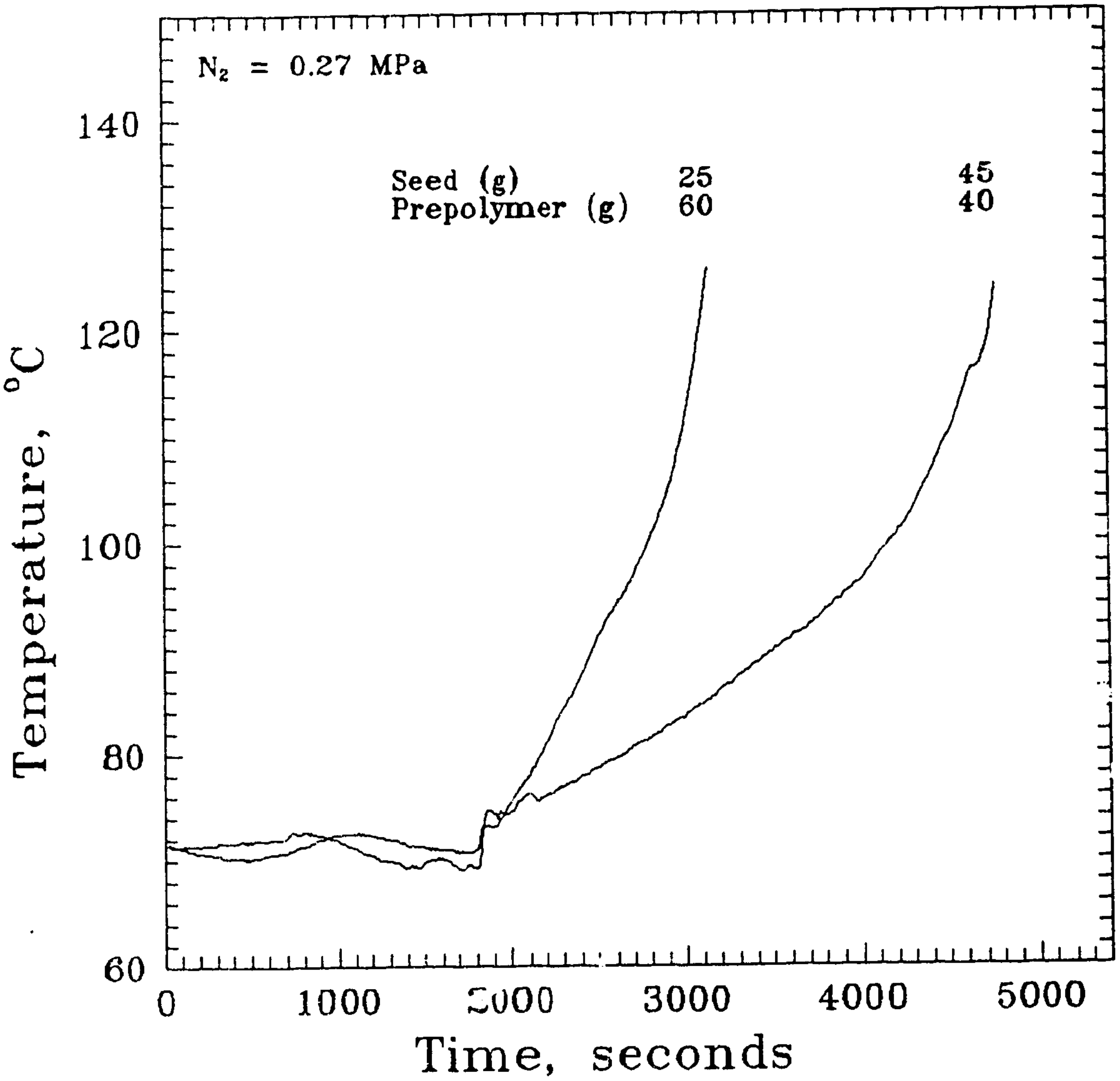


Figure 4.15 Variation of seed and prepolymer at constant total of 85 g

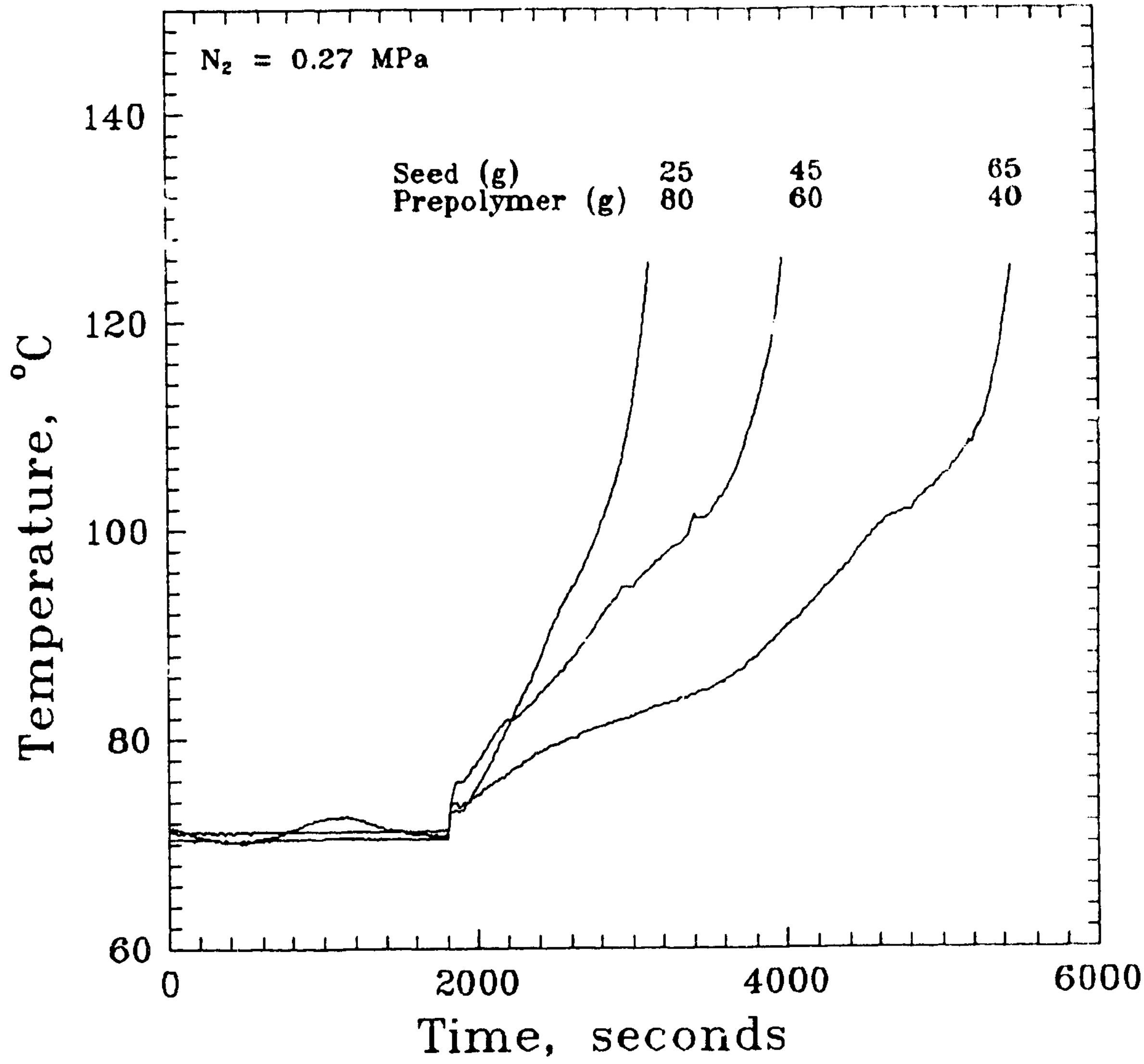


Figure 4.16 Variation of seed and prepolymer at constant total of 105 g

added initially in the form of a seed bed or produced during the course of the reaction. Figure 4.16 shows the temperature profile for the runs when the polymer amount was kept constant at 105 g but different combinations of seed and prepolymer levels were used. Results were similar to that observed in Figure 4.15. Thermal runaway occurred faster with increasing prepolymerization levels. The temperature profile for 125 g total polymer inside the reactor is shown in Figure 4.17.

The temperature profiles seen in Figures 4.15, 4.16 and 4.17 for 85, 105 and 125 g total polymer amounts, indicate that the thermal behaviour with 25 g and 45 g seed beds became similar as the total amount of polymer was increased. However, the rate of temperature rise for 65 g seed bed was still lower than those with large amounts of prepolymerization.

The cause for the unexpected effect of the amount of prepolymer on thermal runaway, i.e., faster thermal runaway with increasing amounts of prepolymer in reactor, is not known. However, this phenomenon is probably related to the concentration of catalyst on the seed particles (seed bed to catalyst ratio) and the catalyst fracture mechanism. Detailed examination of the morphology of the polymer particles and catalyst distribution on the seed bed particles are required to gain insight into this behaviour.

4.5 Effect of Background Gas

The effect of background gas on thermal runaway was studied by replacing nitrogen with helium. The partial pressure of helium was kept constant at 0.27 MPa. The effect of variation in mass of seed bed with different amounts of prepolymerization with helium as the inert gas is shown in Figures 4.18 to 4.20. The behaviour is similar to that observed with nitrogen as the background gas, i.e., increasing the amount of seed bed delays the onset of thermal runaway. It should be noted that the stirrer speed was increased from 670 rpm to 885 rpm for Run GAS9221 (25 g seed bed) at about 2200 s after increasing the ethylene partial pressure to maintain temperature uniformity in the reactor. This increase in stirring

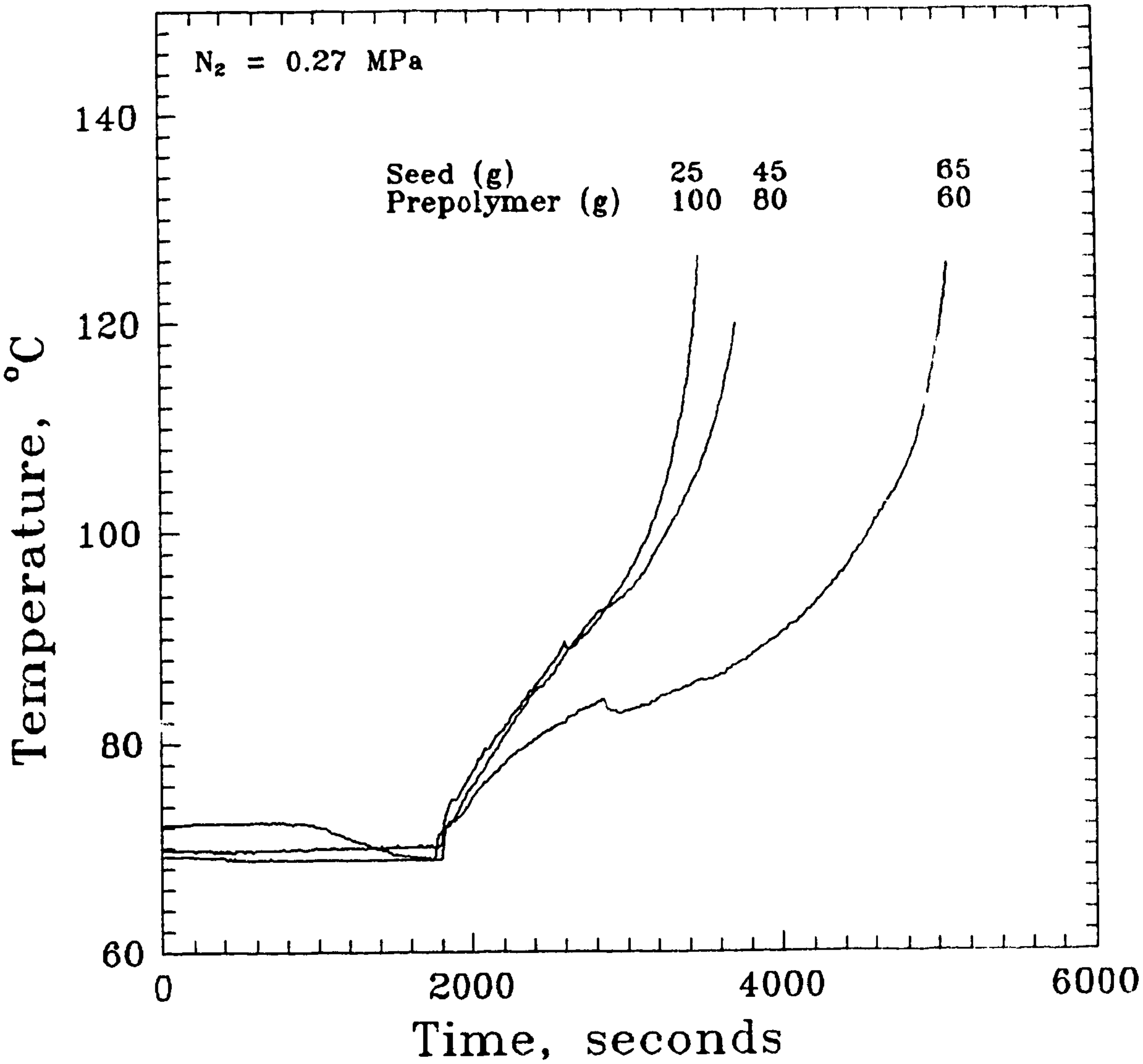


Figure 4.17 Variation of seed and prepolymer at constant total of 125 g

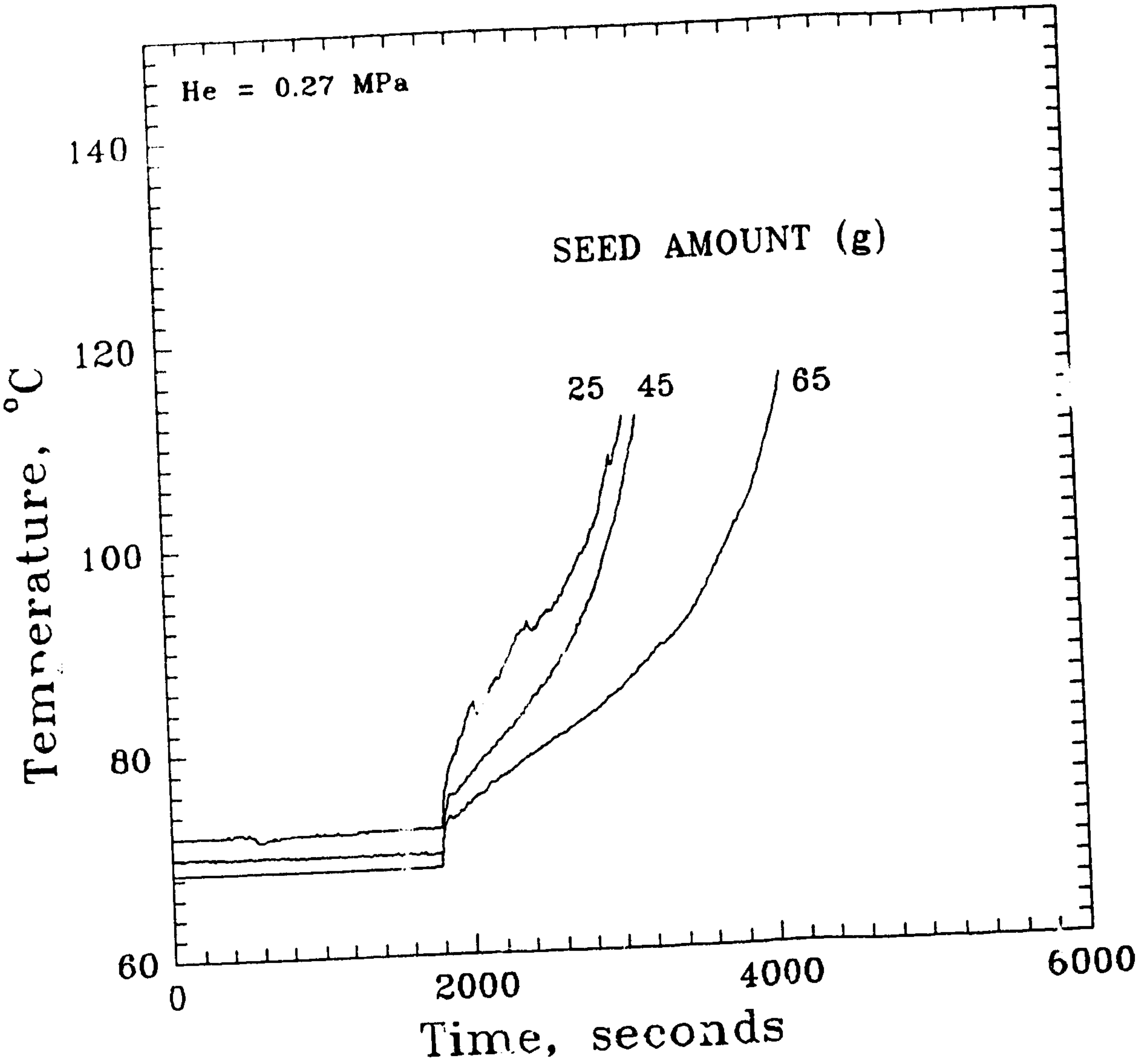


Figure 4.18 Variation of seed amount at 40 g prepolymerization

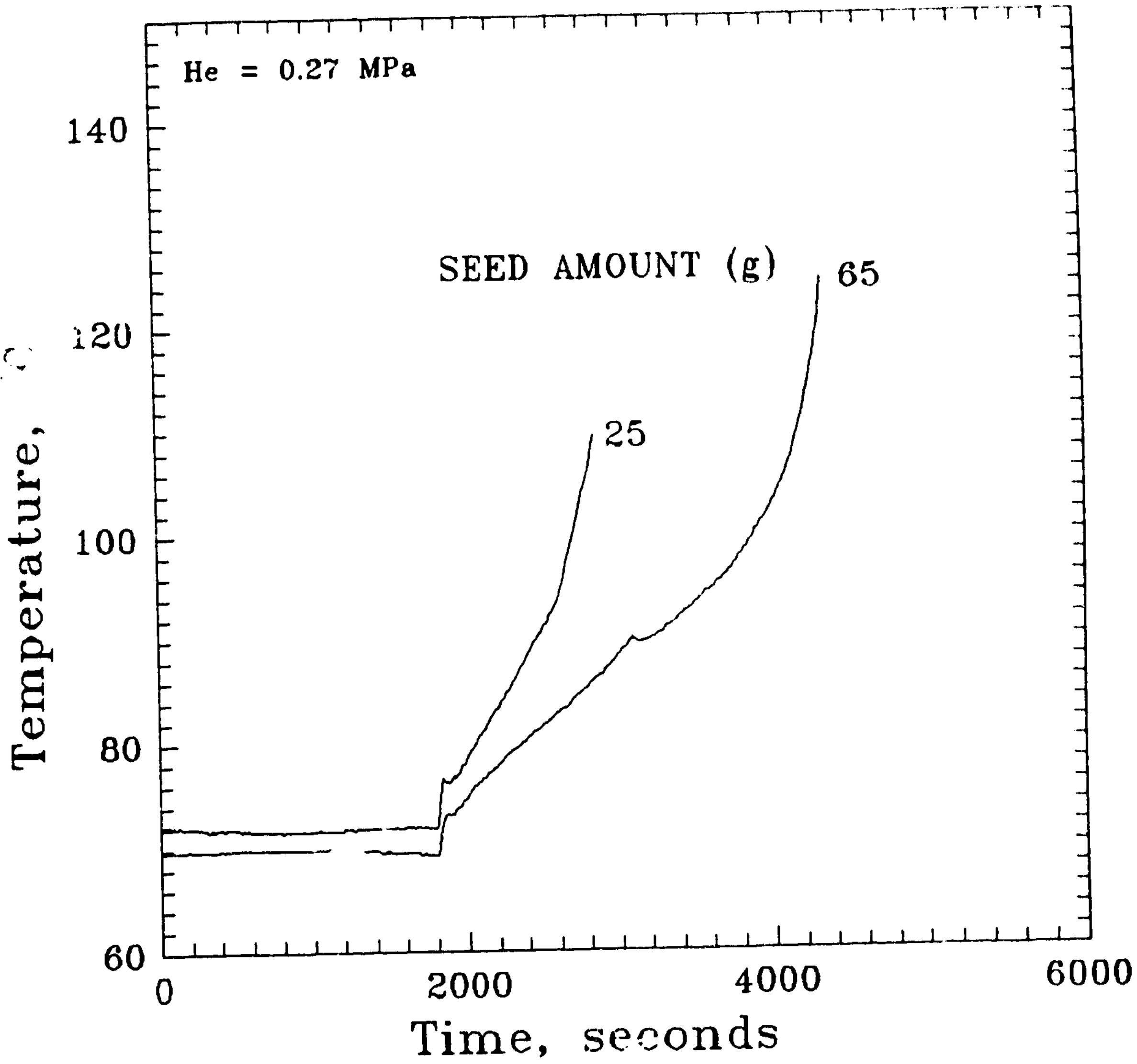


Figure 4.19 Variation of seed amount at 60 g prepolymerization

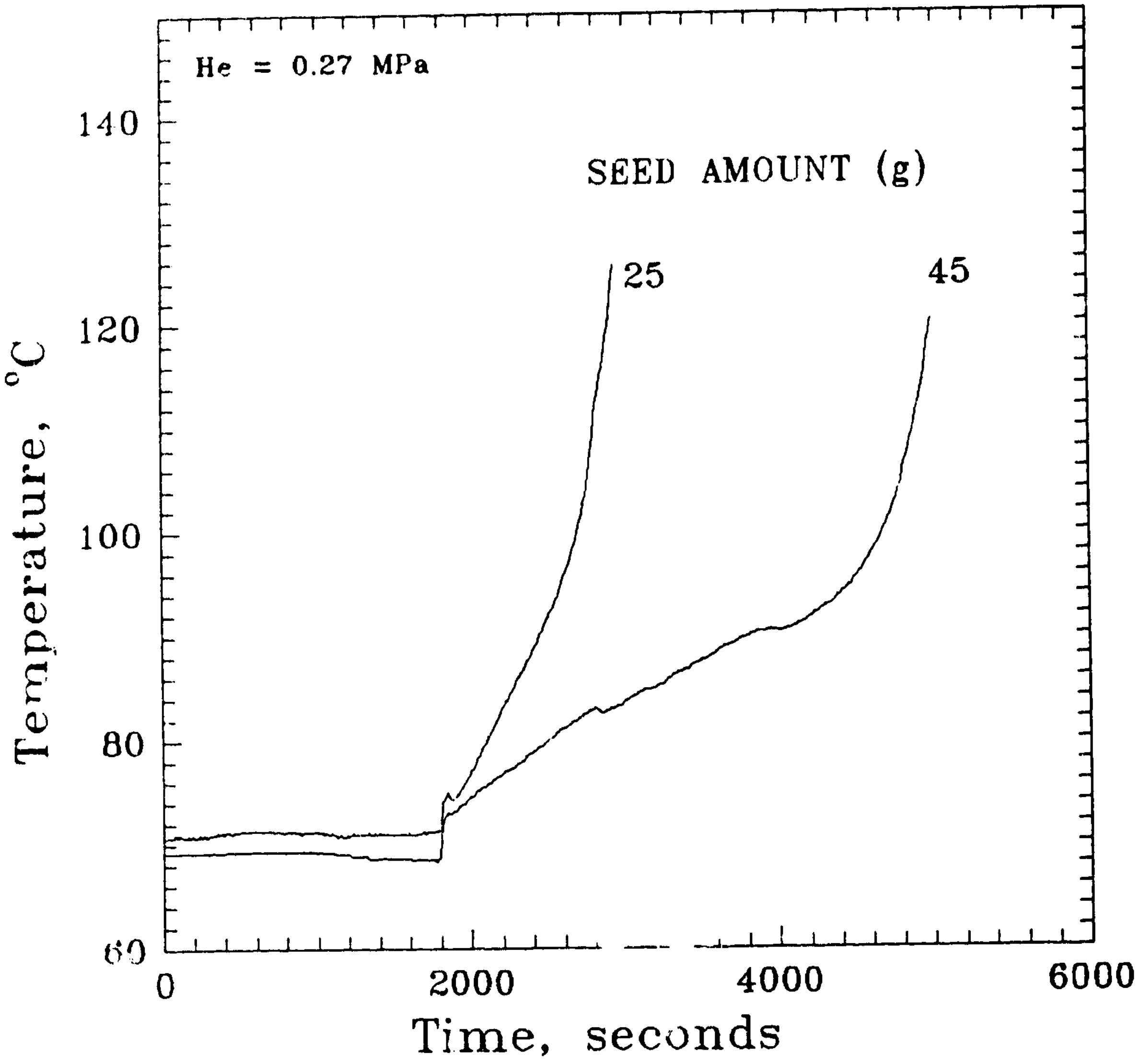


Figure 4.20 Variation of seed amount at 80 g prepolymerization

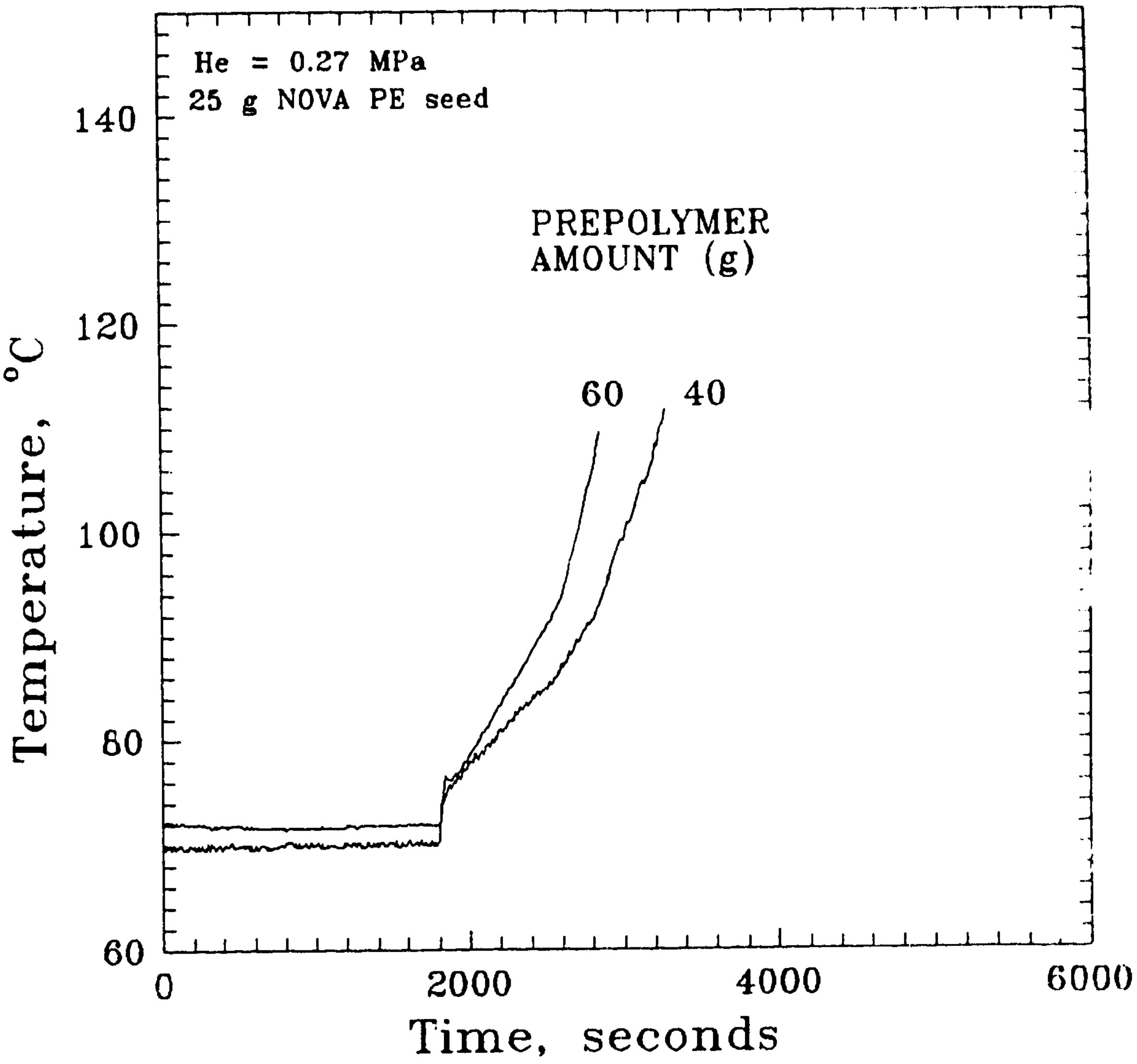


Figure 4.21 Variation in amount of prepolymerization

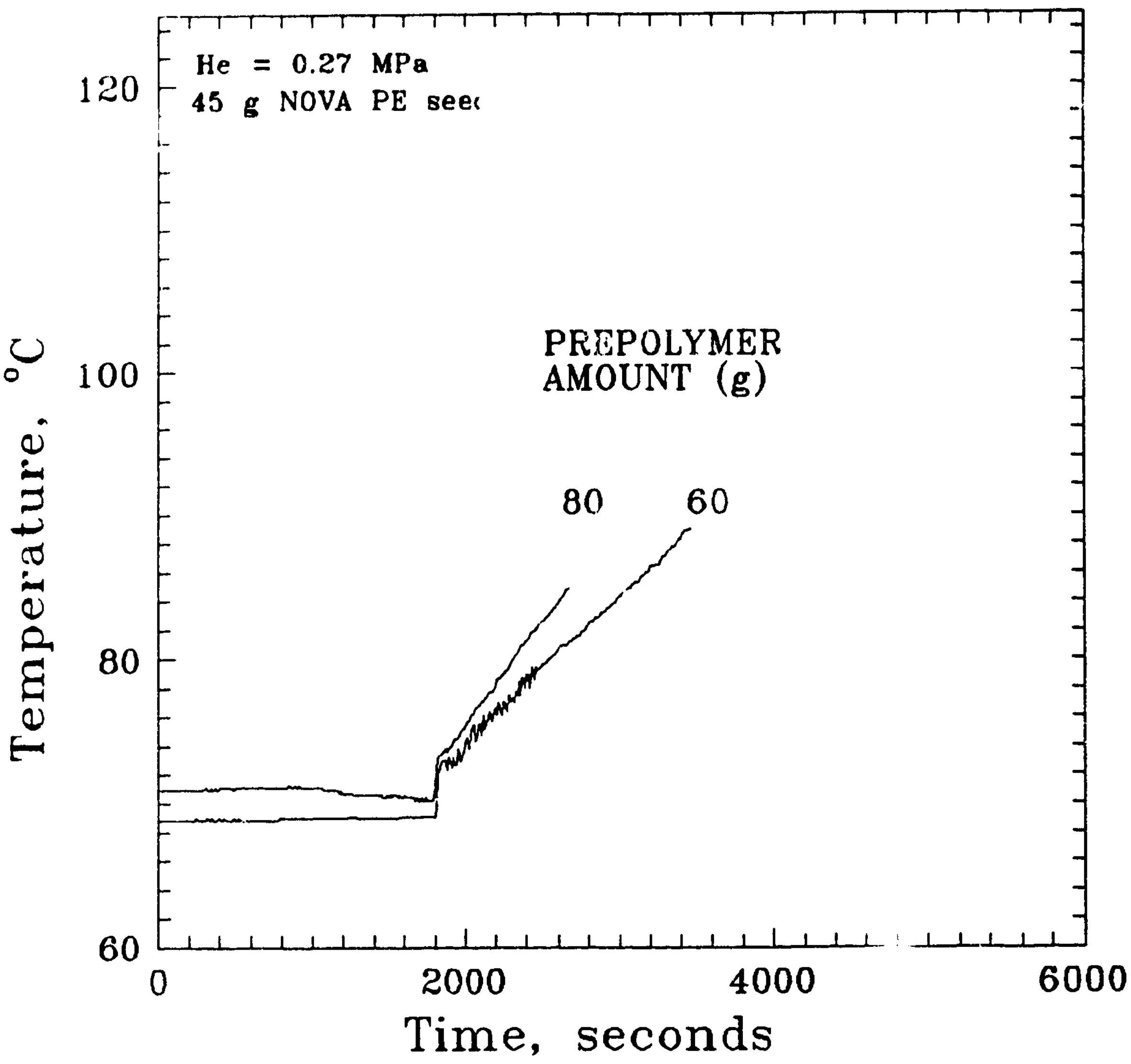


Figure 4.22 Variation in amount of prepolymerization

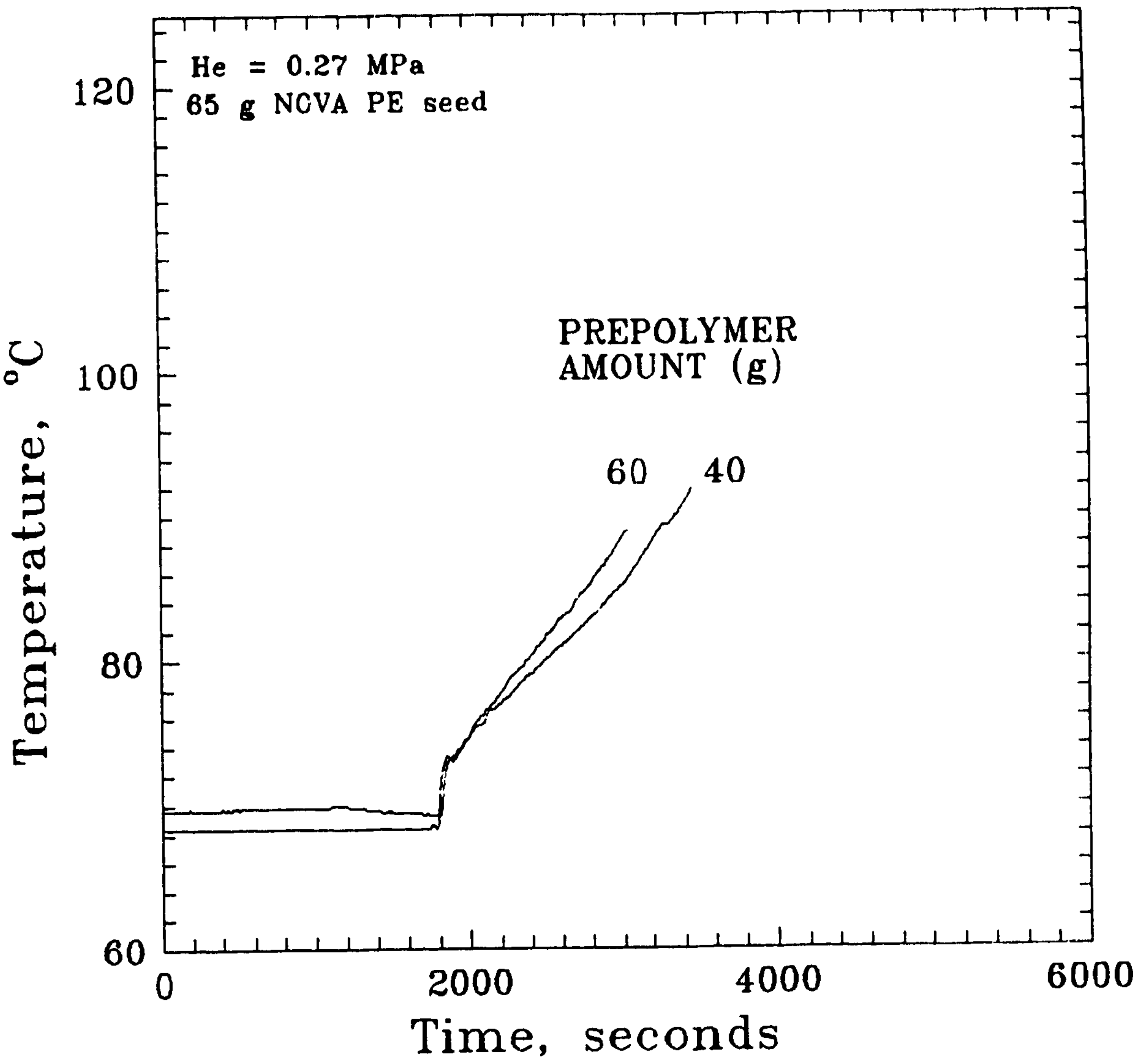


Figure 4.23 Variation in amount of prepolymerization

rate may have caused a slight delay in thermal runaway of Run GAS9221 seen in Figure 4.18.

The effect of prepolymer amounts on the temperature of the reactor contents is shown in Figures 4.21 to 4.23. The experiments (GAS9221 and GAS9224) for 40 and 60 g prepolymer levels, respectively, and at 25 g of seed bed indicated (as seen in Figure 4.21) that temperature increased at a higher rate when the prepolymer amount was changed from 40 g to 60 g. This behaviour is similar to that observed with nitrogen as the background gas.

The combined effect of seed bed and prepolymerization amounts on the thermal behaviour of the gas-phase reactor is shown in Figure 4.24 where the temperature profile for the runs GAS9224 (25 g seed & 60 g prepolymer) and GAS9223 (45 g seed & 40 g prepolymer) are plotted. The results are analogous to the observation made for the runs when nitrogen was used as the inert background gas, i.e., increasing the prepolymer amount hastened the runaway process as compared with increasing the mass of seed bed while keeping the total amount of polymer inside the reactor at 85 g. Similar results were obtained for total polymer amounts of 105 and 125 g. This can be seen in Figures 4.25 and 4.26 respectively.

The thermal conductivity of nitrogen is 0.31 mW/(cm.K) and of helium is 1.72 W/(cm.K). Therefore, it was expected that heat transfer from the heated polymer icles to the surrounding gas phase would be increased by replacing nitrogen with helium as the background gas. However, most of the runs with different seed bed and prepolymerization levels showed that the time required for reaching the melting point of the polymer was longer with nitrogen than with helium. Figure 4.27 shows the temperature profile for the Runs GAS9224 (helium background) and GAS9263 (nitrogen background). The mass of seed bed in both the runs was 25 g and the prepolymerization amount was 60 g. As indicated in this figure, the rate of temperature rise was higher with helium than with nitrogen. Similar results were observed for different seed bed and prepolymer amounts.

In order to determine the effect of inert partial pressure at constant polymerization rate, it was decided to keep the total pressure constant and vary the

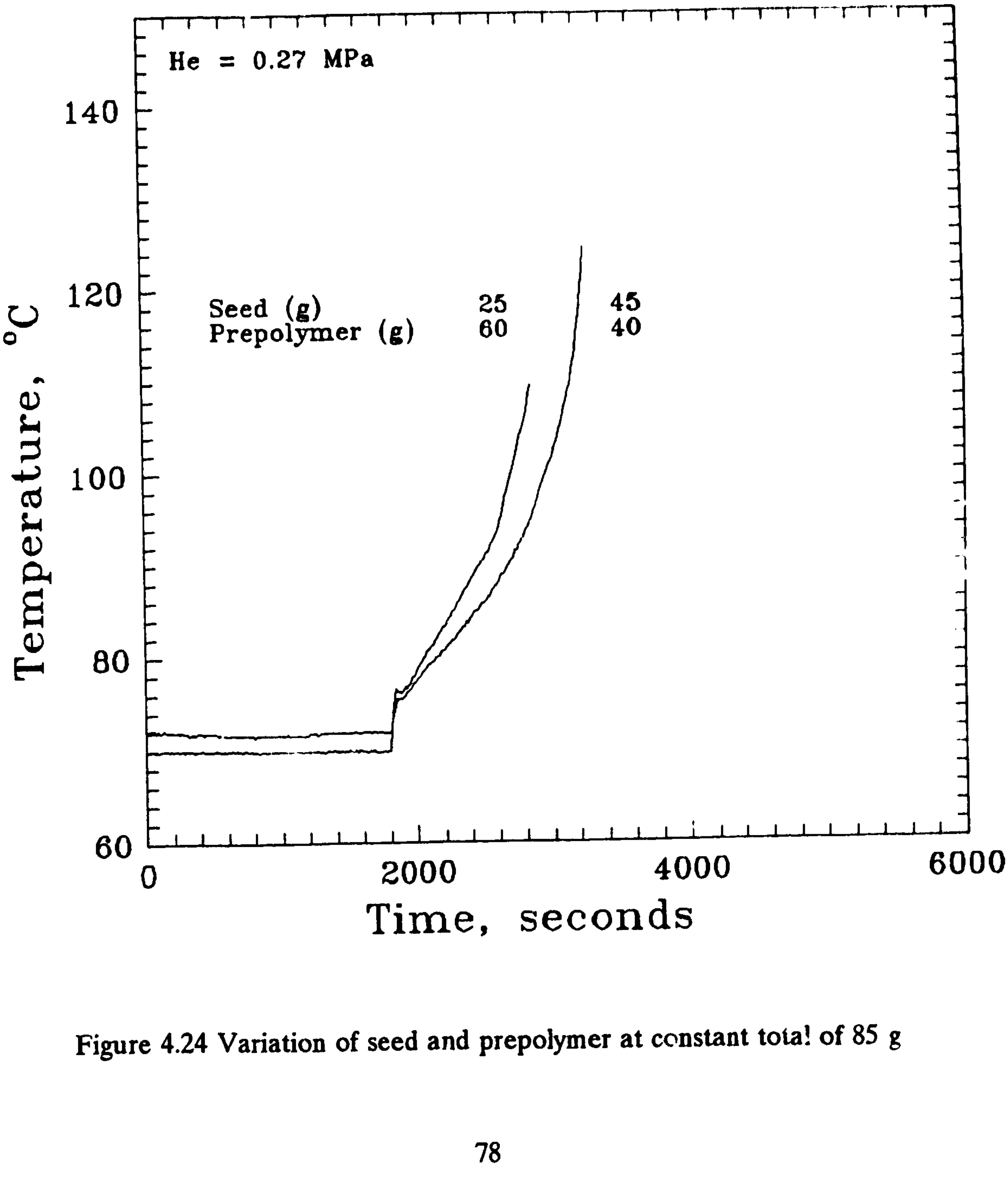


Figure 4.24 Variation of seed and prepolymer at constant total of 85 g

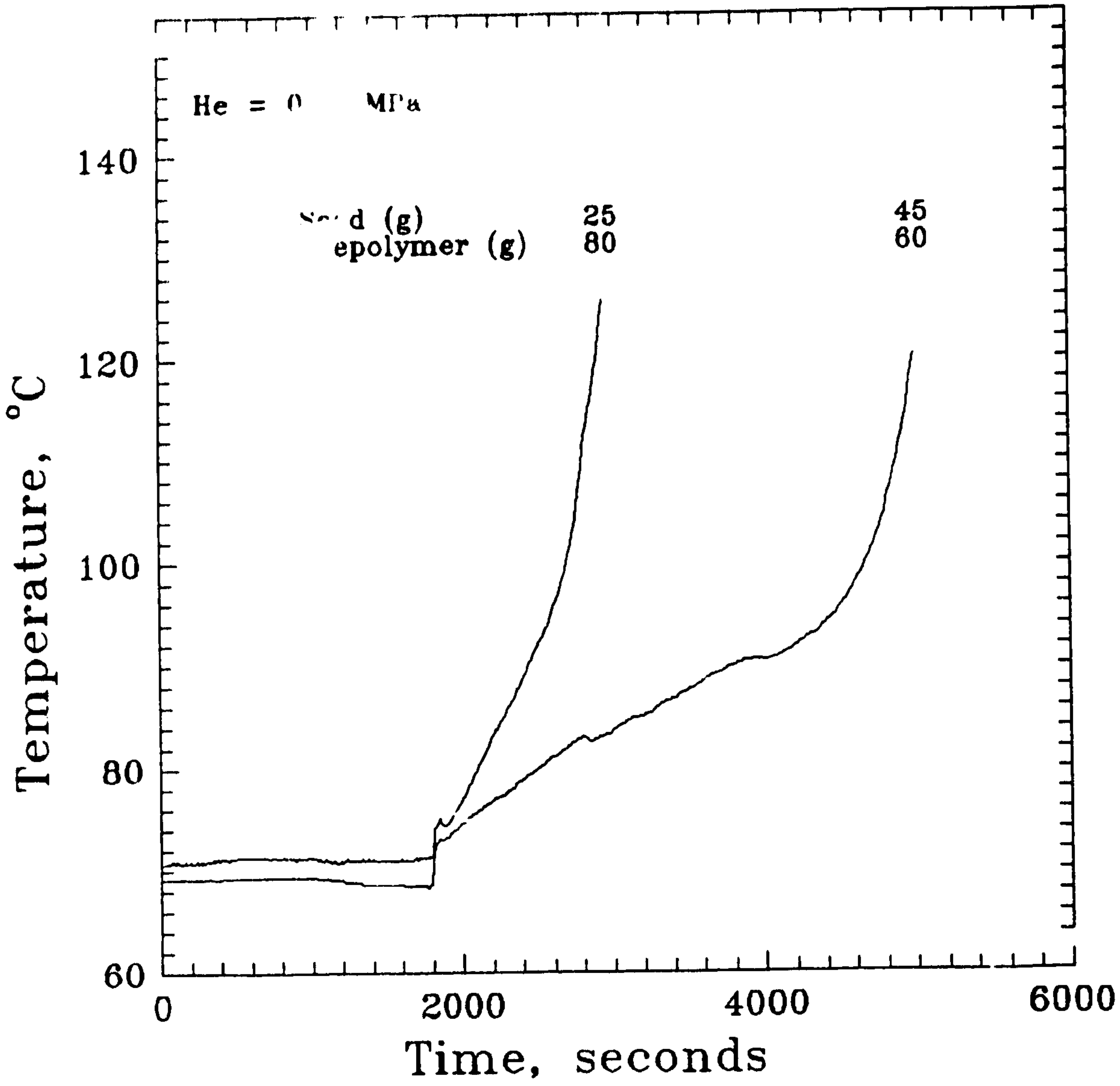


Figure 4.25 Variation of seed and prepolymer at constant total of 105 g

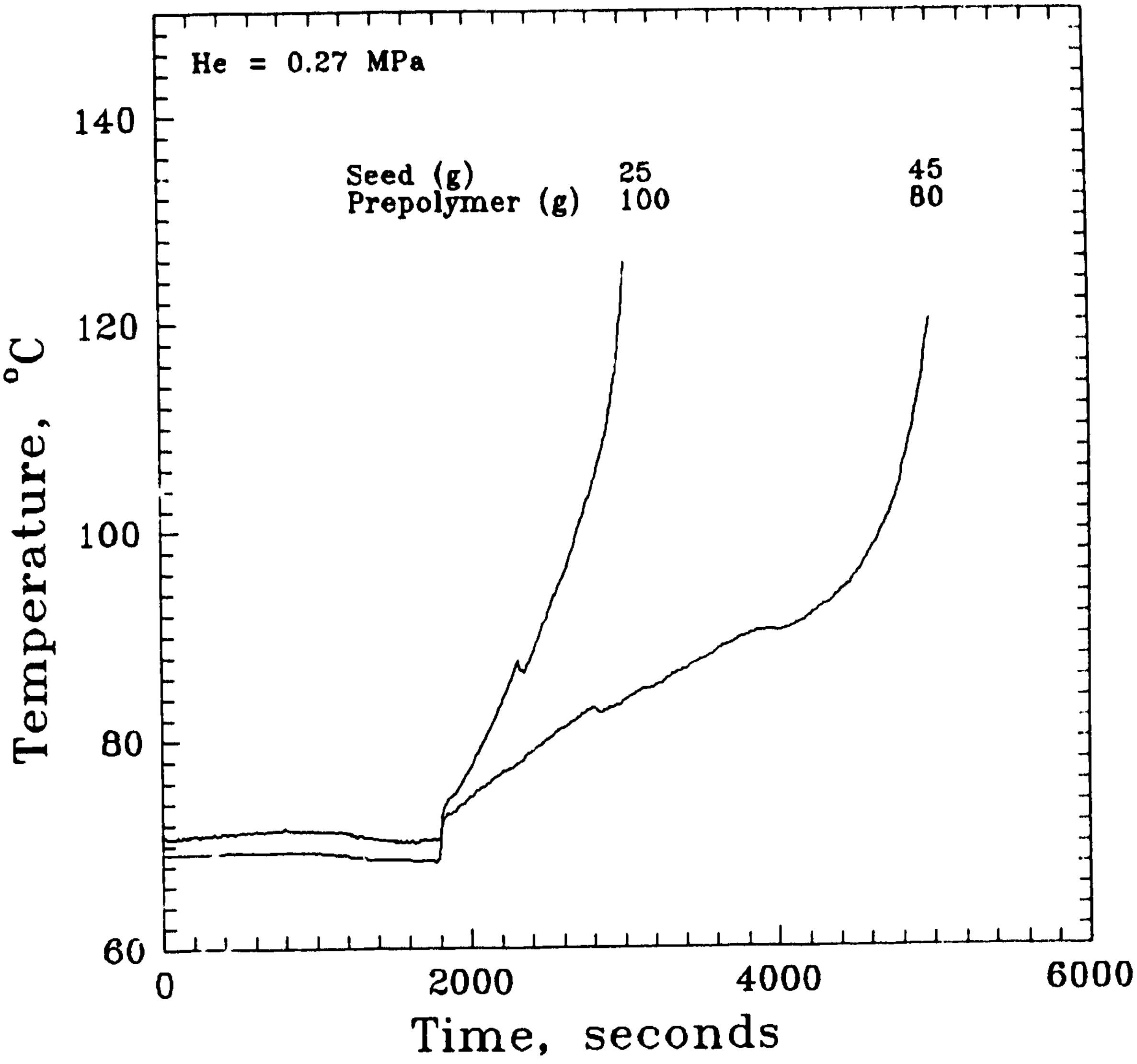


Figure 4.26 Variation of seed and prepolymer at constant total of 125 g

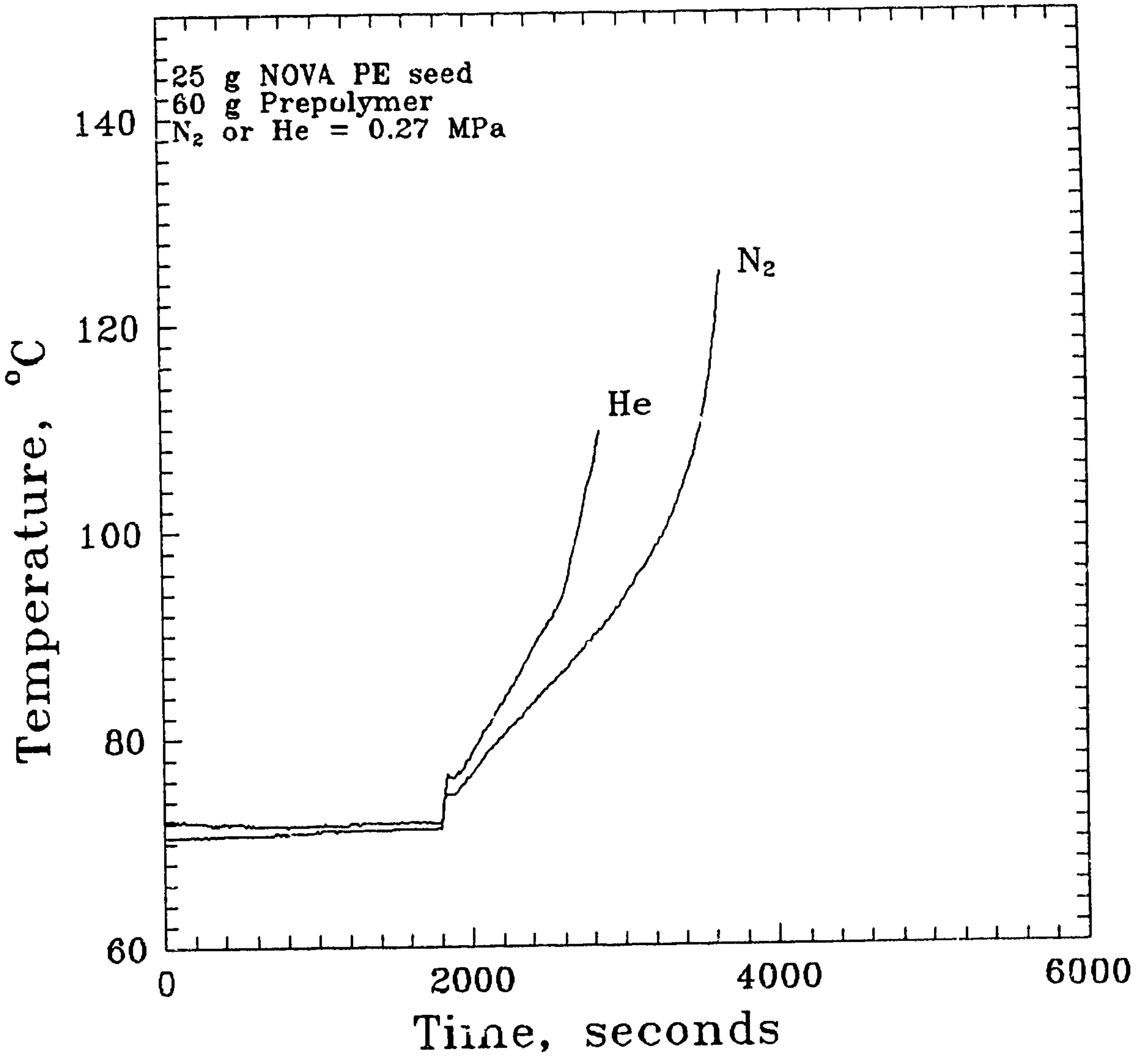


Figure 4.27 Variation of background gas at constant seed and prepolymer amount

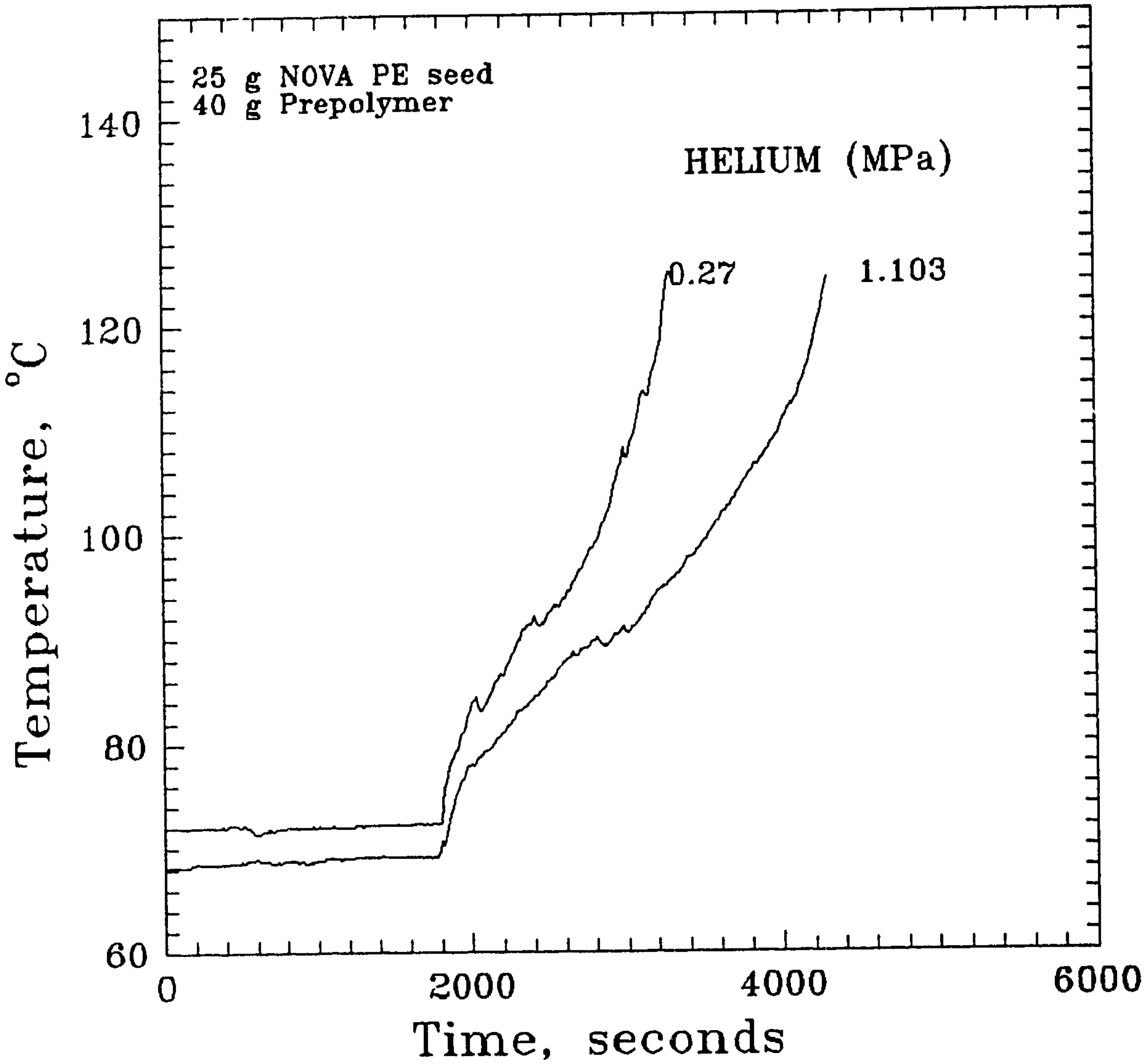


Figure 4.28 Variation in inert gas pressure at constant seed and prepolymer amount

amount of catalyst to compensate for the change in the ethylene partial pressure. For Run GAS9260, about 0.22 g of catalyst was used. Figure 4.28 compares the temperature profile obtained at helium partial pressure of 1.14 MPa (GAS9260) and 0.27 MPa (GAS9221). The behaviour is as expected; the higher thermal conductivity of the gas phase delayed the onset of thermal runaway.

4.6 Effect of Reaction Temperature

The gas-phase experiments were carried out with the oil bath at 70°C. It is important to study the effect of changing the reactor operating temperature because it could have a strong effect on the thermal runaway (parametric sensitivity) phenomena. Runs GAS9257 and GAS9256 were carried out at 50°C and 85°C respectively. The seed bed and prepolymer amounts were 25 g and 40 g, respectively, in both the experiments. As seen in Figure 4.29, thermal runaway did not occur when the reaction was carried at 50°C. Increasing the temperature to 85°C nearly doubled the rate of temperature rise when compared with the run GAS9221 carried out at 70°C.

4.7 Summary of Experimental Observations

On the basis of the results presented in this chapter, the following general observations can be made:

1. The onset of thermal runaway was delayed with increase in the mass of seed bed. This effect was as expected, i.e., the addition of inert solids inside the reactor acts as thermal capacitance and increasing the amount of seed bed delays the runaway behaviour.
2. The effect of prepolymer amount on the thermal behaviour of the reactor was unexpected. The cause of faster thermal runaway with increasing amounts of prepolymer in the reactor is not known. However, this phenomenon is probably related to the morphology of the catalyst-polymer particles on the seed bed and the catalyst fracture mechanism.
3. The effect of background gas on runaway rate was also unexpected. Thermal

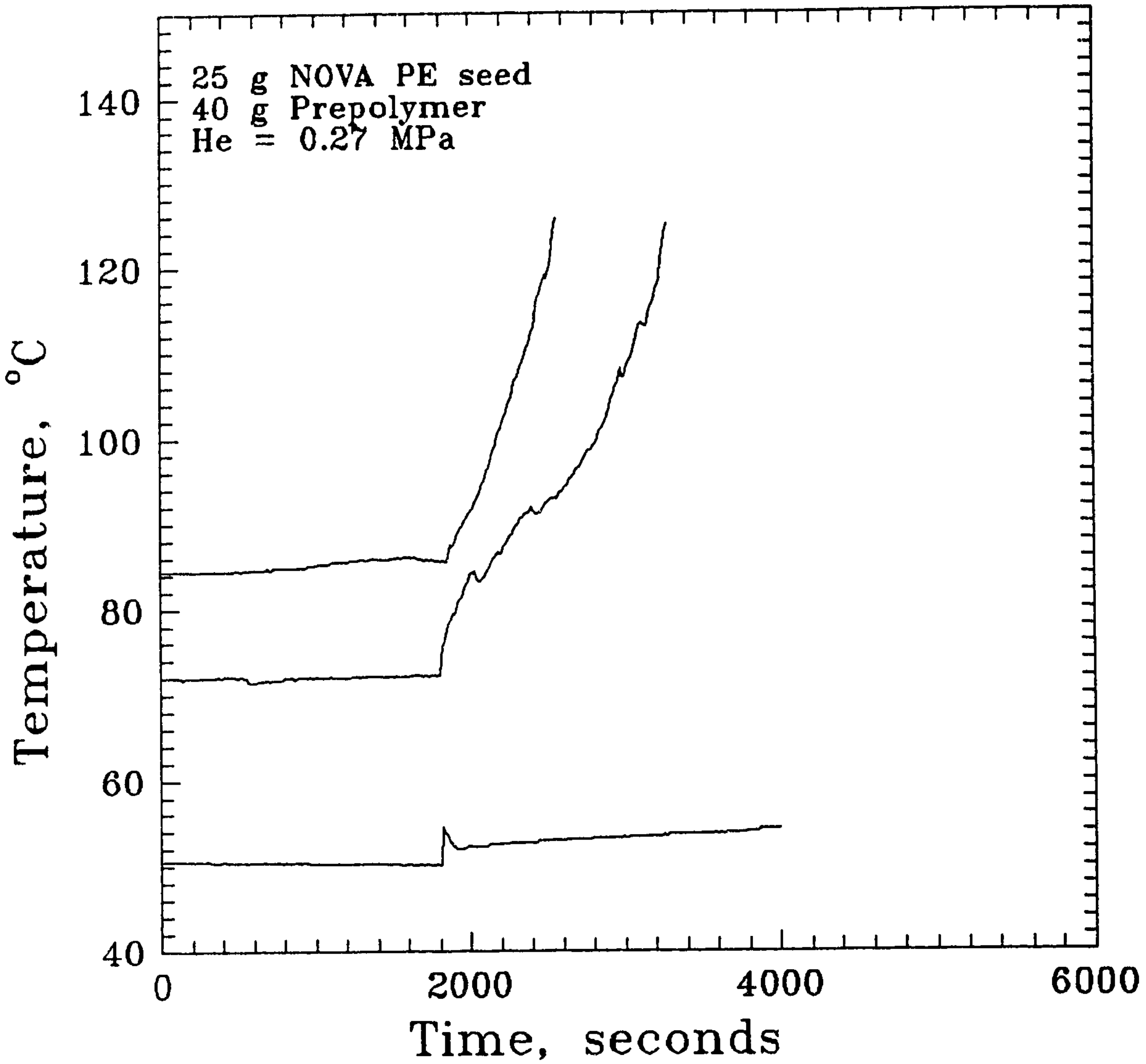


Figure 4.29 Variation in reaction temperature at constant seed and prepolymer amount.

conductivity of helium is nearly 6 times that of nitrogen. Therefore, it was expected that heat transfer from the heated polymer to the surrounding gas phase would be increased by replacing nitrogen with helium. However, the results showed that the onset of thermal runaway occurred earlier with helium than with nitrogen.

4. The oil bath temperature is an important parameter for controlling thermal runaway. The time for thermal runaway was considerably lower at the bath temperature of 85°C than at 70°C. At a bath temperature of 50°C, thermal runaway did not occur.

Table 4.1

Gas-phase Experiments GAS9108-9273

Run	Catalyst		Co-catalyst		Seed	Reaction Conditions		
GAS	Type	(g)	Type	(ml)	Bed	T(°C)	$P_{C_2H_4}$ (MPa)	P_{IN}(MPa)
9108*	AA 2.1	0.183	DEAC	0.5	40g TE	70	0.14-0.77	0.27 N_2
9109	AA 2.1	0.184	DEAC	0.5	18g PE	70	0.24-0.89	0.31 N_2
9110	AA 2.1	0.190	DEAC	0.5	80g PE	70	0.25-0.95	0.30 N_2
9111	AA 2.1	0.170	DEAC	0.5	18g PE	70	0.29-2.00	0.35 N_2
9201	AA 2.1	0.188	DEAC	1.0	50g PE	70	0.27-0.83	0.27 N_2
9202	AA 2.1	0.104	DEAC	0.5	25g PE	70	0.27-0.86	0.27 N_2
9203	AA 2.1	0.103	DEAC	0.5	25g PE	70	0.27-0.83	0.27 N_2
9204	AA 2.1	0.104	DEAC	0.5	25g PE	70	0.27-2.13	0.27 N_2
9205	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.27-2.13	0.27 N_2
9206	AA 2.1	0.099	DEAC	0.5	25g PE	70	0.26-2.22	0.29 N_2
9207	AA 2.1	0.106	DEAC	0.5	25g PE	70	0.27-2.65	0.27 N_2
9208	AA 2.1	0.104	DEAC	0.5	25g PE	70	0.27-2.55	0.27 N_2
9209	AA 2.1	0.110	DEAC	0.5	25g PE	70	0.55-2.46	0.27 N_2
9210	AA 2.1	0.108	DEAC	0.5	25g PE	70	0.55-2.55	0.27 N_2
9211	AA 2.1	0.108	DEAC	0.5	25g PE	70	0.55-2.31	0.27 N_2
9212	AA 2.1	0.108	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9213	AA 2.1	0.104	DEAC	0.5	25g PE	70	0.55-2.53	0.29 N_2
9214	AA 2.1	0.108	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9215	AA 2.1	0.103	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9216	AA 2.1	0.110	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9217	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.55-2.56	0.27 N_2
9218	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9219	AA 2.1	0.110	DEAC	0.5	25g PE	70	0.55-2.54	0.27 N_2
9220	AA 2.1	0.111	DEAC	0.5	65g PE	70	0.55-2.54	0.27 N_2
9221	AA 2.1	0.113	DEAC	0.5	25g PE	70	0.56-2.59	0.27 He
9222	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.55-2.54	0.27 He
9223	AA 2.1	0.113	DEAC	0.5	45g PE	70	0.55-2.55	0.27 He
9224	AA 2.1	0.110	DEAC	0.5	25g PE	70	0.56-2.57	0.27 He
9235	AA 2.1	0.114	DEAC	0.5	25g PE	70	0.55-2.55	0.27 He

Table contd.

Run	Catalyst		Co-catalyst		Seed	Reaction Conditions		
GAS	Type	(g)	Type	(ml)	Bed	T(°C)	$P_{C_2H_4}$(MPa)	P_{IN}(MPa)
9236	AA 2.1	0.113	DEAC	0.5	25g PE	70	0.55	0.27 He
9237	AA 2.1	0.112	DEAC	0.5	25g PE	70	0.55-2.52	0.27 He
9238	AA 2.1	0.112	DEAC	0.5	25g PE	70	0.56-2.55	0.27 He
9239	AA 2.1	0.113	DEAC	0.5	25g PE	70	0.55-2.55	0.27 He
9240	AA 2.1	0.113	DEAC	0.5	25g PE	70	0.55-2.55	0.27 He
9250	AA 2.1	0.109	DEAC	0.5	45g PE	70	0.55-2.55	0.27 He
9251	AA 2.1	0.109	DEAC	0.5	45g PE	70	0.55-2.57	0.28 He
9252	AA 2.1	0.109	DEAC	0.5	45g PE	70	0.55-2.41	0.27 He
9253	AA 2.1	0.111	DEAC	0.5	45g PE	70	0.55-2.55	0.27 He
9254	AA 2.1	0.107	DEAC	0.5	65g PE	70	0.55-2.55	0.27 He
9255	AA 2.1	0.107	DEAC	0.5	65g PE	70	0.55-2.55	0.27 He
9256	AA 2.1	0.110	DEAC	0.5	25g PE	85	0.55-2.55	0.27 He
9257	AA 2.1	0.108	DEAC	0.5	25g PE	50	0.56-2.55	0.27 He
9258	AA 2.1	0.200	DEAC	1.0	25g PE	70	0.27-1.28	1.55 He
9259	AA 2.1	0.200	DEAC	1.0	50g PE	70	0.27-1.32	1.55 He
9260	AA 2.1	0.218	DEAC	1.0	25g PE	70	0.28-1.69	1.14 He
9261	AA 2.1	0.220	DEAC	1.0	50g PE	70	0.27-1.59	1.23 He
9262	AA 2.1	0.116	DEAC	0.5	25g PE	70	0.55-2.55	0.27 N_2
9263	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.55-2.55	0.27 N_2
9264	AA 2.1	0.108	DEAC	0.5	25g PE	70	0.56-2.55	0.27 N_2
9265*	AA 2.1	0.109	DEAC	0.5	25g PE	70	0.55-2.55	0.27 N_2
9266	AA 2.1	0.108	DEAC	0.5	45g PE	70	0.55-2.58	0.27 N_2
9267	AA 2.1	0.110	DEAC	0.5	45g PE	70	0.55-2.57	0.27 N_2
9268	AA 2.1	0.109	DEAC	0.5	45g PE	70	0.56-2.54	0.27 N_2
9269	AA 2.1	0.109	DEAC	0.5	65g PE	70	0.55-2.55	0.27 N_2
9270	AA 2.1	0.110	DEAC	0.5	65g PE	70	0.55-2.52	0.27 N_2
9271	AA 2.1	0.111	DEAC	0.5	45g PE	70	0.55-2.55	0.27 N_2
9272	AA 2.1	0.111	DEAC	0.5	25g PE	70	0.55-2.55	0.27 N_2
9273	AA 2.1	0.110	DEAC	0.5	45g PE	70	0.55-2.55	0.27 N_2

+ Seed bed used: PTFE (-600, +425μm) ; * Seed bed used: PE (-600, +425 μm)
Rest of the runs, seed bed used: PE (-841, +355 μm)

5 REACTOR MODEL

The prediction of thermal runaway in gas-phase ethylene polymerization reactors has immediate consequences in industrial operations. The occurrence of thermal excursion followed by agglomeration of product can result in major breakdown of plant operation. It is critical to be able to predict the effect of various operating parameters on the thermal runaway of the reactor.

The various macroscopic models proposed for the gas-phase polymerization reactors have been discussed in Chapter 2. Although there has been some study on the modelling of semibatch stirred-bed reactors, most of the models have assumed isothermal operation. The focus here was on developing a macroscale reactor model with emphasis on heat removal limitations and resultant nonisothermalities of the contents of the reactor. The model predictions were compared with the experimental results.

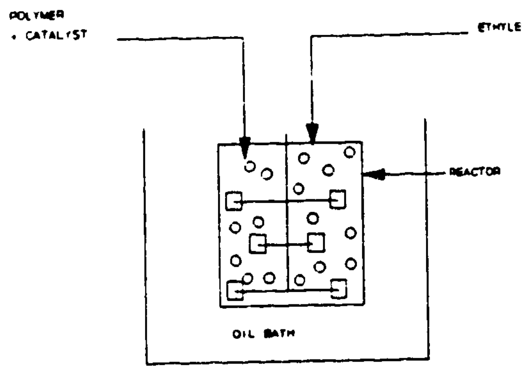


Figure 5.1 Semibatch stirred-bed reactor for gas-phase polymerization

5.1 Description of Reactor Model

The schematic of the reactor used for modelling, is shown in Figure 5.1. The following assumptions were made to formulate the simplified macroscale model of the reactor.

1. The reactor consists of a solid-free gas-phase zone and a reacting powder bed

of catalyst, seeds and polymer product. Perfect backmixing of gas and solids is assumed. The distribution of Stauffer catalyst on the surface of the polyethylene seed bed is assumed to be uniform.

2. Active catalyst is added to the reactor at the beginning of the run. Stable activity is assumed throughout the polymerization reaction. The initial acceleration period observed for Stauffer AA Type 2.1 catalyst is neglected.
3. The solid phase is at the uniform temperature T_p. The gas phase consisting of ethylene and inert gas (nitrogen or helium) is at the uniform temperature T_g. The reactor contents are well mixed.
4. The temperature T_p and T_g of the solid phase and gas phase are different depending on the heat transfer coefficient (h.t.c) between the solid and the gas phase; and the overall h.t.c between the bed and the wall.
5. There are no diffusional resistances within the growing polymer particles. Hence, there are no concentration and temperature gradients within the polymer particles.
6. The polymerization reaction proceeds equally on the seed particles.
7. There is no ethylene transfer resistance to the active sites on the catalyst.
8. The temperature dependence of the polymerization reaction is described by the Arrhenius expression.
9. The physical properties of the gas and solid phases are those of gaseous monomer and solid polymer, respectively. The ideal gas law is applicable to the gas phase.
10. There is no catalyst deactivation until the temperature reaches the melting point of the polymer.

The agglomeration of product due to melting polymer was observed only after the final temperature exceeded the melting point of polyethylene. Appendix D summarizes the catalyst activity profile for some runs after thermal runaway occurred in the reactor.

With these assumptions, the following independent variables are identified for the well-mixed, semibatch, stirred-bed reactor.

$N_{C_2H_4}$ = amount (moles) of C_2H_4 in reactor

m_{PE} = mass of PE in reactor

V_g = gas phase volume in reactor

T_p = temperature of solid phase

T_g = temperature of gas phase

R_p = radius of solid particles

The material and energy balance equations for the reactor of volume *V* takes the following form:

1. Mass of PE in Reactor (m_{PE})

$$\frac{dm_{PE}}{dt} = m_{cat}\, r_p \tag{5.1}$$

2. Volume of Gas in Reactor (V_g)

$$\frac{dV_g}{dt} = -\frac{m_{cat}\, r_p}{\rho_{PE}} \tag{5.2}$$

3. Ethylene in Gas Phase ($N_{C_2H_4}$)

$$\frac{dN_{C_2H_4}}{dt} = \frac{P_t}{RT_g}\frac{dV_g}{dt} - \frac{P_t V_g}{RT_g^2}\frac{dT_g}{dt} \tag{5.3}$$

4. Solid Particle Temperature (T_p)

$$\frac{dT_p}{dt} = \frac{h_{pg}\, N_p\, A_p\, (T_g - T_p) - \Delta U_R\, m_{cat}\, r_p}{m_{seed}\, C_{v,seed} + m_{PE}\, C_{v,PE}} \tag{5.4}$$

5. Gas-Phase Temperature (T_g)

$$\frac{dT_g}{dt} = \frac{h_{pg}\, N_p\, A_p\, (T_p - T_g) - U_w\, A_w\, (T_g - T_{bath})}{N_{C_2H_4}\, C_{P,ethylene} + N_{inerts}\, C_{P,inerts}} + \frac{F_g\, C_{P,ethylene}\, (T_{in} - T_g) + R\, T_g \dfrac{dN_{C_2H_4}}{dt}}{N_{C_2H_4}\, C_{P,ethylene} + N_{inerts}\, C_{P,inerts}} \tag{5.5}$$

6. Radius of Solid Particle (R_p)

$$\frac{dR_p}{dt} = \frac{m_{cat}\, r_p}{A_p\, \rho_{PE}} \tag{5.6}$$

h_{pg} represents the heat transfer coefficient from a single growing polymer particle to the surrounding gas phase. U_w represents the overall heat transfer coefficient from the bed to the outside oil bath. It is represented by the following equation:

$$U_w = \frac{1}{\dfrac{1}{h_o} + \dfrac{1}{h_w} + \dfrac{x\, A_w}{k_w\, A_{w,m}}} \tag{5.7}$$

where

h_w = bed-wall heat transfer coefficient

h_o = outside heat transfer coefficient of the oil bath

x = thickness of the wall

A_w = outside heat transfer area

$A_{w,m}$ = mean heat transfer area

k_w = thermal conductivity of the reactor vessel material (SS 316)

Since the catalyst distribution was assumed to be uniform on the surface of the seed bed particles, the size of all growing polymer particles is equal. In the case of the number of seed particles being more than the number of catalyst particles, the number of growing polymer particles (N_p) is always limited to the number of catalyst particles, the rest of the seed particles were assumed not to be taking part in the growth process, i.e., N_p is constant.

The ideal gas ethylene heat capacity $C_{p,o}$ relation given by Equation 5.8 was corrected for variation in pressure and temperature. Equation 5.10 represents the correlation used for the specific heat of ethylene gas.

$$\frac{C_{p,o}}{R} = 4.0 + \sum_{i=1}^{12} u_i^2 \frac{e^{u_i}}{(e^{u_i} - 1)^2} \tag{5.8}$$

where

$$u_i = \frac{a_i}{T} \tag{5.9}$$

$$\frac{C_{p,ethylene}}{R} = \frac{C_{p,o}}{R} + 0.17*P + \frac{5.5}{T^2} \tag{5.10}$$

The program used to obtain the correlation of specific heat of ethylene gas as a function of temperature and pressure is given in Appendix E.

Equations 3.1 and 3.2 describe the average polymerization rate (r_p) and the pseudo-first-order rate constant (k) of ethylene polymerization on Stauffer AA type 2.1 catalyst.

A_p is the surface area of the growing polymer particle. The polymer particle was assumed to be spherical and the surface area was calculated knowing the radius of the polymer particle (from Equation 5.6). A_w is the external surface area available for thermal energy transfer from the reactor to the oil bath. It was calculated assuming the whole reactor to be immersed in the oil bath. The temperature across the oil bath was assumed to be uniform. The detailed calculation of A_w is shown in Appendix F. The numerical values of all the physical constants and the standard reactor operating parameters are tabulated in Table 5.1.

The numerical values of h_{pg} and U_w also had to be obtained for the model. For determining the overall heat transfer coefficient (U_w), it is necessary to know the bed-wall heat transfer coefficient (h_w) and outside (oil bath) heat transfer coefficient (h_o).

5.2 Particle-Gas Heat Transfer (h_{pg})

There has not been much study on particle-fluid heat transfer in stirred-bed reactors. Therefore, the correlations available for particle-fluid heat transfer in fluidized bed reactors were used. For particle-gas heat transfer in a fluidized bed, many correlations, statements, and conclusions are found in literature because of the complicated flow characteristics that make the experiments difficult to perform. Various correlations which have been proposed in the literature for particle-fluid heat transfer are listed below.

The following correlation for a single sphere in a fluid medium moving with relative velocity u was proposed by Ranz and Marshall (1952):

$$N_u = 2 + 0.6\, N_{Re}^{1/2}\, N_{Pr}^{1/3} \tag{5.11}$$

where

$$N_u = \frac{h_{pg}\, d_p}{k_f} \tag{5.12}$$

$$N_{Re} = \frac{\rho u d_p}{\mu} \tag{5.13}$$

$$N_{Pr} = \frac{\mu C_{p,ethylene}}{k_f} \tag{5.14}$$

Kunii and Levenspiel (1969) proposed the following correlation for fluidized beds:

$$N_u = 0.03\, N_{Re}^{1.3} \tag{5.15}$$

Similar correlations were proposed by Kettenring et al. (1950):

$$N_u = 0.0135\, N_{Re}^{1.3} \tag{5.16}$$

Zenz and Othmer (1960)

$$N_u = 0.017\, N_{Re}^{1.21} \tag{5.17}$$

and Borodulya et al. (1980)

$$N_u = 0.37\, N_{Re}^{0.71}\, N_{Pr}^{0.31} \tag{5.18}$$

5.3 Bed-Wall Heat Transfer (h_w)

Three correlations were examined for the bed-wall heat transfer coefficient.

These were the Dow and Jacob correlation for a fluidized bed with particle diameters between 0.007-0.017 cm (Kunii and Levenspiel, 1969):

$$N_u^{\,w} = 0.55\, N_{Re}^{0.8} \left(\frac{\rho_{PE} C_{p,PE}}{\rho_g C_{p,ethylene}}\right)^{0.25} \left(\frac{d_t}{d_p}\right)^{0.03} \left(\frac{L_f}{d_t}\right)^{-0.65} \left(\frac{1-\epsilon_f}{\epsilon_f}\right)^{0.25} \tag{5.19}$$

and correlations by
Van Heerden et al. (Kunii and Levenspiel, 1969):

$$N_u^{\,w} = 0.058\, N_{Pr}^{\,0.5} (\beta N_{Re})^{0.45} \left(\frac{C_{p,PE}}{C_{p,ethylene}}\right)^{0.36} \left(\frac{\rho_{PE}\,(1-\epsilon_f)}{\rho_g}\right)^{0.18} \tag{5.20}$$

and Kunii and Levenspiel (1969):

$$N_u^{\,w} = 0.6\, N_{Pr}\, N_{Re}^{\,0.3} \tag{5.21}$$

where,

$$N_u^{\,w} = \frac{h_w d_p}{k_f} \tag{5.22}$$

β = Shape factor of the particles
ϵ_f = Voidage
L_f = Length (height) of fluidized bed

The outside heat transfer coefficient (h_o) was considered to be constant for the polymerization reaction. The lower range of h_o is the value obtained for natural convection inside the oil bath. The contents of the oil bath were stirred vigorously with the help of a constant speed stirrer which was placed inside the bath. The value of the heat transfer coefficient in the case of vigorous stirring (forced convection) can be as much as 10 times higher than the value obtained with natural convection. The value of h_o estimated assuming natural convection is nearly 500 J/(m^2.s.K). In Appendix G numerical calculations for natural convection heat transport are shown.

During the simulation study, the value of h_o was assumed to be 5000 J/(m^2.s K), 10 times the natural convection heat transfer coefficient.

Equations 5.1 to 5.6 were solved using various correlations for h_{pg}, h_w and U_w so as to obtain the values of the dependent variables as a function of time. The six coupled ordinary differential equations were solved using the Runge-Kutta-Fehlberg variable step size (4th and 5th order) routine. Initial conditions and more details on the method of solution are given in Appendix H. The computer program for the solution is shown in Appendix I.

In order to use correlations 5.11 through 5.21 for h_{pg} and h_w, it is necessary to determine the solid/gas relative velocity u. From physical reasoning, it could be assumed that the relative velocity of particle and gas is roughly that of free fall due to gravity. But mechanical agitation of the reactor contents can increase the relative velocity considerably. A relative velocity of 20 cm/s has been predicted for some regions in industrial sized fluidized beds. But at the high agitation speed (>500 rpm) of the experimental stirred-bed reactor, the (radial) tip speed calculated at the stirrer blade is nearly 700 cm/s. The average speed of the liquid jet across the vessel interior is about 15-20% of the tip speed. In case of agitation in the presence of gas, the average relative speed could be considerably lower than the above value (up to 10% of the tip speed), i.e., the value of u could be about 70 cm/s. It was decided to use the average of the value predicted by tip speed (70 cm/s) and that reported for industrial fluidized beds (20 cm/s). For all the further simulation studies, the relative velocity u was assumed constant at 45 cm/s.

The predicted values of solid-gas heat transfer coefficient (h_{pg}) for the various correlations are plotted in Figure 5.2. Note that the Ranz-Marshall correlation predicts the lowest value of h_{pg} and most of the fluidized bed correlations (Kettenring, Zenz-Othmer & Borodulya) predict very similar values. As noted earlier, heat transfer coefficients may be larger than those estimated using the terminal velocity of the particles. Also, there is uncertainty about the accuracy of the correlations for the stirred-bed mode of fluidization. Thus, more definitive research

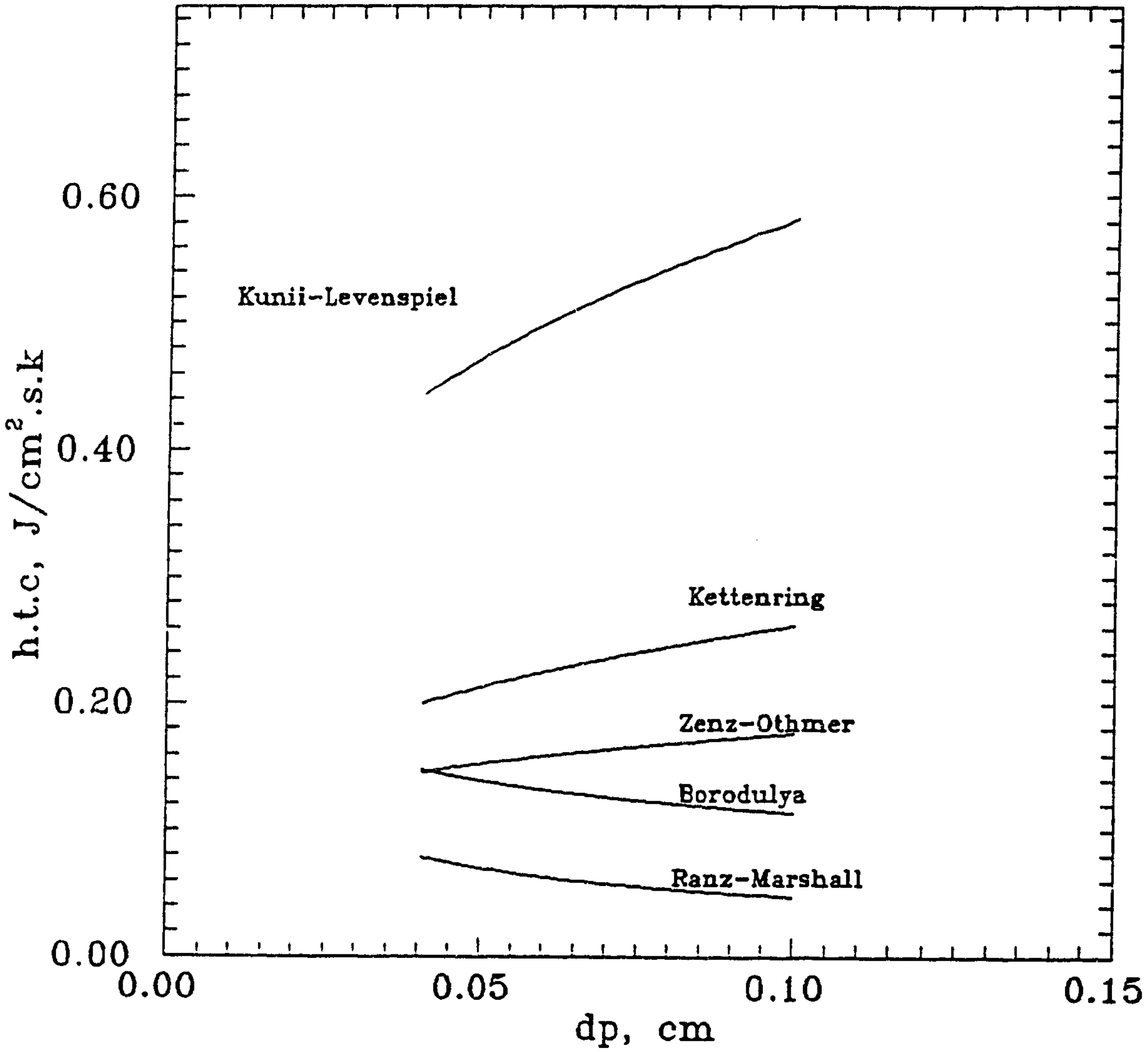


Figure 5.2 Solid-gas heat transfer coefficients for various correlations

is required to confirm the actual heat transfer coefficients for particles in solid/gas stirred-bed systems. The Zenz-Othmer correlation was chosen to obtain the values of h_{pg}, for comparing the predictions of the model with the experimental results, because this correlation is "average" in its prediction of solid/gas heat transfer coefficient.

Of all the various correlations examined for the prediction of the bed-wall heat transfer coefficient in fluidized beds, the Kunii-Levenspiel correlation gave the smallest value of the heat transfer coefficient. Thus, to be conservative, the Kunii-Levenspiel correlation was used to predict the bed-wall heat transfer coefficient (h_w) values. Hence, the value obtained for the overall heat transfer coefficient (U) for the reactor would be a highly conservative "worst case". In reality, the temperatures of solid and gas phases could be considerably lower than the simulation results.

A sensitivity analysis was carried out for u and h_o. The effect of relative velocity of solid and gas on the final temperature of the gas phase predicted by the model, is shown in Figure 5.3. In order to facilitate comparison with the experimental results, the gas phase temperatures are shown in all further model predictions, since the temperatures measured by the thermocouples at the various locations (2 to 6) during the experiments are essentially for the gas phase.The model predictions were obtained with the same initial conditions as that used for experiments. The outside heat transfer coefficient was fixed at 5000 J/(m^2.s.K), the seed bed at 65 g and the amount of prepolymer at 40 g. After modelling the prepolymerization period, the ethylene partial pressure was increased from 0.55 MPa to 2.55 MPa, which is same as that which occurred in the experiments.

As shown in Figure 5.3, the predicted temperatures of the gas phase during prepolymerization was approximately equal to the oil bath temperature (70°C) at velocities above 35 cm/s. Experimentally, it was observed that the reactor temperature was approximately the same as the oil bath temperature during prepolymerization. Hence, the relative velocities for the correlation should be above 35 cm/s.

The thermal runaway phenomena occurred very rapidly when the relative

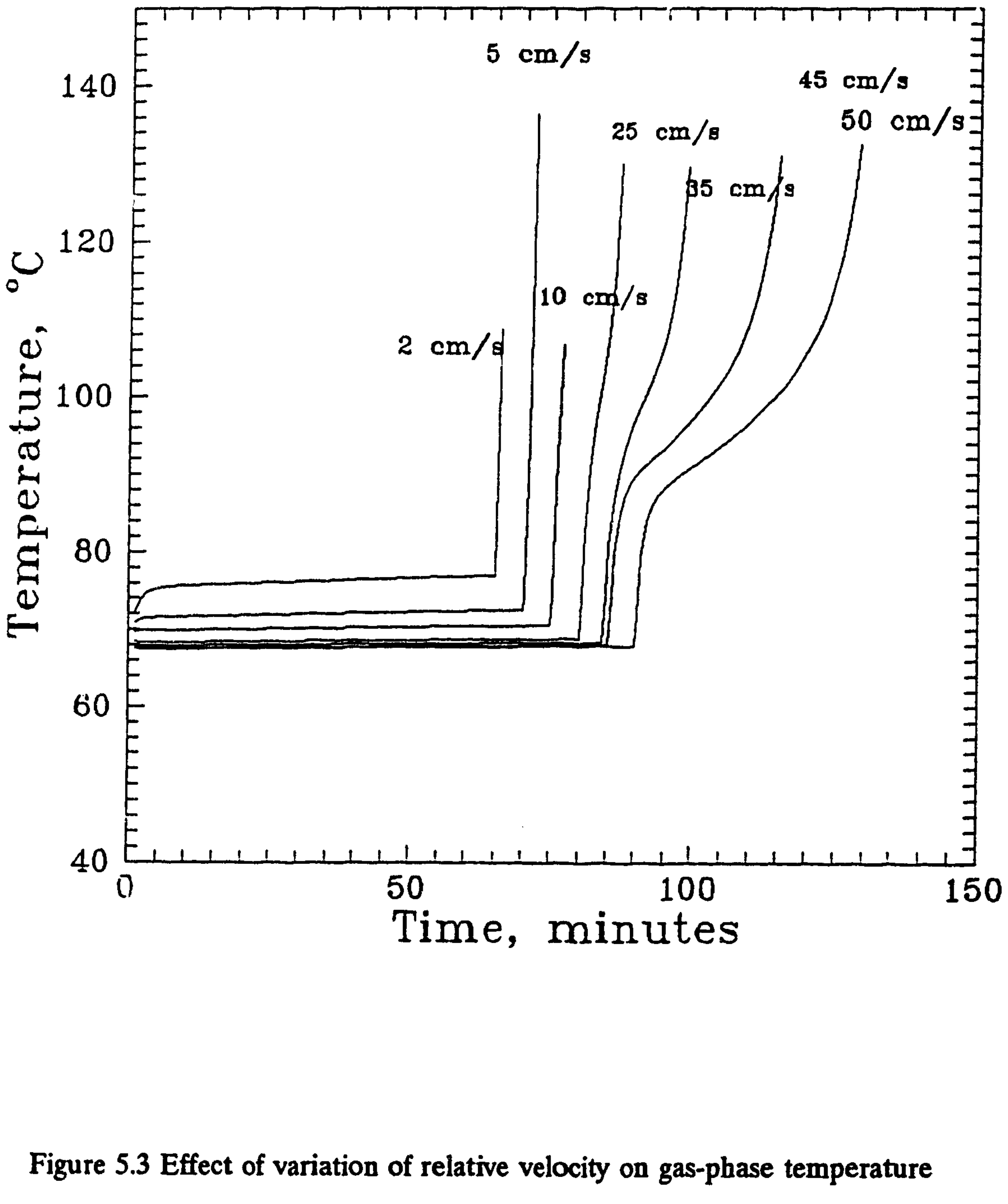


Figure 5.3 Effect of variation of relative velocity on gas-phase temperature

velocity of the solid particles was less than 35 cm/s. For simulations with u of 2, 5 and 10 cm/s, the time required for reaching the melting point of the polymer after increasing the ethylene pressure to the final value, was 1, 2 and 3 minutes, respectively. In the experimental runs, the time required for thermal runaway to occur in the reactor was much longer. When a relative velocity, u, of 35 cm/s or greater was used, the predicted thermal behaviour of the gas phase started resembling the experimentally observed profiles. The time required for the reactor temperature to reach the melting point of polymer when u is 35, 45 and 50 cm/s, was 16, 30 and 39 minutes, respectively. These times are similar to the experimentally observed values. Therefore, it was decided to use a relative velocity (u) of the solid/gas phase of 45 cm/s.

The choice of the outside (oil bath) heat transfer coefficient h_o was also subjected to careful inspection. Figure 5.4 shows the simulation results when the value of h_o was varied from 500 J/(m^2.s.K), obtained for natural convection flows, to 5000 J/(m^2.s.K) obtained in case of forced convection of the oil inside the bath. In all the model predictions described in Figure 5.4, the relative velocity was 45 cm/s, and the amounts of seed and prepolymer were 65 g and 40 g, respectively. Also, the initial and final values of ethylene partial pressure were the same as the values used for the experimental study. As shown in Figure 5.4, for the values of 500 and 1000 J/(m^2.s.K) of h_o, the time required for the reactor temperature to reach the melting point of the polymer was 5 and 11 minutes, respectively. The thermal behaviour predicted by the model, approached the experimentally observed profile for values of h_o greater than 2500 J/(m^2.s.K). Also, above 2500 J/(m^2.s.K), the runaway temperature of the reactor was not very sensitive to the value of the oil-bath heat transfer rate. Hence, the value of 5000 J/(m^2.s.K) was chosen for the outside heat transfer coefficient. Typical values of parameters used in the model are listed in Table 5.1.

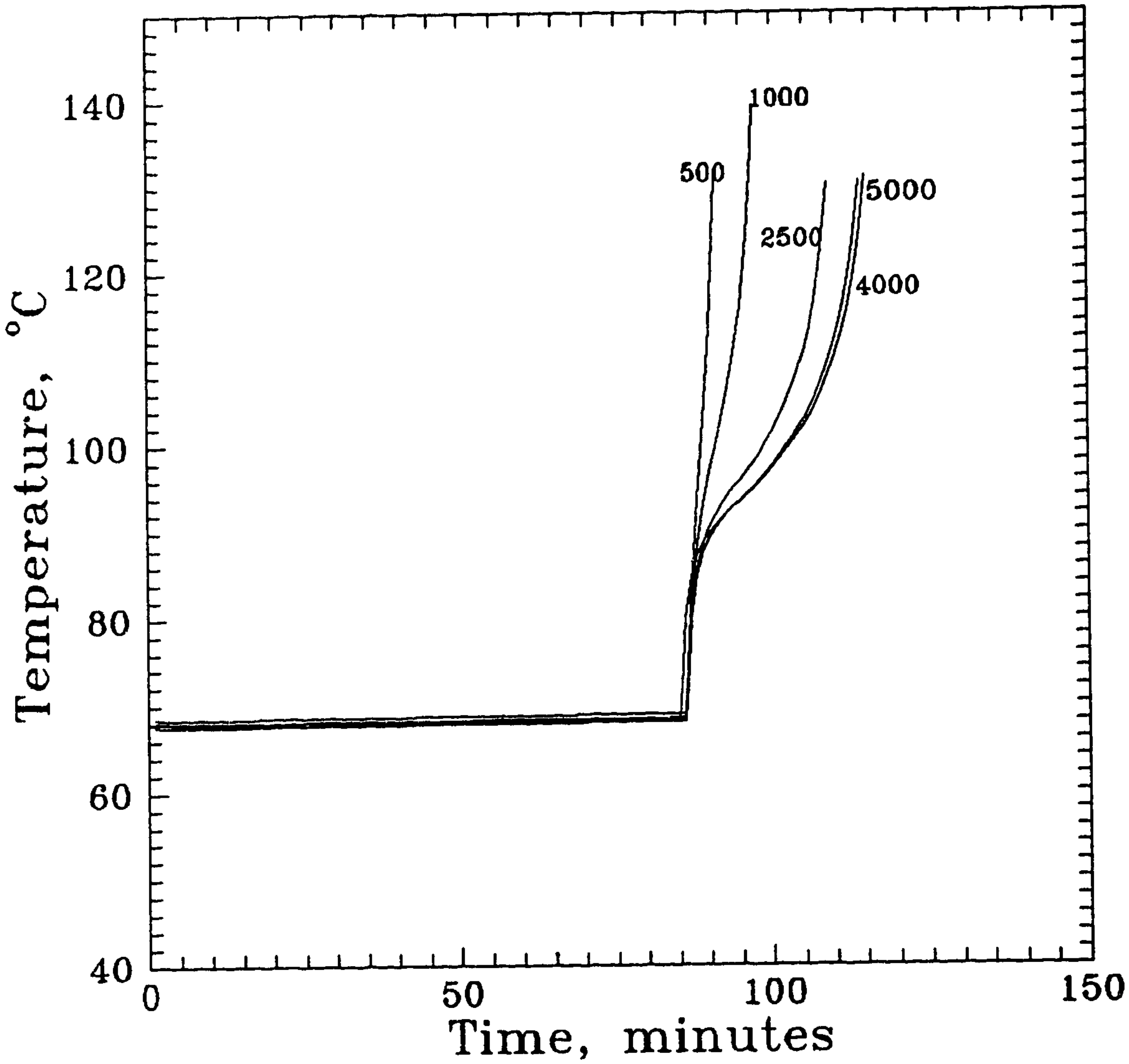


Figure 5.4 Effect of variation of outside heat transfer coefficient (h_o J/m^2.s.K) on gas-phase temperature

Table 5.1

Physical Constants and Standard Reactor Operating Parameters

Parameters	Symbols	Units	Values
Volume of Reactor	V	m^3	0.001
Mass of catalyst (typical)	m_{cat}	g	0.1
Mass of seed bed	m_{seed}	g	25
Average size of seed particles	d_p	μm	598
Reaction temperature	T	K	343
Density of polyethylene	ρ_{PE}	g/cm^3	0.9549
Specific heat of seed	$C_{v,seed}$	J/g K	2.4267
Specific heat of polyethylene	$C_{p,PE}$	J/g K	2.4267
Inlet temperature	T_{in}	K	298
Reference temperature	T_R	K	298
Heat of reaction at 298 K	$\Delta H(T_R)$	J/g C_2H_4	-3863.3
Universal Gas Constant	R	J/gmol K	8.314
Average molecular weight of polyethylene	MW_{PE}	g/gmol	144000
Average size of catalyst particles		μm	55
Density of Stauffer catalyst		g/cm^3	2.6
Mass of one catalyst particle	m_p	g	2.26495×10^{-7}
Relative velocity of fluid/particles	u	cm/s	45
Outside (oil) heat transfer coefficient	h_o	J/m^2 s K	5000
Molecular weight of ethylene	MW_{ethy}	g/gmol	28.05
Density of ethylene gas	ρ_g	g/cm^3	0.028
Thermal conductivity of nitrogen	$k_{nitrogen}$	mW/cm K	0.31
Thermal conductivity of helium	k_{helium}	mW/cm K	1.72
Thermal conductivity of ethylene	k_f	mW/cm K	0.2853
Viscosity of ethylene	μ	g/cm s	0.012×10^{-2}
External surface area of reactor	A_w	cm^2	730.1
Voidage	ϵ_f		0.7
Shape factor of the particles	β		1.0
Length of fluidized bed	L_f	cm	7.15
Thickness of the wall	x	cm	0.013
Inside heat transfer area	A_i	cm	537.0
Thermal conductivity of SS 316	k_w	W/m K	16.26

6 COMPARISON OF SIMULATION RESULTS WITH EXPERIMENTS

In this chapter, the experimental observations presented in Chapter 4 are compared to the predictions by the model described in Chapter 5. Before beginning these comparisons, it should be reiterated that the model is a simple macro-model which does not describe any of the processes occurring inside the growing polymer particles. Furthermore, no attempts were made to 'fit' parameters to the experimental data. The objective of the comparison of the model and experimental results is to determine whether the simple model predicts the correct trends in the observed experimental behaviour. Experiments had shown that the thermal behaviour critically depends on the concentration of ethylene in the reactor. The experimentally observed thermal behaviour of the reactor and the temperature profiles predicted by the model are compared in Figure 6.1 for various ethylene partial pressures. The amount of seed bed, amount of prepolymer and nitrogen pressure were the same for the simulation and experiments.

The model predictions and the experimental results were in excellent agreement during the prepolymerization stage (ethylene pressure of 0.55 MPa), i.e., the reactor temperature in both cases was essentially equal to the oil bath temperature. The predicted and experimentally observed behaviours had similarities when the ethylene pressure was increased to 2.55 MPa, i.e., thermal runaway occurred in both cases, but the predicted runaway occurred much more rapidly than the experimentally observed runaway. However, at ethylene pressures of 2.14 MPA, the model still predicted thermal runaway, while no thermal runaway was observed experimentally at this ethylene pressure. Moreover, the predicted temperature profile for an ethylene pressure of 2.14 MPa was very similar to the experimentally observed profile at an ethylene pressure of 2.55 MPa. Stable thermal behaviour (no thermal runaway) was predicted by the model when the ethylene pressure was lowered to 1.96 MPa (see Figure 6.1).

These results indicate that the model displays parametric sensitivity to ethylene pressure (i.e. small changes in ethylene pressure caused large changes in

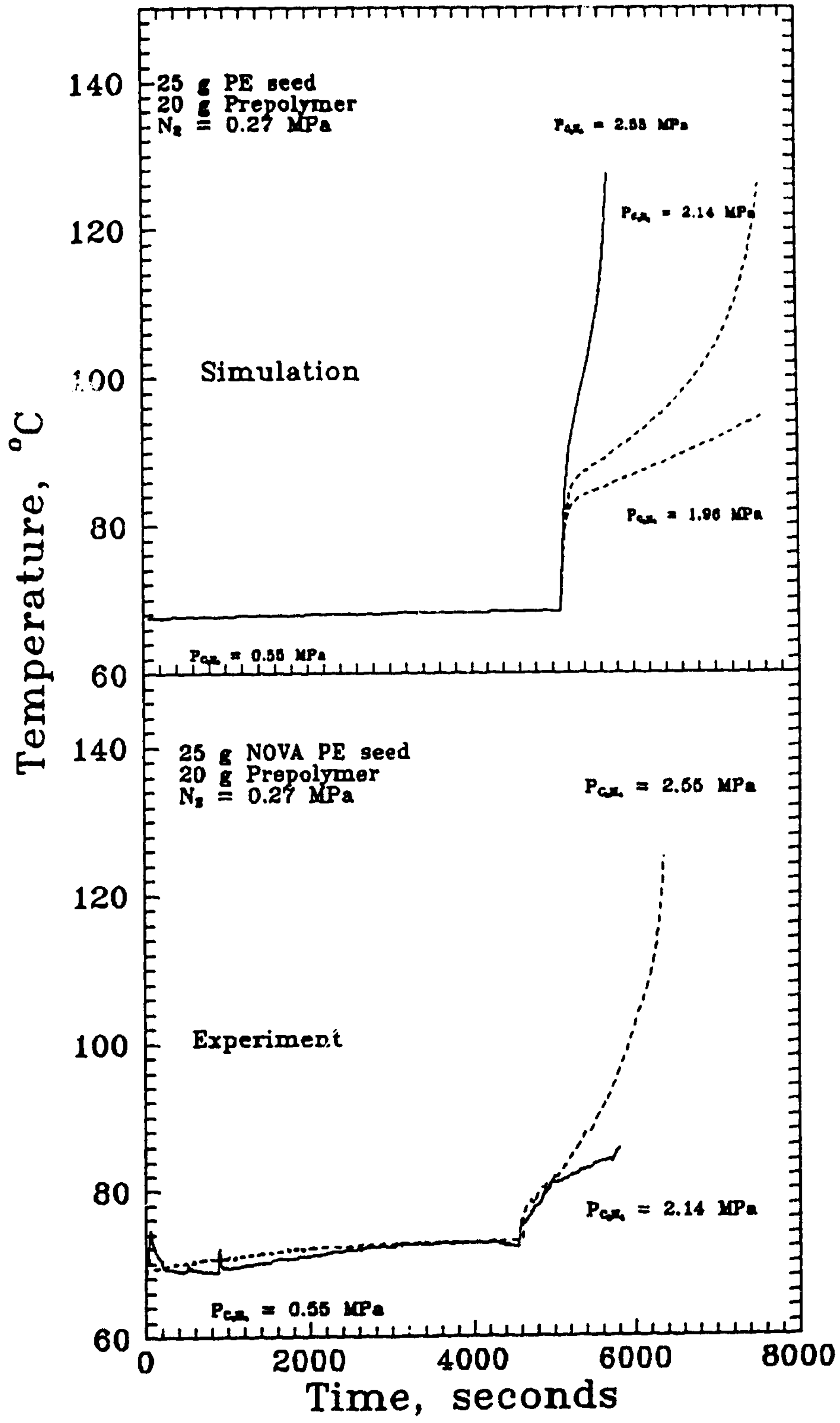


Figure 6.1 Effect of ethylene pressure

reactor temperature). The results also show that the model does a reasonably good job of predicting the qualitative behaviour of the temperature profile and better correspondence between measured and experimental temperature profiles shown in Figure 6.1 could be obtained by fine tuning the heat transfer parameters. However, the objective was to determine whether the model predicts the correct trends for variation in reactor operating parameter; hence, no fine tuning of heat transfer parameters was done.

The next operating parameter examined was the influence of the amount of polymer in the reactor at the time that the ethylene pressure was increased from the prepolymerization level of 0.55 MPa. Comparison of the bottom panel in Figure 6.1 with Figure 6.2 shows the effect of increasing both the amount of the seed bed (from 25 to 65 g) and the amount of prepolymer (20 to 40 g). Comparison of these two figures shows that according to the predictions of the model, thermal runaway is totally suppressed or the rate at which runaway occurs is decreased as the mass of polymer in the reactor is increased. This behaviour is the expected behaviour since increased polymer mass in the reactor provides increased thermal mass which would decrease the rate of temperature rise.

The effects of increasing the amount of seed bed at constant amount of prepolymer is shown in Figures 6.3 to 6.5. The temperature profiles from the experiments and those predicted by the model display similar behaviour for variations in the seed bed amount from 25 to 65 g with 40 and 60 g prepolymer (Figures 6.3 and 6.4, respectively). In these cases, increases in the amount of seed bed resulted in delayed onset of thermal runaway both in experimental observations and model predictions. However, for 80 g of prepolymer, thermal runaway was observed experimentally but the model predicted stable thermal behaviour (Figure 6.5). Comparison of the experimental results in Figures 6.4 and 6.5 shows that the thermal runaway for 80 g prepolymer and 25 g of seed bed occurred more rapidly than for 60 g prepolymer and 25 g of seed bed. This was very unexpected behaviour and a more detailed comparison of model predictions and experimental results for variations in the amount of prepolymer are presented in Figures 6.6 to 6.8.

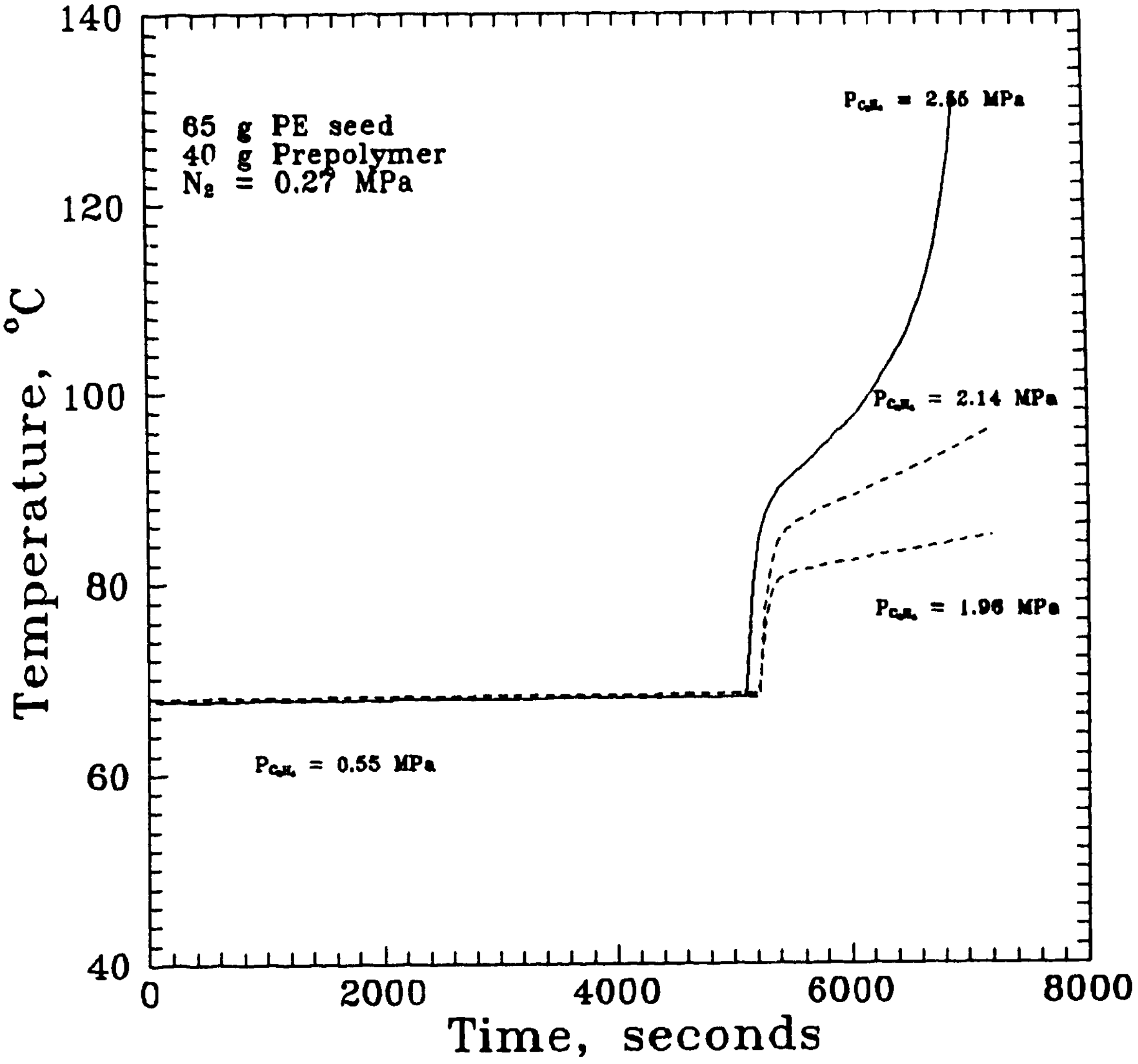


Figure 6.2 Effect of ethylene pressure on gas-phase temperature

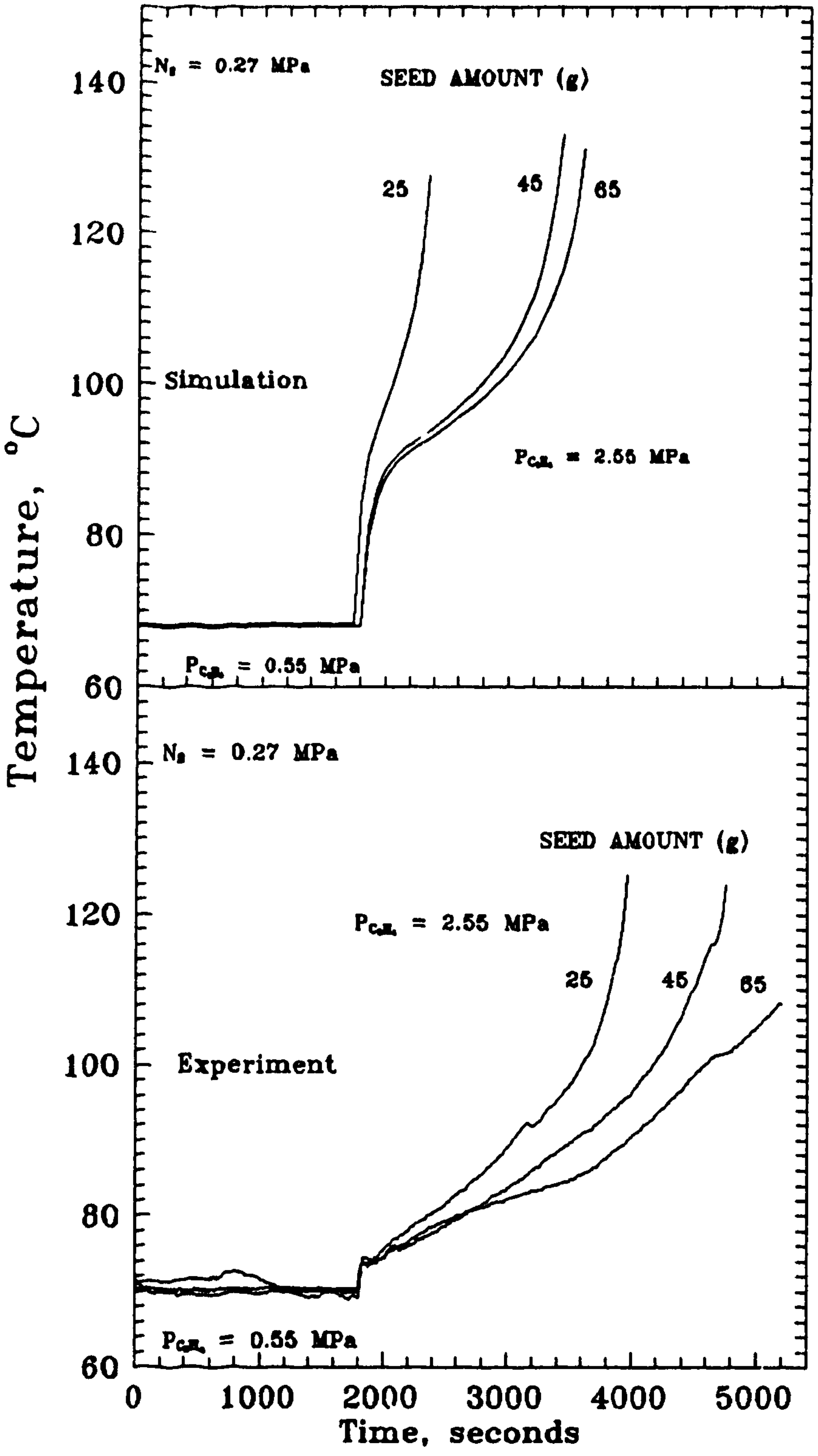


Figure 6.3 Variation of seed amount at 40 g prepolymerization

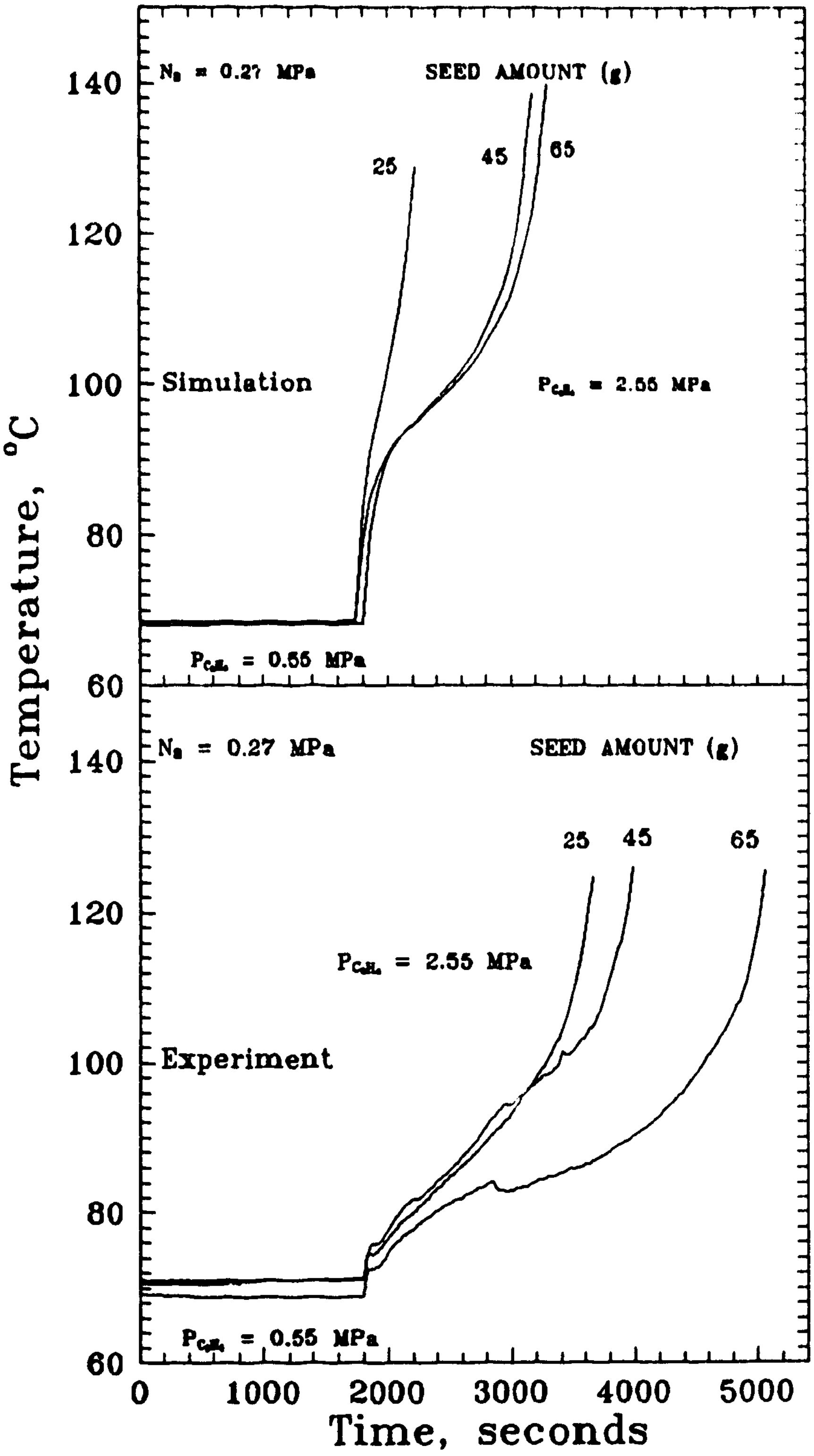


Figure 6.4 Variation of seed amount at 60 g prepolymerization

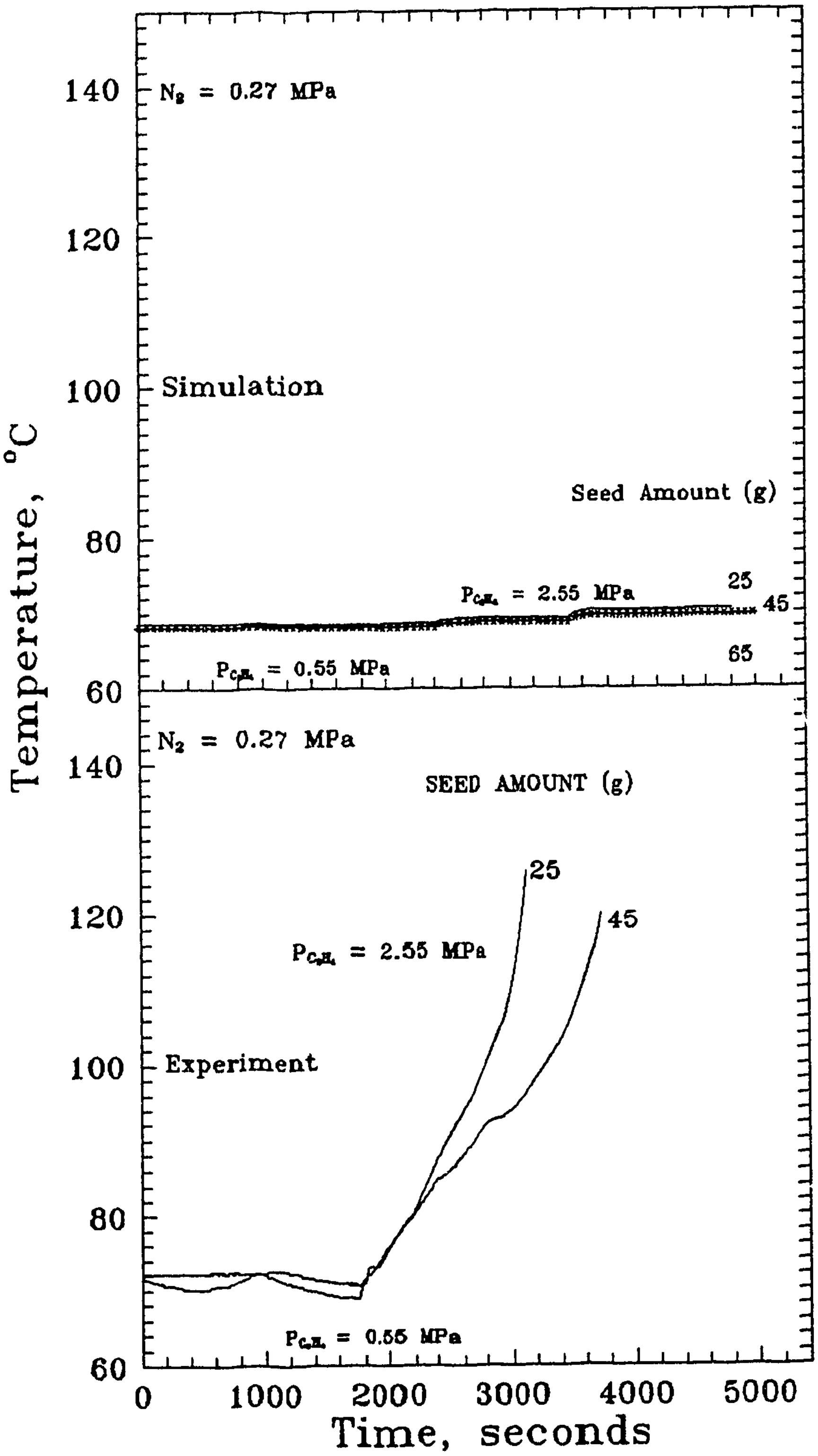


Figure 6.5 Variation of seed amount at 80 g prepolymerization

Figure 6.6 compares the experimental thermal behaviour and the model predictions for different prepolymer amounts (40, 60 and 80 g). The amount of seed bed was kept fixed at 25 g. The model predictions were in excellent qualitative agreement with the experimentally observed thermal behaviour for prepolymerization levels of 40 and 60 g; but the experimental temperature profile when the prepolymer amount was raised to 80 g is much different than the model prediction. It was observed experimentally that at prepolymer amounts of 80 g, the runaway occurred rapidly, but simulation results show that for 80 g prepolymer, the temperature of the gas phase remains practically isothermal even after raising the ethylene pressure to 2.55 MPa. This difference between observation and prediction could be attributed to effects taking place in the polymer particle. As the prepolymer amount is increased, polymer particles grow considerably and at large sizes, intraparticle thermal gradients could exist. In the simulation results, the growing polymer particle becomes quite large (size >1.0 mm) at 80 g of prepolymer. Even at such sizes, the polymer particles are assumed to be at a constant temperature and intraparticle effects were neglected. This is a possible reason for the observed difference in the temperature profiles at higher prepolymerization levels of 80 g. Errors in the heat transfer correlations are also a possible cause for the difference in observed and predicted behaviour.

Figures 6.7 and 6.8 further substantiate the necessity for accounting the intraparticle gradients in predicting the thermal behaviour of the reactor at the prepolymerization level of 80 g. Similar to the earlier observation (see Figure 6.6), it was noted that the model predicted qualitatively that the time required for reaching the melting point of the polymer decreased when the prepolymer amount was raised from 40 g to 60 g; but failed to predict thermal runaway at 80 g of prepolymer. In Figures 6.7 and 6.8, the amount of seed bed was kept constant at 45 and 65 g, respectively.

The combined effect of seed bed and prepolymer amounts on the thermal runaway was shown in the previous experimental study. The macroscale model was examined to check whether the results were in agreement with the observed

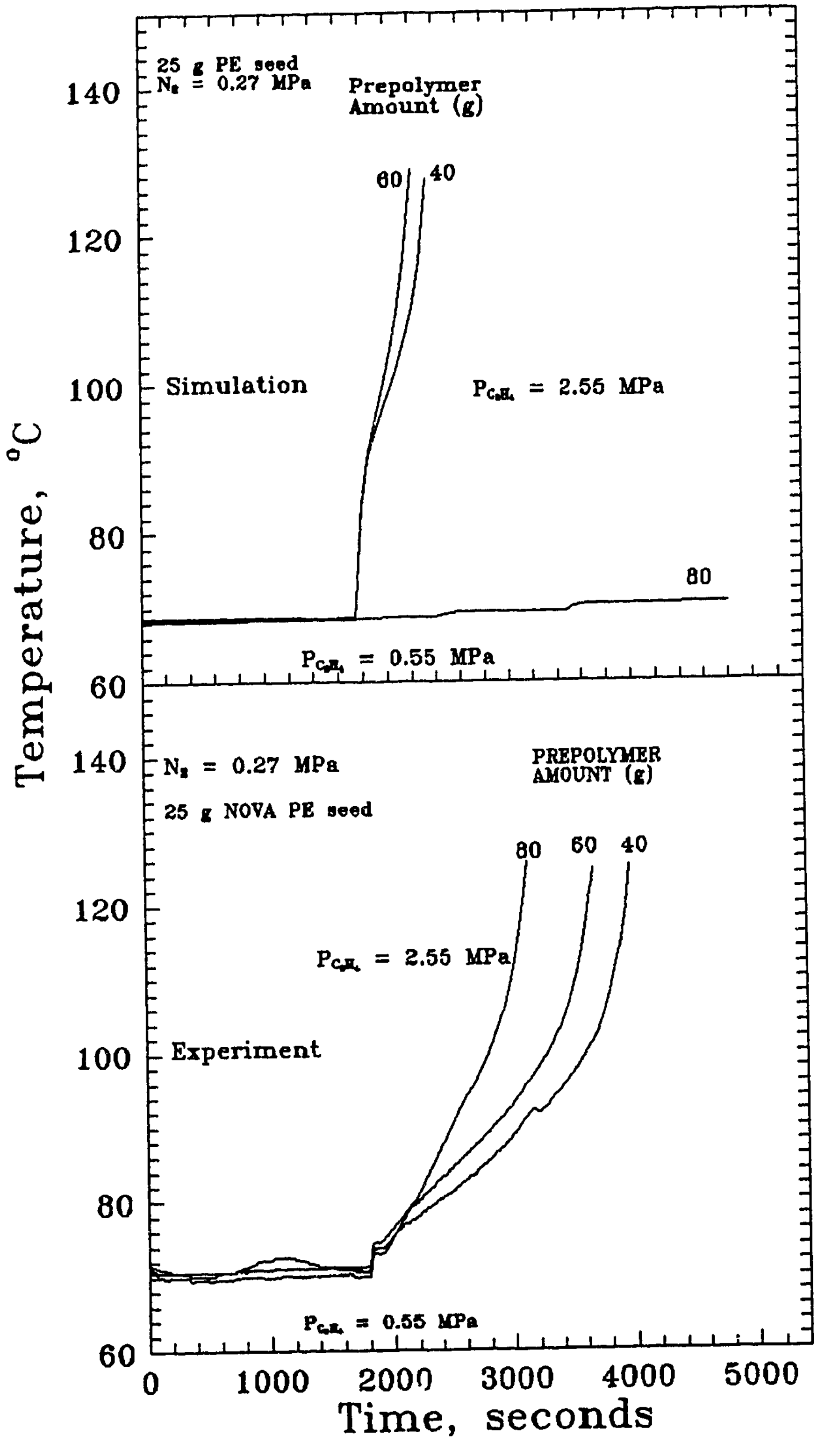


Figure 6.6 Variation in amount of prepolymerization

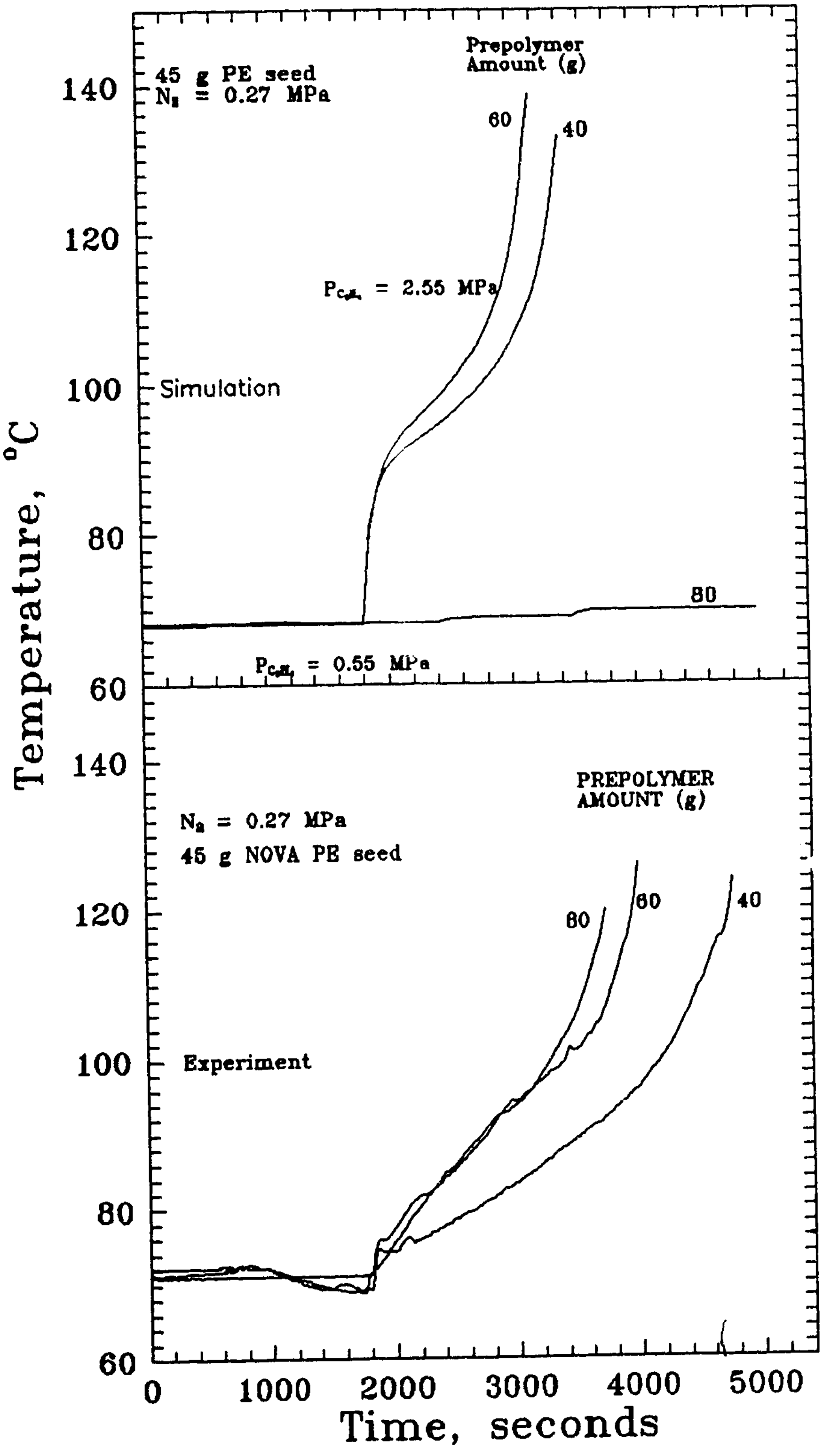


Figure 6.7 Variation in amount of prepolymerization

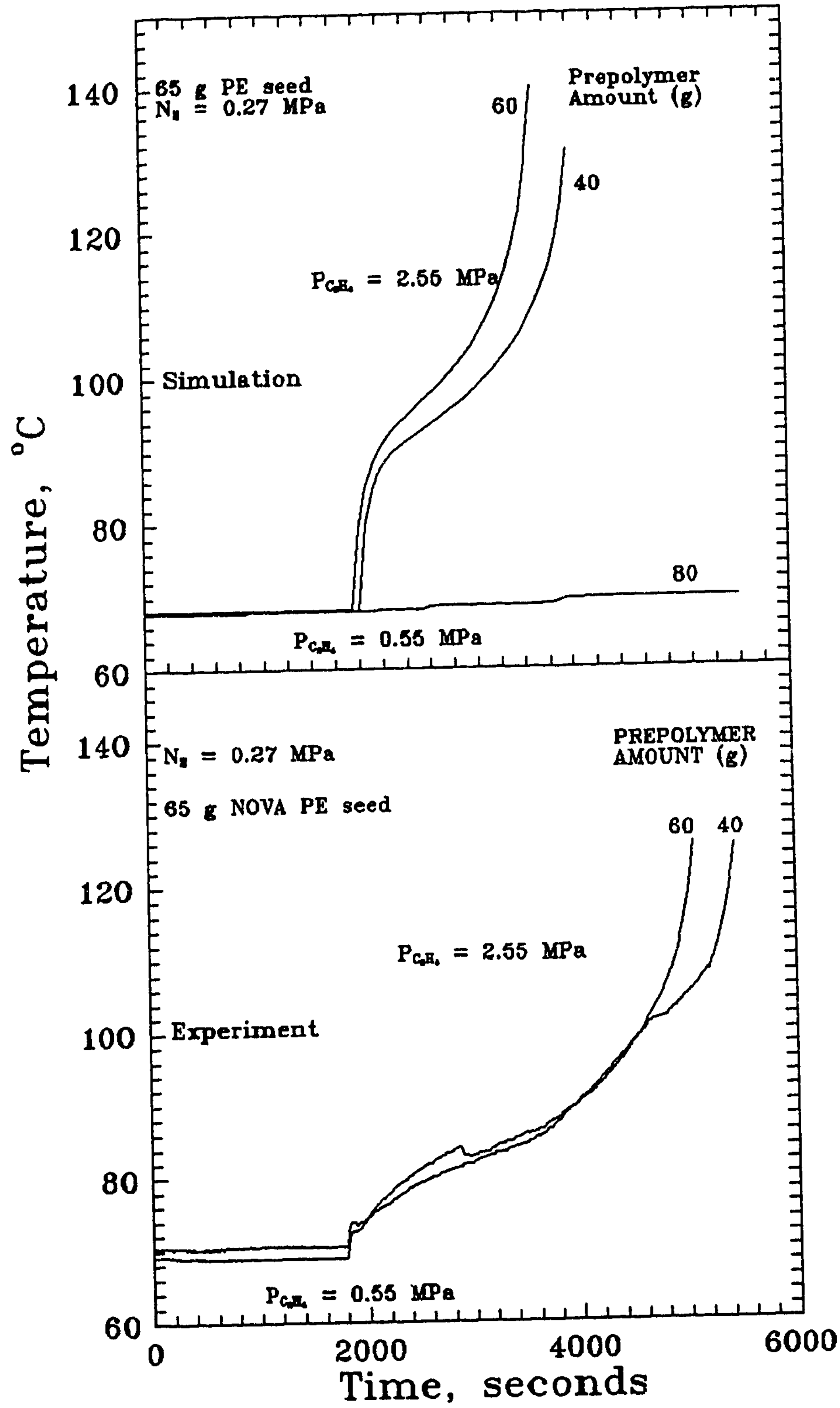


Figure 6.8 Variation in amount of prepolymerization

behaviour. The effects of changing the amount of the seed bed and prepolymer keeping their combined mass constant, at the time of change in ethylene pressure from 0.55 MPa to 2.55 MPa, is shown in Figures 6.9 and 6.10. Comparison of the experimental results with the predicted behaviour at the same total mass of 85 g and 105 g (see Figures 6.9 and 6.10, respectively), indicate that the model does a good job of predicting the qualitative behaviour of the temperature profile. The results indicate that the rate of temperature rise inside the reactor differs considerably depending on whether the solids are added initially in the form of seed bed or produced during the course of the reaction.

The effect of initial reaction temperature on the temperature profile of the gas-phase reactor at constant seed and prepolymer amount is illustrated in Figure 6.11. Model simulations were carried out with 25 g seed and 40 g prepolymerization and initial reactor temperatures of 55°C, 70°C and 85°C. The comparison of experimental results and simulations again shows that the model predictions are in qualitative agreement with the experimental observations, and with better correlations, closer agreement between the experimental and predicted profiles should be obtainable. Both experiments and simulations indicated that no runaway occurred when the initial temperature was kept fixed at about 50°C. However, the simulation indicated a higher temperature in the gas phase of the reactor (≈80°C) after ethylene pressure was increased to 2.55 MPa than the experimentally observed value of about 55°C.

In conclusion, the two-phase heterogeneous model for the gas-phase polymerization of ethylene has been shown to agree with the general experimentally observed results. For more accurate prediction of the profile, better estimation of the solid-gas, bed-wall and oil bath heat transfer rates are necessary. The lack of agreement of the model-experiment results at higher prepolymerization levels of 80, and 100 g, are possibly due to temperature gradients in the interior of the growing particles. The two-phase macro-model does not account for such gradients and a more detailed meso or micro model is required to model such behaviour.

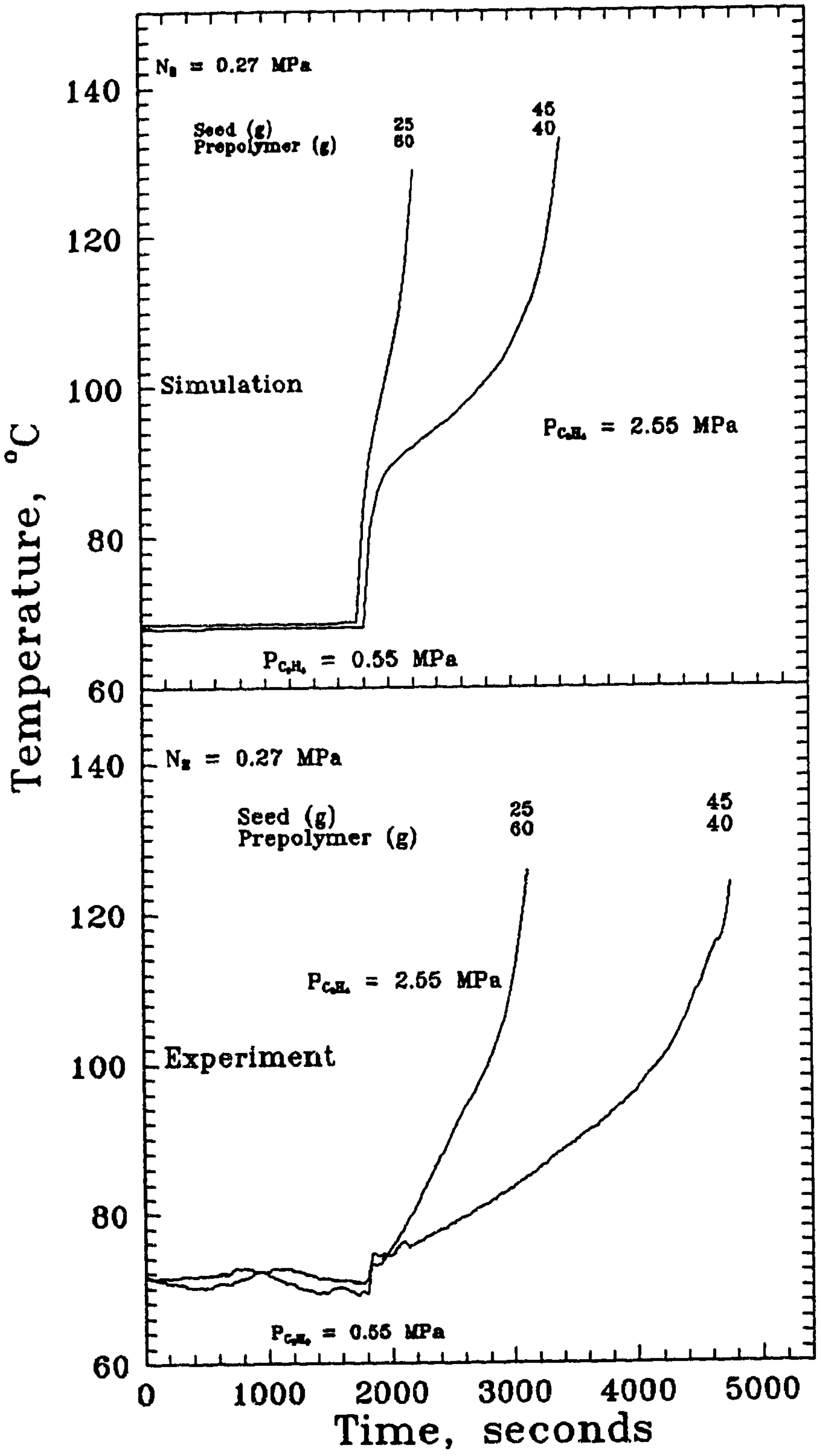


Figure 6.9 Variation of seed and prepolymer at constant total of 85 g

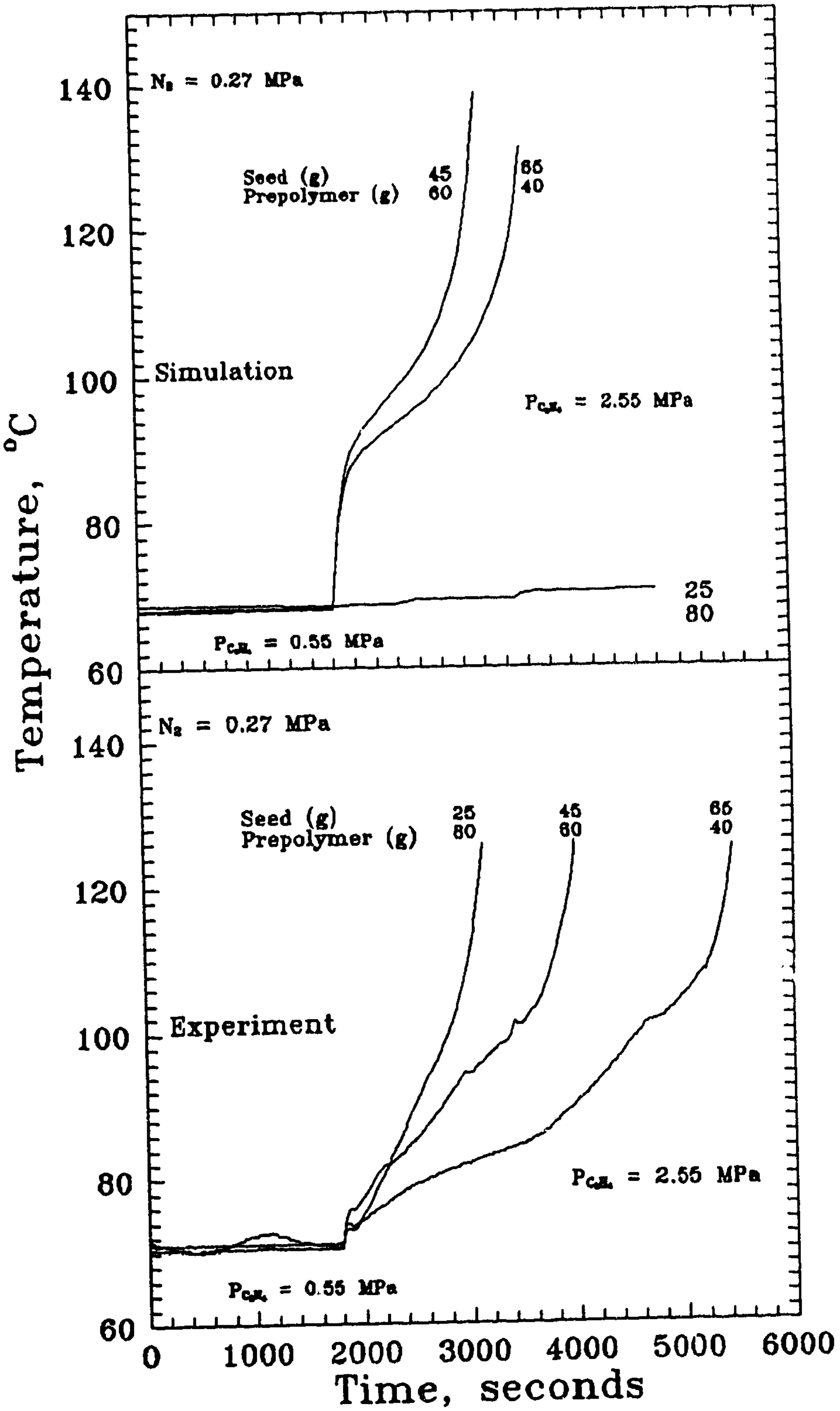


Figure 6.10 Variation of seed and prepolymer at constant total of 105 g

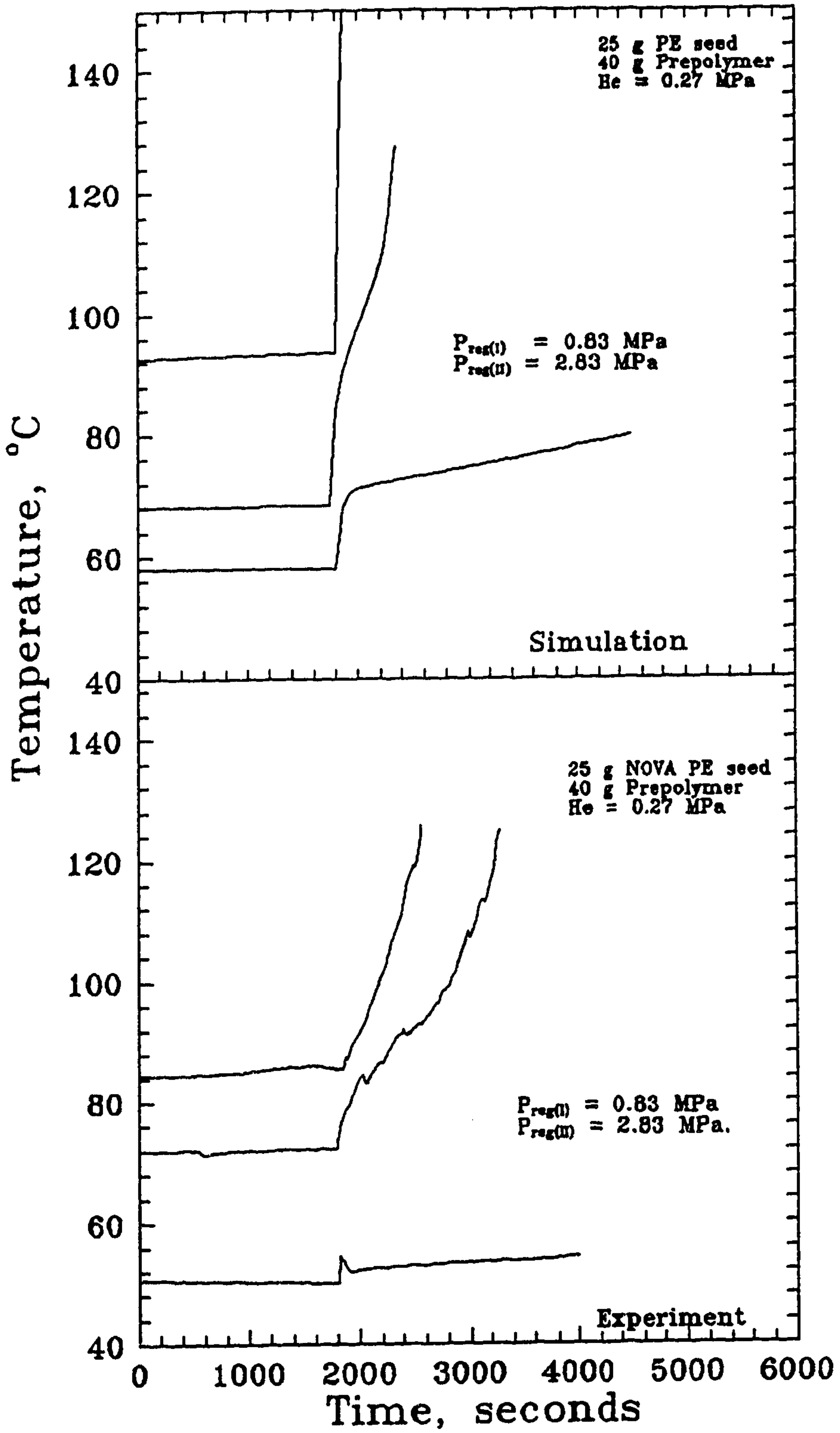


Figure 6.11 Variation of reaction temperature at constant seed and prepolymer amount

7 CONCLUSIONS

The design and operation of a well-instrumented, semi-batch stirred-bed reactor for gas-phase polymerization of ethylene have been described.

The thermal behaviour of the gas-phase homopolymerization of ethylene has been studied using the semi-batch stirred-bed reactor. The main limitation encountered with this reactor is the relatively low rates of heat transfer which can be achieved between the growing polymer particles and the gas-phase, and between the reactor contents and the walls of the reactor. The inadequate removal of the heat of reaction results in an uncontrolled increase in the reactor temperature, commonly called as "thermal runaway". The effects of various operating parameters such as maximum ethylene feed rate to the reactor, amount of catalyst used, amount and size of seed bed, length of prepolymerization, agitation speed, outside heat transfer rates, reaction temperature and the concentration of background inert gas, on the onset of thermal runaway of the reactor, have been studied in detail.

A simplified two-phase macroscopic heterogeneous model has been developed to describe mathematically the instability of the reactor due to limited heat transfer rates at the operating conditions. The model predictions are in good qualitative agreement with most of the experimental observations. The solid-gas (h_{pg}) and bed-wall (h_w) heat transfer coefficients have been estimated using Zenz-Othmer and Kunii-Levenspiel correlations respectively, available from literature. The heat transfer coefficients estimated from literature have been found to be generally conservative in nature. Actual heat transfer rates obtained during reaction are much higher.

The lack of agreement of the experimental observation of thermal behaviour and the results obtained with the model at prepolymerization levels greater than 80 g suggest that steady state thermal gradients exist on the growing polymer particles and these gradients become critical as particle size increases. Therefore, effects taking place on the single growing polymer particle have to be incorporated in the current model for the model to predict completely the observed thermal behaviour.

The lack of reproducibility of catalyst activity for gas-phase polymerization creates difficulty in comparing the results obtained for different runs. The uniform distribution of catalyst on the surface of the seed bed is very difficult to achieve. Hence, local "hot spots" are often created which results in the formation of polymer lumps inside the reactor.

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APPENDIX A

Description of Gas-Phase Experiments

Brief description of the start-up and operating procedures used for experiments GAS9108 to GAS9111, and GAS9201 to GAS9273, are given in this appendix. These experiments were carried out under gas-phase conditions. Figures showing the time dependence of the total reactor pressure, ethylene feed flow rates and temperatures for each experiment are collected at the end of this appendix.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9108	**DATE:** JUNE 18, 1991
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.183 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.248 g of Teflon placed into bottom of injection port
0.183 g of catalyst placed into port
0.240 g of Teflon placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: Teflon (-600, +425μm)
AMOUNT OF SOLIDS PRECHARGED: 40 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 35 minutes
Time to Start of Olefin Feed: 6 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 59 psia
Reaction Temperature: 70°C
Length of Run: 4.5 hours
Additional Comments: This run was first conducted at constant pressure (59 psia) and temperature (70°C) for 1.2 hours, then pressure was increased step by step till flow rate dropped rapidly. The temperature reached as high as 200°C. The stirrer ran at speed of 30% whole range.

TOTAL AMOUNT OF PRODUCT: 360 g

COMMENTS:

Product became a big solid chunk

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9109 **DATE:** JUNE 25, 1991

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.184 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.207 g of Teflon placed into bottom of injection port
0.184 g of catalyst placed into port
0.267 g of Teflon placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: NOVA PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 18 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 80°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 62 minutes
Time to Start of Olefin Feed: 6 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 45 psia
Total Initial Reactor Pressure: 80 psia
Reaction Temperature: 70°C
Length of Run: 5.5 hours
Additional Comments: This run was first conducted at constant pressure (80 psia) and temperature (70°C) for 1.6 hours, then pressure was increased step by step till flow rate dropped rapidly. The temperature reached as high as 200°C. A half hour later catalyst activity was checked. Stirrer ran at speed of 30% whole range. The activity was checked again after night.

TOTAL AMOUNT OF PRODUCT: 172 g

COMMENTS:

Product became a big solid chunk stuck on wall and bottom of reactor.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9110	**DATE:** JULY 5, 1991
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.190 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.240 g of NOVA PE placed into bottom of injection port
0.190 g of catalyst placed into port
0.164 g of NOVA PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: NOVA PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 80 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 80°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 45 minutes
Time to Start of Olefin Feed: 8 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 44 psia
Total Initial Reactor Pressure: 80 psia
Reaction Temperature: 70°C
Length of Run: 5.4 hours
Additional Comments: This run was first conducted at constant pressure (80 psia) and temperature (70°C) for 0.5 hour, then pressure was increased step by step till flow rate dropped rapidly. The temperature#4 reached as high as 220°C. Stirrer ran at speed of 30% whole range. The activity was checked next morning.

TOTAL AMOUNT OF PRODUCT: 202 g

COMMENTS:

Product became a big solid chunk stuck on wall and bottom of reactor.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9111 **DATE:** JULY 11, 1991

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.170 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.215 g of NOVA PE placed into bottom of injection port
0.170 g of catalyst placed into port
0.141 g of NOVA PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: NOVA PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 18 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 80°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 32 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 51 psia
Total Initial Reactor Pressure: 93 psia
Reaction Temperature: 70°C
Length of Run: 2.5 hours
Additional Comments: This run was conducted at constant temperature (70°C). The pressure was increased step by step till flow rate dropped rapidly. The temperature#4 reached as high as 220°C. Stirrer ran at speed of 30% whole range. The catalyst activity was checked at the end of run.

TOTAL AMOUNT OF PRODUCT: 141 g

COMMENTS:

Product became a big solid chunk stuck on wall and bottom of reactor.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9201	**DATE:** JAN 15, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.188 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 1.0 cm^3

LOADING OF CATALYST INJECTION PORT:
0.149 g of PE placed into bottom of injection port
0.188 g of catalyst placed into port
0.165 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 50 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 12 minutes
Time to Start of Olefin Feed: 4 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 80.1 psia
Reaction Temperature: 70°C
Length of Run: 1.5 hours
Additional Comments: This run was first conducted at constant pressure (80 psia) and temperature (70°C) for 1 hour, then pressure was increased step by step till flow rate dropped rapidly. The temperature reached as high as 206°C. The stirrer ran at speed of 30% for 30 minutes and then at speed of 40% whole range.

TOTAL AMOUNT OF PRODUCT: 136.8 g

COMMENTS:

Product became a big solid chunk
Catalyst dispersion not uniform.
Stirrer blade broken.

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9202	**DATE:** JAN 17, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.104 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.156 g of PE placed into bottom of injection port
0.104 g of catalyst placed into port
0.185 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 80 psia
Reaction Temperature: 70°C
Length of Run: 2.33 hours
Additional Comments: This run was first conducted at constant pressure (80 psia) and temperature (70°C) for 1 hour, then pressure was increased step by step till flow rate dropped rapidly. The temperature reached as high as 200°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 136.8 g

COMMENTS:

Product became a big solid chunk

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9203	**DATE:** JAN 21, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.103 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.150 g of PE placed into bottom of injection port
0.103 g of catalyst placed into port
0.165 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 10 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 79.2 psia
Reaction Temperature: 70°C
Length of Run: 40 minutes
Additional Comments: This run was first conducted at constant pressure (79 psia) and temperature (70°C) for 10 minutes, then pressure was increased (163 psia). The temperature reached as high as 220°C before flow rate dropped. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 97.8 g

COMMENTS:

Initial activity very high.
Product became a big solid chunk
Polymer formed grey balls at the bottom.
Stirrer blade had fallen.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9204	**DATE:** JAN 23, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.104 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.176 g of PE placed into bottom of injection port
0.104 g of catalyst placed into port
0.107 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 6 minutes
Time to Start of Olefin Feed: 1 minute

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 81 psia
Reaction Temperature: 70°C
Length of Run: 3 hours
Additional Comments: This run was first conducted at constant pressure (81 psia) and temperature (70°C) for 1.4 hours, then pressure was increased step by step till temperature reached 125°C. Flow was stopped. The temperature reached as high as 130°C. The stirrer ran at speed of 40% for whole range. The activity was checked after the product cooled down to 70°C.

TOTAL AMOUNT OF PRODUCT: 134.5 g

COMMENTS:

Product was uniform powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9205 **DATE:** JAN 27, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.109 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.183 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.157 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 6 minutes
Time to Start of Olefin Feed: 2 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 42 psia
Total Initial Reactor Pressure: 80 psia
Reaction Temperature: 70°C
Length of Run: 1.75 hours
Additional Comments: This run was first conducted at constant pressure (81 psia) and temperature (70°C) for 1.25 hours, then pressure was increased (350 psia). Flow was stopped after temperature reached 150°C. The temperature reached as high as 200°C. The stirrer ran at speed of 40% for whole range. The activity was checked after the product cooled down to 70°C.

TOTAL AMOUNT OF PRODUCT: 114.8 g

COMMENTS:

Product was a big solid chunk stuck on the stirrer.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9206	**DATE:** JAN 29, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.99 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.163 g of PE placed into bottom of injection port
0.99 g of catalyst placed into port
0.153 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 8 minutes
Time to Start of Olefin Feed: 2 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 43 psia
Total Initial Reactor Pressure: 80 psia
Reaction Temperature: 70°C
Length of Run: 3 hours
Additional Comments: This run was first conducted at constant pressure (81 psia) and temperature (70°C) for 1.67 hours, then pressure was increased step by step. Flow was stopped after temperature reached 150°C. The temperature reached as high as 230°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 197.2 g

COMMENTS:

Product was a big solid chunk stuck on the stirrer.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9207	**DATE:** JAN 31, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.106 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.177 g of PE placed into bottom of injection port
0.106 g of catalyst placed into port
0.191 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 10 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 81 psia
Reaction Temperature: 70°C
Length of Run: 2.67 hours
Additional Comments: This run was first conducted at constant pressure (81 psia) and temperature (70°C) for 1.25 hours, then pressure was increased step by step. Flow was stopped after temperature reached 150°C. The temperature reached as high as 175°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 140.6 g

COMMENTS:

Product was a big solid chunk stuck at the bottom.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9208	**DATE:** FEB 4, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.104 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.168 g of PE placed into bottom of injection port
0.103 g of catalyst placed into port
0.163 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 79.4 psia
Reaction Temperature: 70°C
Length of Run: 2.16 hours
Additional Comments: This run was first conducted at constant pressure (79 psia) and temperature (70°C) for 1.33 hours, then pressure was increased step by step. Flow was stopped after temperature reached 135°C. The temperature reached as high as 150°C. The stirrer ran at speed of 40% for whole range. Catalyst activity checked after temperature lowered to 70°C.

TOTAL AMOUNT OF PRODUCT: 174.9 g

COMMENTS:

Product was a big solid chunk stuck on the stirrer.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9209 **DATE:** FEB 6, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.110 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.167 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.170 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119.5 psia
Reaction Temperature: 70°C
Length of Run: 2.42 hours
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 1.08 hours, then pressure was increased step by step. Flow was stopped after temperature reached 125°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for whole range. Catalyst activity checked after temperature lowered to 70°C.

TOTAL AMOUNT OF PRODUCT: 129.4 g

COMMENTS:

Product was fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9210	**DATE:** FEB 10, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.108 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.156 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.170 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less than 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 6 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.5 psia
Reaction Temperature: 70°C
Length of Run: 2 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 1.33 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 132°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 133.3 g

COMMENTS:

Product was fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9211

DATE: FEB 12, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.108 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.156 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.163 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355µm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 10 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 120.1 psia
Reaction Temperature: 70°C
Length of Run: 55 minutes
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 40 minutes, then pressure was increased (375 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 160°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 98.4 g

COMMENTS:

Product was loose chunk.
Reactor vent valve was leaking.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9212

DATE: FEB 14, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.108 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.142 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.137 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 7 minutes
Time to Start of Olefin Feed: 6 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 119.8 psia
Reaction Temperature: 70°C
Length of Run: 50 minutes
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 34 minutes, then pressure was increased (410 psia). Flow was stopped after temperature reached 129°C. The temperature reached as high as 183°C. The stirrer ran at speed of 40% for whole range. Catalyst activity checked after temperature lowered to 70°C.

TOTAL AMOUNT OF PRODUCT: 91.3 g

COMMENTS:

Very few chunks.
Thin film cover on the walls.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9213	**DATE:** FEB 18, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.104 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.164 g of PE placed into bottom of injection port
0.104 g of catalyst placed into port
0.156 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 43 psia
Total Initial Reactor Pressure: 122.6 psia
Reaction Temperature: 70°C
Length of Run: 2.33 hours
Additional Comments: This run was first conducted at constant pressure (122 psia) and temperature (70°C) for 2 hours, then pressure was increased (409 psia). Flow was stopped after temperature reached 124°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 138.9 g

COMMENTS:

Product very fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9214

DATE: FEB 21, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.108 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.185 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.143 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 118.8 psia
Reaction Temperature: 70°C
Length of Run: 52 minutes
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 24 minutes, then pressure was increased (409 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 141°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 103.9 g

COMMENTS:

Product very fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9215

DATE: FEB 25, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.103 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.156 g of PE placed into bottom of injection port
0.103 g of catalyst placed into port
0.181 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 7 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 121.6 psia
Reaction Temperature: 70°C
Length of Run: 50 minutes
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 20 minutes, then pressure was increased (411 psia). Flow was stopped after temperature reached 126°C. The temperature reached as high as 134°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 113.9 g

COMMENTS:

Product very fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9216	**DATE:** FEB 28, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.11 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.163 g of PE placed into bottom of injection port
0.11 g of catalyst placed into port
0.157 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 6 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 120.6 psia
Reaction Temperature: 70°C
Length of Run: 1.16 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 40 minutes, then pressure was increased (410 psia). Flow was stopped after temperature reached 126°C. The temperature reached as high as 138°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 115.8 g

COMMENTS:

Very soft chunks formed along the stirrer blades.
Thin film covering the side of the reactor.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9217

DATE: MAR 03, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.163 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.157 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 120.9 psia
Reaction Temperature: 70°C
Length of Run: 54 minutes
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 23 minutes, then pressure was increased (415 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 130°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 115.01 g

COMMENTS:

Product fine powder except for a small chunk on the thermocouple T, because of which it recorded a maximum temperature of 160°C.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9218

DATE: MAR 06, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.150 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.160 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 39 psia
Total Initial Reactor Pressure: 120.9 psia
Reaction Temperature: 70°C
Length of Run: 3.4 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 3.13 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 140.61 g

COMMENTS:

Product not fine powder but also not chunky. Incipient fusing observed.
Thin film covering the reactor wall.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9219	**DATE:** MAR 10, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.11 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.151 g of PE placed into bottom of injection port
0.11 g of catalyst placed into port
0.170 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N[illegible]ed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.5 psia
Reaction Temperature: 70°C
Length of Run: 4.74 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 4.5 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 138°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 150.66 g

COMMENTS:

Product fusing more prevalent.
A relatively thicker film formed along the sides of the reactor.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9220 **DATE:** MAR 13, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.111 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.180 g of PE placed into bottom of injection port
0.111 g of catalyst placed into port
0.137 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 65 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.7 psia
Reaction Temperature: 70°C
Length of Run: 2.75 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 2.33 hours, then pressure was increased (411 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 160°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 140.0 g

COMMENTS:

A big solid chunk formed attached to the stirrer.
Rest of the product was fine powder.
No film formation.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9221

DATE: MAR 17, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.113 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.165 g of PE placed into bottom of injection port
0.113 g of catalyst placed into port
0.148 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.7 psia
Reaction Temperature: 70°C
Length of Run: 3 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 2.56 hours, then pressure was increased (420 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 137.5 g

COMMENTS:

Film formation was prominent.
Very few solid chunks.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9222	**DATE:** MAR 19, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.109 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.166 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.143 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355µm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 7 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 3.75 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 3.43 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 146.4 g

COMMENTS:

Product fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9223 **DATE:** MAR 25, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.113 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.154 g of PE placed into bottom of injection port
0.113 g of catalyst placed into port
0.149 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 3 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 2.66 hours, then pressure was increased (415 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 138°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 111.0 g

COMMENTS:

Product fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9224

DATE: MAR 26, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.110 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.171 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.148 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 122 psia
Reaction Temperature: 70°C
Length of Run: 4 hours
Additional Comments: This run was first conducted at constant pressure (122 psia) and temperature (70°C) for 3.66 hours, then pressure was increased (417 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 158.6 g

COMMENTS:

Product fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9235	**DATE:** APR 29, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.114 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.160 g of PE placed into bottom of injection port
0.114 g of catalyst placed into port
0.148 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 7 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121.0 psia
Reaction Temperature: 70°C
Length of Run: 4.25 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 3.75 hour, then pressure was increased (411 psia). Flow stopped after temperature reached 125°C. The temperature reached as high as 126°C. The stirrer ran at speed of 30% for whole range. The activity was checked after the product was cooled to 70°C.

TOTAL AMOUNT OF PRODUCT: 189.4 g

COMMENTS:

Product was uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9236

DATE: MAY 1, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.113 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.160 g of PE placed into bottom of injection port
0.113 g of catalyst placed into port
0.130 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 2.5 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 2.5 hours. The temperature reached as high as 138°C. The stirrer ran at speed of 25% for whole range. Flow was stopped.

TOTAL AMOUNT OF PRODUCT: 65.4 g

COMMENTS:

Bottom stirrer blade fallen down.
Polymer agglomerated at the bottom.
Catalyst dispersion not uniform.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9237	**DATE:** MAY 3, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.112 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.145 g of PE placed into bottom of injection port
0.112 g of catalyst placed into port
0.121 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 2.6 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 2.25 hours, then pressure was increased (405 psia). Flow stopped after temperature reached 125°C. The temperature reached as high as 141°C. Stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 119.5 g

COMMENTS:

Product became a big solid chunk
Thick film across the wall.
Stirrer blade had fallen.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9238

DATE: MAY 4, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.112 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.145 g of PE placed into bottom of injection port
0.112 g of catalyst placed into port
0.150 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C

Reactor pressurized with He, and evacuated overnight

Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place

Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 8 minutes
Time to Start of Olefin Feed: 5 minute

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 3.67 hours

Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 2.88 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 130°C. The stirrer ran at speed of 30% for whole range.

TOTAL AMOUNT OF PRODUCT: 163.6 g

COMMENTS:

Product was uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9239 **DATE:** MAY 6, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.113 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.148 g of PE placed into bottom of injection port
0.113 g of catalyst placed into port
0.159 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 7 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119 psia
Reaction Temperature: 70°C
Length of Run: 5.33 hours
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 5 hours, then pressure was increased (411 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 136°C. The stirrer ran at speed of 30% for whole range.

TOTAL AMOUNT OF PRODUCT: 153.5 g

COMMENTS:

Product was uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9240	**DATE:** MAY 8, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.113 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.189 g of PE placed into bottom of injection port
0.113 g of catalyst placed into port
0.132 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 µm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 6.67 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 6.33 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 30% for whole range. The activity was checked after the product was cooled to 70°C.

TOTAL AMOUNT OF PRODUCT:

COMMENTS:
Product was a uniform powder.
No loss of activity observed after runaway.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9250 **DATE:** JUN 8, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.109 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.177 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.151 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 3.13 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 2.6 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 129°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 171.8 g

COMMENTS:

Product was a uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9251

DATE: JUN 9, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.160 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.130 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 41 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 5.16 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 4.4 hours, then pressure was increased (414 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 138°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 200.65 g

COMMENTS:

Product was mostly uniform powder.
Incipient fusing observed.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9252 **DATE:** JUN 11, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.109 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.152 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.143 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 6 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 5.35 hours, then pressure was increased (390 psia). Flow dropped because the cylinder became empty. Flow was stopped after pressure dropped to 350 psia. The temperature reached as high as 139°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 215 g

COMMENTS:

Product was fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9253

DATE: JUN 12, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.111 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.156 g of PE placed into bottom of injection port
0.111 g of catalyst placed into port
0.130 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355µm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 7 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 6.12 hours, then pressure was increased (411 psia). Flow was stopped after temperature reached 126°C. The temperature reached as high as 140°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 226.8 g

COMMENTS:

Product was fine powder.
Stirrer blade started making noise at the end.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9254 **DATE:** JUN 15, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.107 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.155 g of PE placed into bottom of injection port
0.107 g of catalyst placed into port
0.134 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 65 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 3.62 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 3 hours, then pressure was increased (410.1 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 145°C. The stirrer ran at speed of 40% for 3.3 hours and then at 50% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 160.65 g

COMMENTS:

Product was mainly uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9255

DATE: JUN 16, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.107 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.170 g of PE placed into bottom of injection port
0.107 g of catalyst placed into port
0.150 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 65 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119.6 psia
Reaction Temperature: 70°C
Length of Run: 4.75 hours
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 4 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 139°C. The stirrer ran at speed of 40% for 4.4 hours and then at 50% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 193.8 g

COMMENTS:

Product mostly uniform powder.
Early stages of fusing observed.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9256

DATE: JUN 17, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.110 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.158 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.130 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119.3 psia
Reaction Temperature: 85°C
Length of Run: 1.75 hours
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (85°C) for 1.42 hours, then pressure was increased (409 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 139°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT:

COMMENTS:

Product very fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9257

DATE: JUN 18, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.108 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.154 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.144 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121.8 psia
Reaction Temperature: 50°C
Length of Run: 7.67 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (50°C) for 6.67 hours, then pressure was increased (410 psia). Flow was stopped after 1 hour. The temperature was constant at 50°C. No runaway was observed.The temperature reached as high as 56°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 68.5 g

COMMENTS:

Product very fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9258

DATE: JUN 22, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.2 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 1.0 cm^3

LOADING OF CATALYST INJECTION PORT:

0.160 g of PE placed into bottom of injection port
0.200 g of catalyst placed into port
0.167 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 80 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 4.62 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 3 hours, then He pressure was increased (265 psia). The final ethylene pressure was increased (412 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 128°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 224.9 g

COMMENTS:

Product very fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9259

DATE: JUN 23, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.2 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 1.0 cm^3

LOADING OF CATALYST INJECTION PORT:

0.161 g of PE placed into bottom of injection port
0.200 g of catalyst placed into port
0.157 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 50 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 10 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Helium Partial Pressure: 80 psia
Total Initial Reactor Pressure: 120.4 psia
Reaction Temperature: 70°C
Length of Run: 4.88 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 3.67 hours, then He pressure was increased (265 psia). The final ethylene pressure was increased (417 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 130°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 210.7 g

COMMENTS:

Product mostly powder.
Stirrer was stopped during addition of Helium after prepolymerization. Temperature reached 89°C.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9260

DATE: JUN 26, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.218 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 1.0 cm^3

LOADING OF CATALYST INJECTION PORT:
0.162 g of PE placed into bottom of injection port
0.218 g of catalyst placed into port
0.153 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355µm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 79 psia
Total Initial Reactor Pressure: 121.5 psia
Reaction Temperature: 70°C
Length of Run: 3.72 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 1.42 hours, then at constant pressure (132 psia) and temperature (70°C) for 1.5 hours.Then He pressure was increased (218 psia). The final ethylene pressure was increased (411 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 125°C. The stirrer ran at speed of 40% for 3.3 hours and then at 50% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 195.8 g

COMMENTS:
Product fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9261

DATE: JUN 29, 1992

TYPE OF CATALYST: Stauffer [illegible]AA

AMOUNT OF CATALYST: 0.220 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 1.0 cm^3

LOADING OF CATALYST INJECTION PORT:
0.150 g of PE placed into bottom of injection port
0.220 g of catalyst placed into port
0.152 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 50 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with He for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with He, and evacuated overnight
Next morning He flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with He and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by cata.
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Helium Partial Pressure: 80 psia
Total Initial Reactor Pressure: 120.9 psia
Reaction Temperature: 70°C
Length of Run: 3.55 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 1.5 hours, then at constant pressure (130 psia) and temperature (70°C) for 1.5 hours. The Helium pressure was increased (229 psia). The final ethylene pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperaturereached as high as 127°C. The stirrer ran at speed of 40% for 3.13 hours and then at 65% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 162.15 g

COMMENTS:
Product was fine powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9262

DATE: JUN 30, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.116 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.175 g of PE placed into bottom of injection port
0.116 g of catalyst placed into port
0.149 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 20 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 122 psia
Reaction Temperature: 70°C
Length of Run: 3.17 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 2.6 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 162.8 g

COMMENTS:

Product fusing more prevalent.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9263

DATE: JUL 2, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.189 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.167 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.9 psia
Reaction Temperature: 70°C
Length of Run: 4.55 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 4 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 131°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 163.8 g

COMMENTS:
Product was uniform powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9264

DATE: JUL 3, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.108 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.180 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.153 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 µm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 5.1 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 4.75 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for 3.33 hours and then at 60% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 137.5 g

COMMENTS:

Product was uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9265

DATE: JUL 6, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.142 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.152 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-600, +425 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121 psia
Reaction Temperature: 70°C
Length of Run: 6.87 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 6.37 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 138°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 204.7 g

COMMENTS:

Product was mainly in chunks.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9266 **DATE:** JUL 7, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.108 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.157 g of PE placed into bottom of injection port
0.108 g of catalyst placed into port
0.138 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat it once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119.5 psia
Reaction Temperature: 70°C
Length of Run: 5.13 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 3.33 hours, then at constant pressure (130 psia) and temperature (70°) for 50 minutes. The pressure was then increased (415 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 135°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 233.7 g

COMMENTS:

Product fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9

DATE: JUL 8, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.110 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.158 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.140 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.6 psia
Reaction Temperature: 70°C
Length of Run: 3.62 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 1 hour, then at constant pressure (133 psia) and temperature (70°C) for 1.76 hours. The ethylene pressure was increased (414 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 143°C. The stirrer ran at speed of 20-40% for whole range because of stirring noise.

TOTAL AMOUNT OF PRODUCT: 175.7 g

COMMENTS:

Product fine powder.

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DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9268

DATE: JUL 10, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.109 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.199 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.140 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 121.3 psia
Reaction Temperature: 70°C
Length of Run: 5.5 hours
Additional Comments: This run was first conducted at constant pressure (121 psia) and temperature (70°C) for 5 hours, then pressure was increased (408 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 138°C. The stirrer ran at speed of 30% for 5.16 hours and at 50% for the remaining period.

TOTAL AMOUNT OF PRODUCT: 180.7 g

COMMENTS:

Product mainly uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9269	**DATE:** JUL 12, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.109 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.150 g of PE placed into bottom of injection port
0.109 g of catalyst placed into port
0.126 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 65 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120.7 psia
Reaction Temperature: 70°C
Length of Run: 4.42 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 3.38 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 30% for whole range.

TOTAL AMOUNT OF PRODUCT: 202.4 g

COMMENTS:
Product was uniform powder.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9270

DATE: JUL 13, 1992

TYPE OF CATALYST: Stauffer 2.1AA

AMOUNT OF CATALYST: 0.110 g

TYPE OF CO-CATALYST: DEAC

AMOUNT OF CO-CATALYST: 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.206 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.196 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 65 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 5.5 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 4.6 hours, then pressure was increased (405 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 150°C. The stirrer ran at speed of 40% for the whole range.

TOTAL AMOUNT OF PRODUCT: 206.7 g

COMMENTS:

Fusing of product was more prevalent.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9271	**DATE:** JUL 14, 1992
TYPE OF CATALYST: Stauffer 2.1AA	**AMOUNT OF CATALYST:** 0.111 g
TYPE OF CO-CATALYST: DEAC	**AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.161 g of PE placed into bottom of injection port
0.111 g of catalyst placed into port
0.138 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 6.12 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 5.55 hours, then pressure was increased (409 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 133°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 180.2 g

COMMENTS:

Product was mainly in chunks.
The chunks were quite hard.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9272 **DATE:** JUL 15, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.111 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:

0.174 g of PE placed into bottom of injection port
0.111 g of catalyst placed into port
0.190 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355 μm)
AMOUNT OF SOLIDS PRECHARGED: 25 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:

Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 4 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:

Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 120 psia
Reaction Temperature: 70°C
Length of Run: 6.77 hours
Additional Comments: This run was first conducted at constant pressure (120 psia) and temperature (70°C) for 6.33 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 136°C. The stirrer ran at speed of 40% for whole range.

TOTAL AMOUNT OF PRODUCT: 198.7 g

COMMENTS:

Large chunks across the stirrer.

Novacor Polymerization Project

DATA SHEET FOR GAS-PHASE POLYMERIZATION RUNS

RUN NUMBER: GAS9273 **DATE:** JUL 19, 1992

TYPE OF CATALYST: Stauffer 2.1AA **AMOUNT OF CATALYST:** 0.110 g

TYPE OF CO-CATALYST: DEAC **AMOUNT OF CO-CATALYST:** 0.5 cm^3

LOADING OF CATALYST INJECTION PORT:
0.155 g of PE placed into bottom of injection port
0.110 g of catalyst placed into port
0.130 g of PE placed on top of catalyst

SOLIDS PRECHARGED TO REACTOR: PE (-841, +355μm)
AMOUNT OF SOLIDS PRECHARGED: 45 g

EVACUATION PROCEDURE OF REACTOR SYSTEM:
Reactor pressurized with N_2 for checking leaks, then evacuated and placed in oil bath at 90°C
Reactor pressurized with N_2, and evacuated overnight
Next morning N_2 flowed through reactor and connecting lines while catalyst injection holder put into place
Reactor was pressurized with N_2 and then evacuated less then 0.2 Torr. Repeat once

START-UP PROCEDURE

Sequence of Injections: DEAC followed by catalyst
Time Between Injections: 5 minutes
Time to Start of Olefin Feed: 5 minutes

CONDITIONS DURING POLYMERIZATION RUN:
Feed: pure ethylene
Initial Nitrogen Partial Pressure: 40 psia
Total Initial Reactor Pressure: 119.5 psia
Reaction Temperature: 70°C
Length of Run: 4.75 hours
Additional Comments: This run was first conducted at constant pressure (119 psia) and temperature (70°C) for 4.15 hours, then pressure was increased (410 psia). Flow was stopped after temperature reached 125°C. The temperature reached as high as 139°C. The stirrer ran at speed of 40% for 4.6 hours and then at 60% for the remaining period.

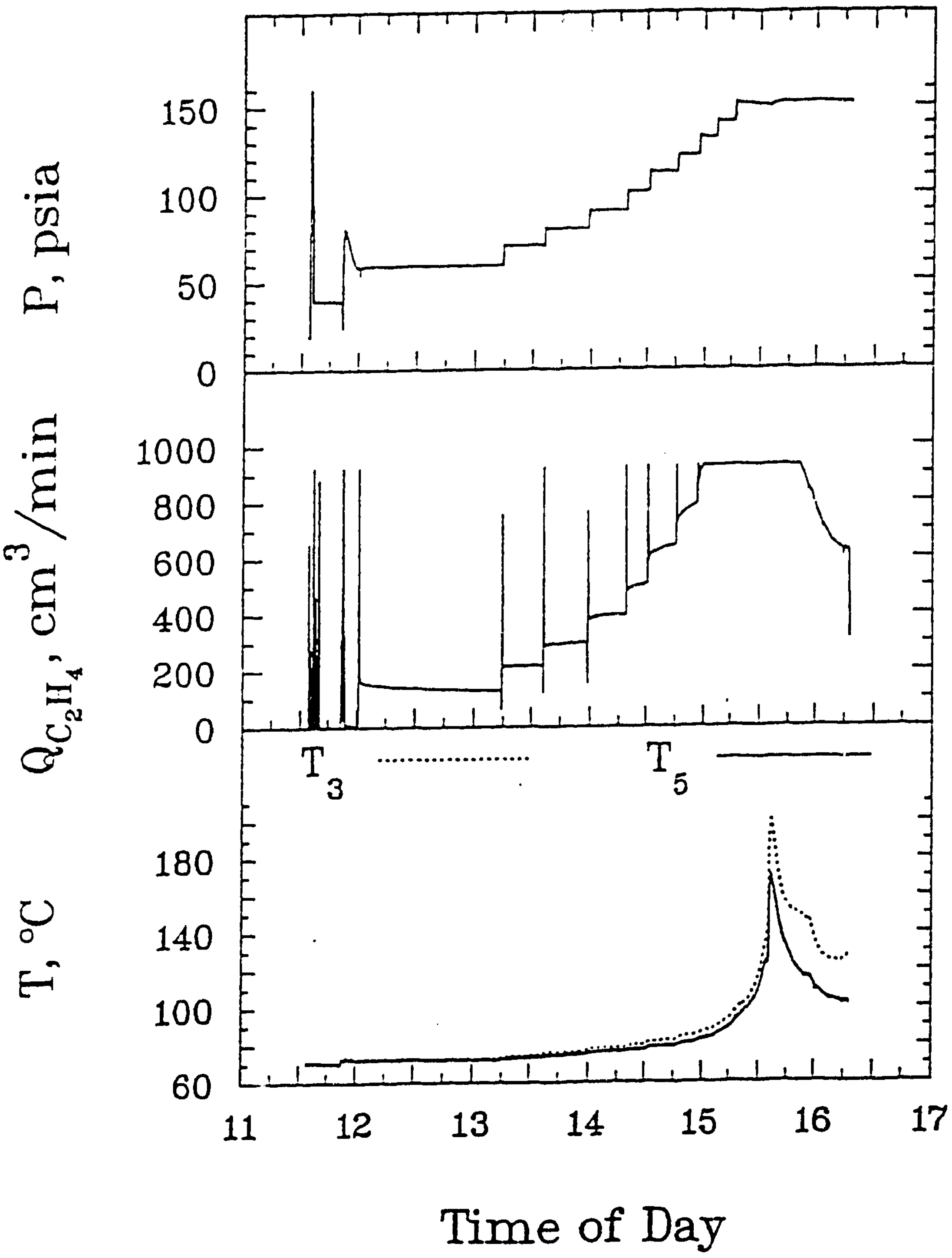
TOTAL AMOUNT OF PRODUCT: 186.3 g

COMMENTS:

Large scale fusing observed.

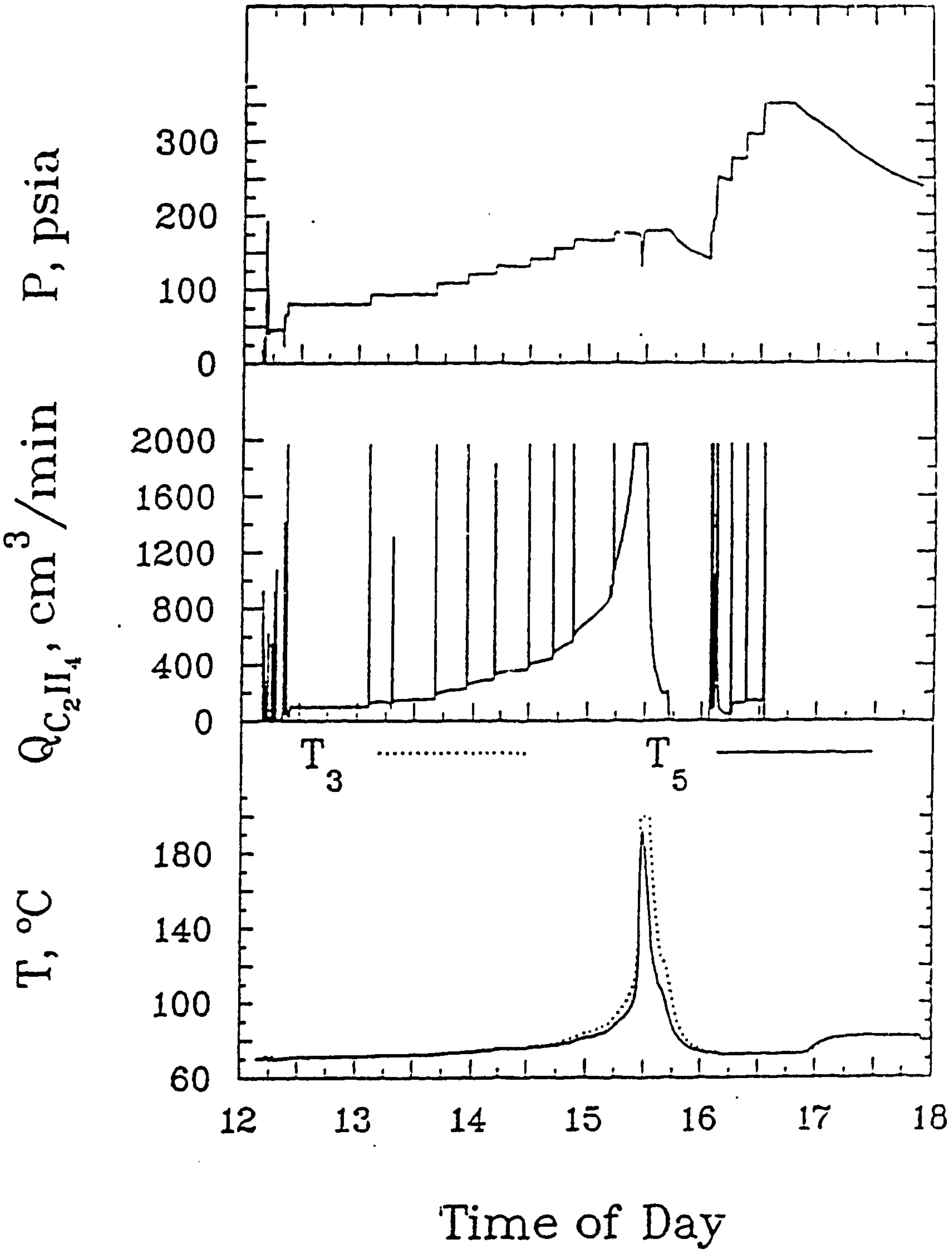
18 JUNE 1991 40 g TEFLON GAS9108

0.50 ml DEAC 0.183 g STAUFFER 2.1 AA

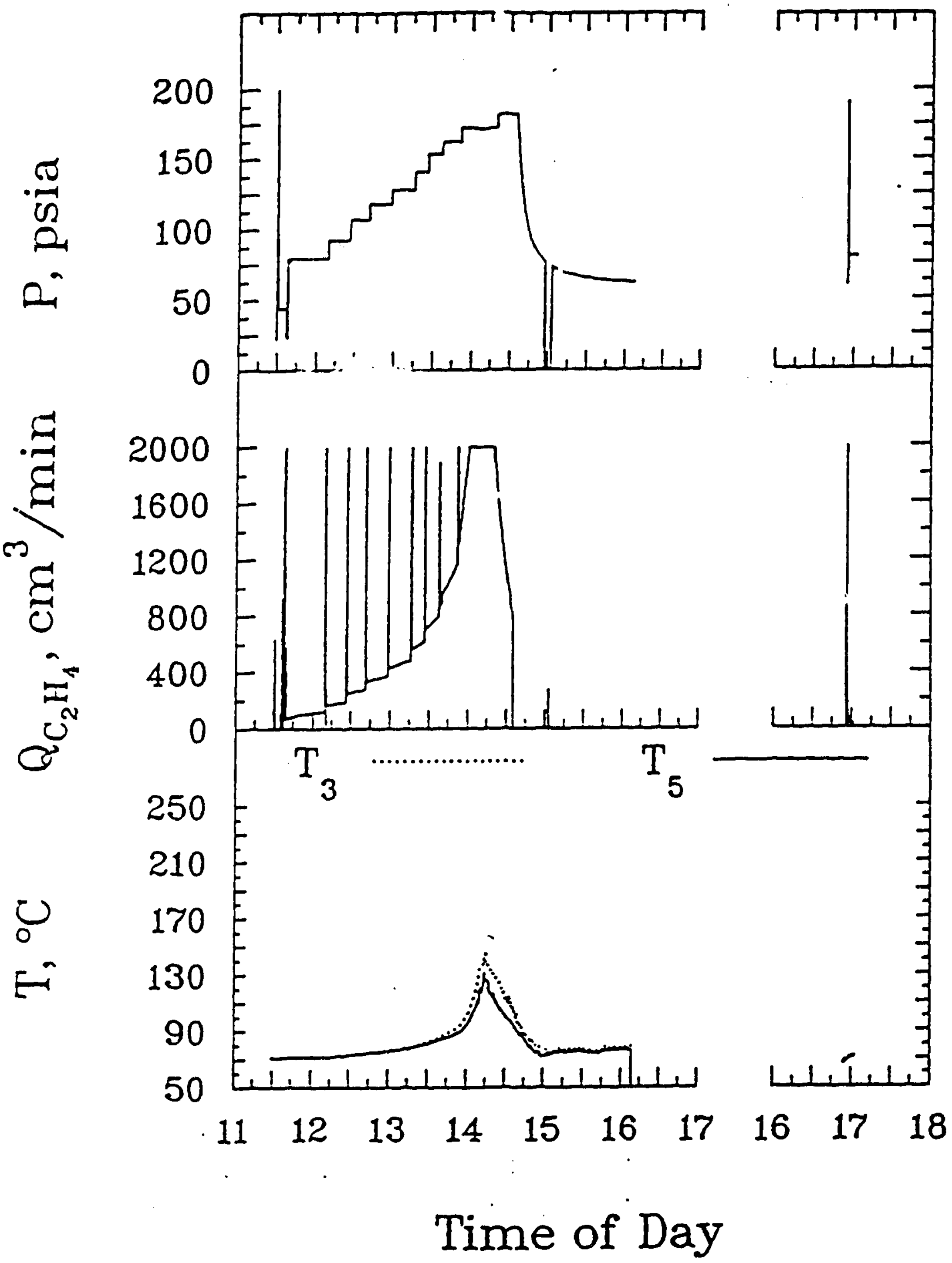


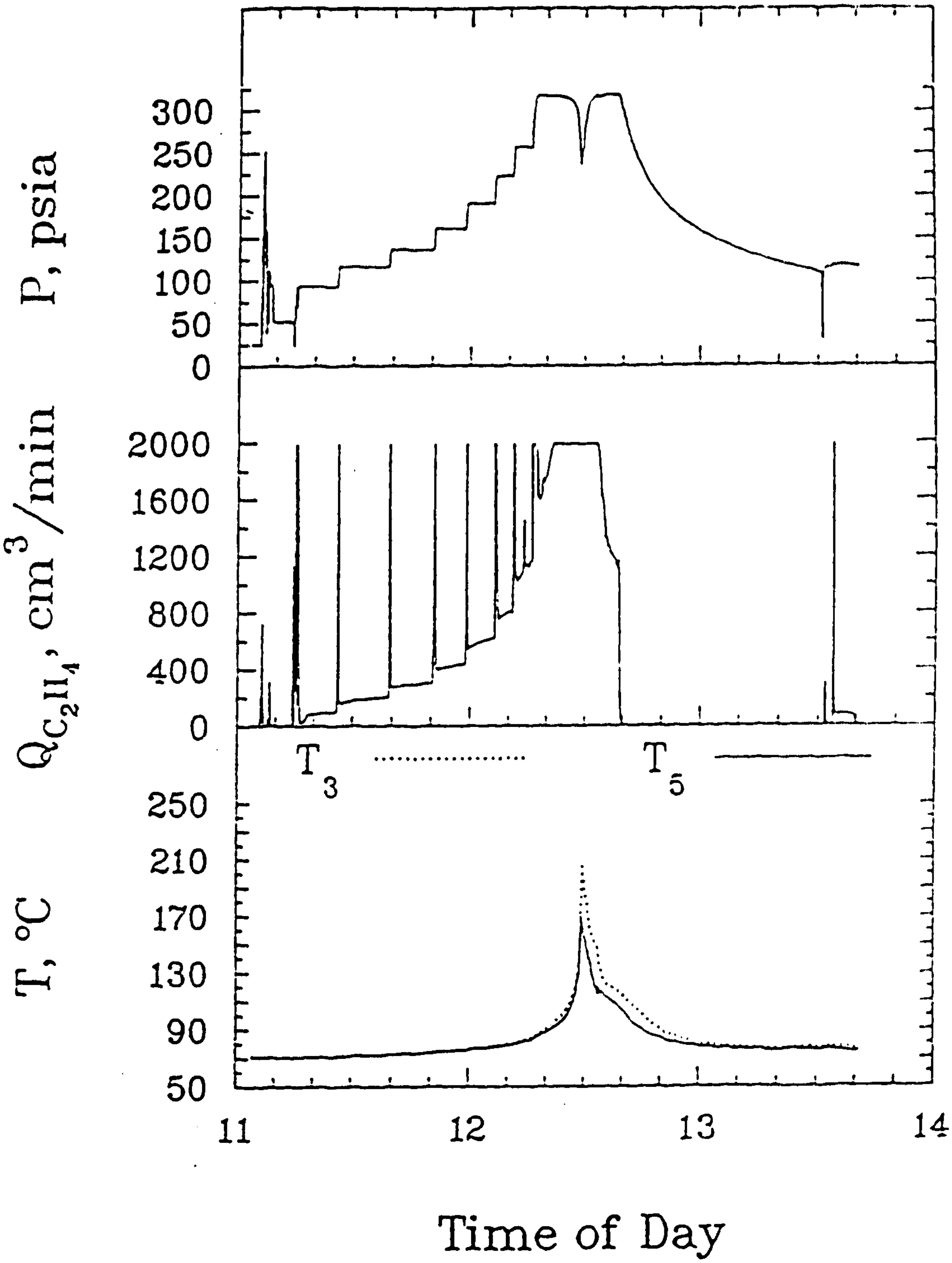
25 JUNE 1991 18 g NOVA PE GAS9109

0.50 ml DEAC 0.184 g STAUFFER 2.1 AA



5 JULY 1991 80 g NOVA PE GAS9110
0.50 ml DEAC 0.190 g STAUFFER 2.1 AA

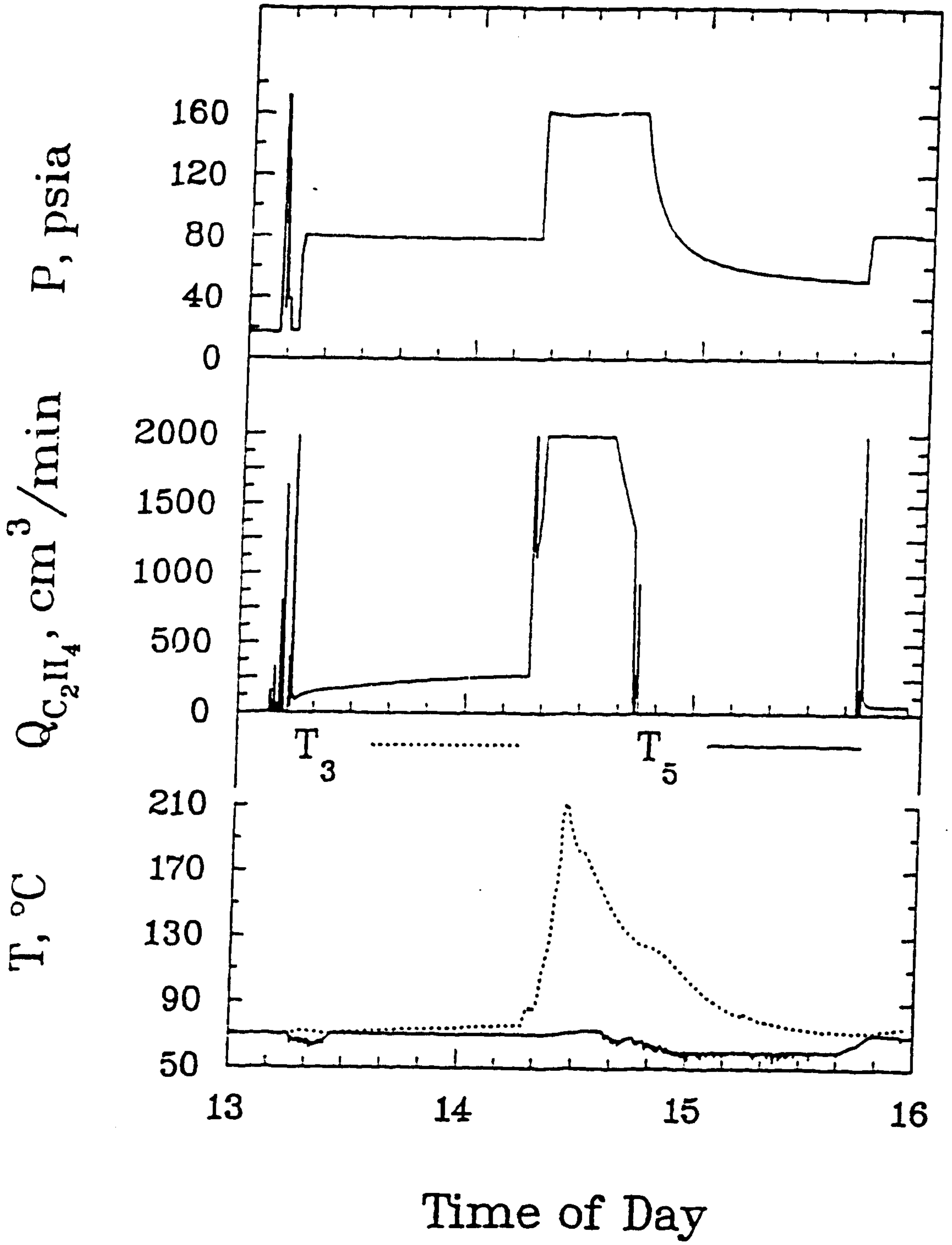



11 JULY 1991 18 g NOVA PE GAS9111

0.50 ml DEAC 0.170 g STAUFFER 2.1 AA

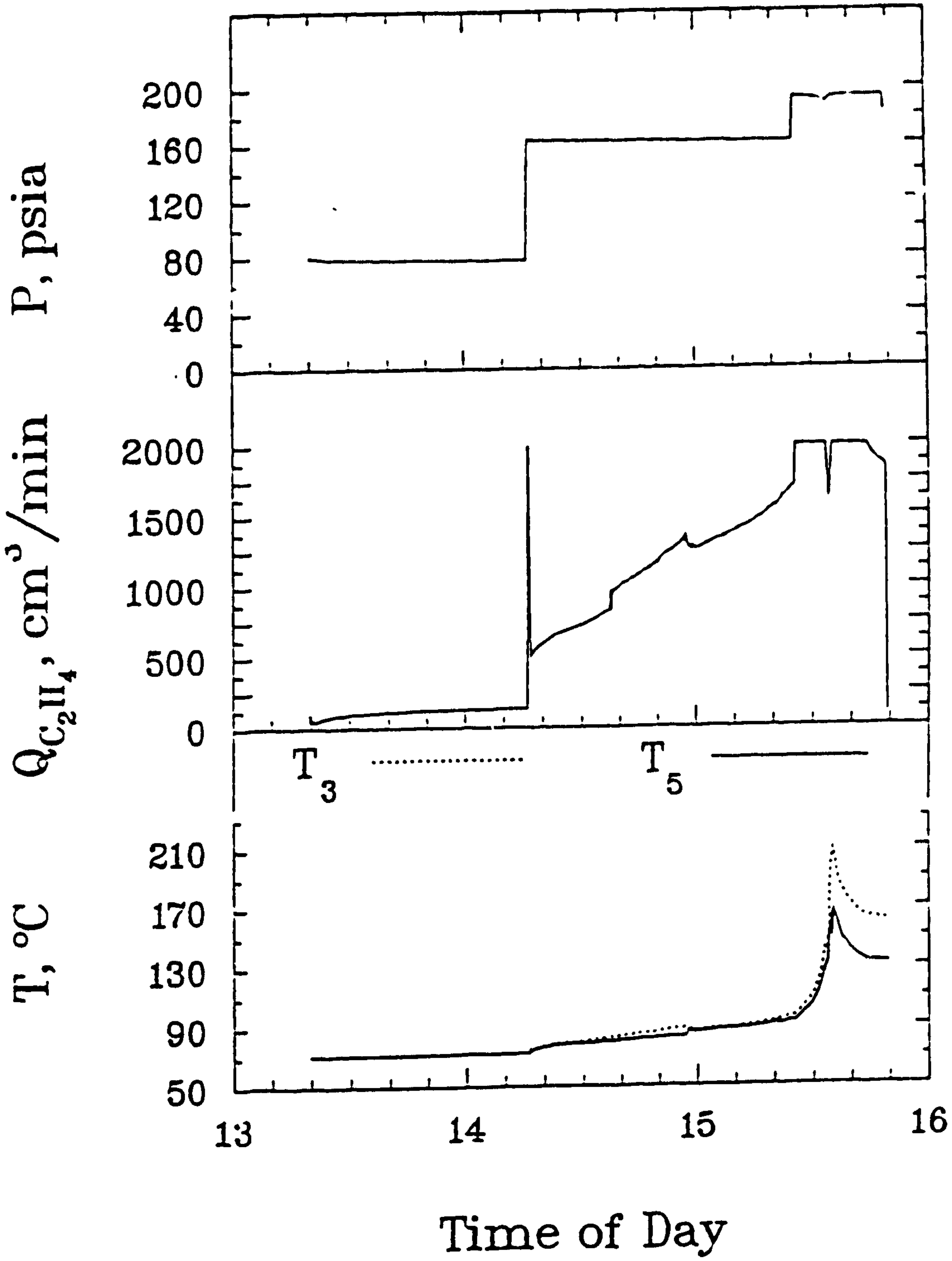
16 JANUARY 1992 50 g NOVA PE GAS9201

1.0 ml DEAC 0.188 g STAUFFER 2.1AA



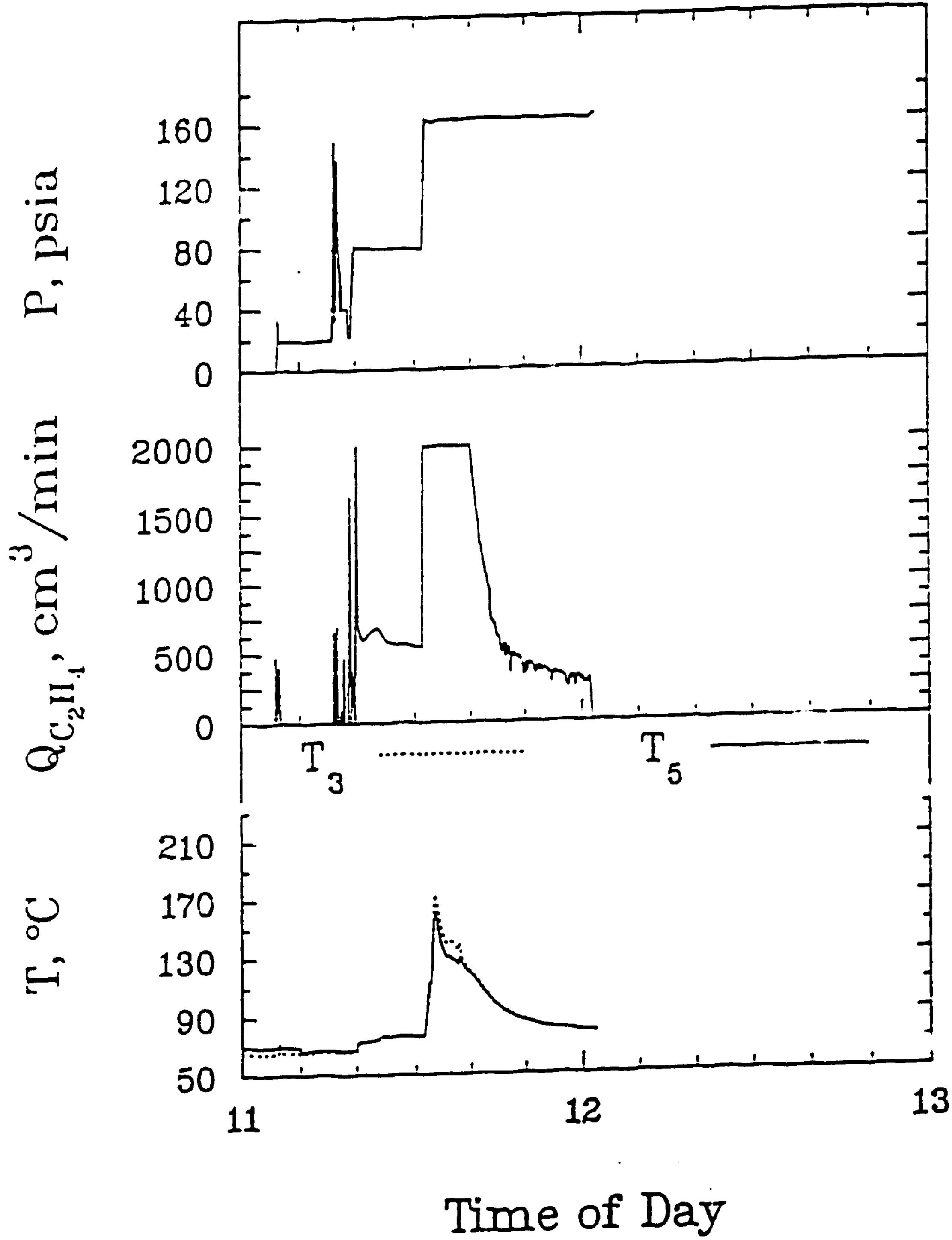
18 JANUARY 1992 25 g NOVA PE GAS9202

0.5 ml DEAC 0.104 g STAUFFER 2.1AA



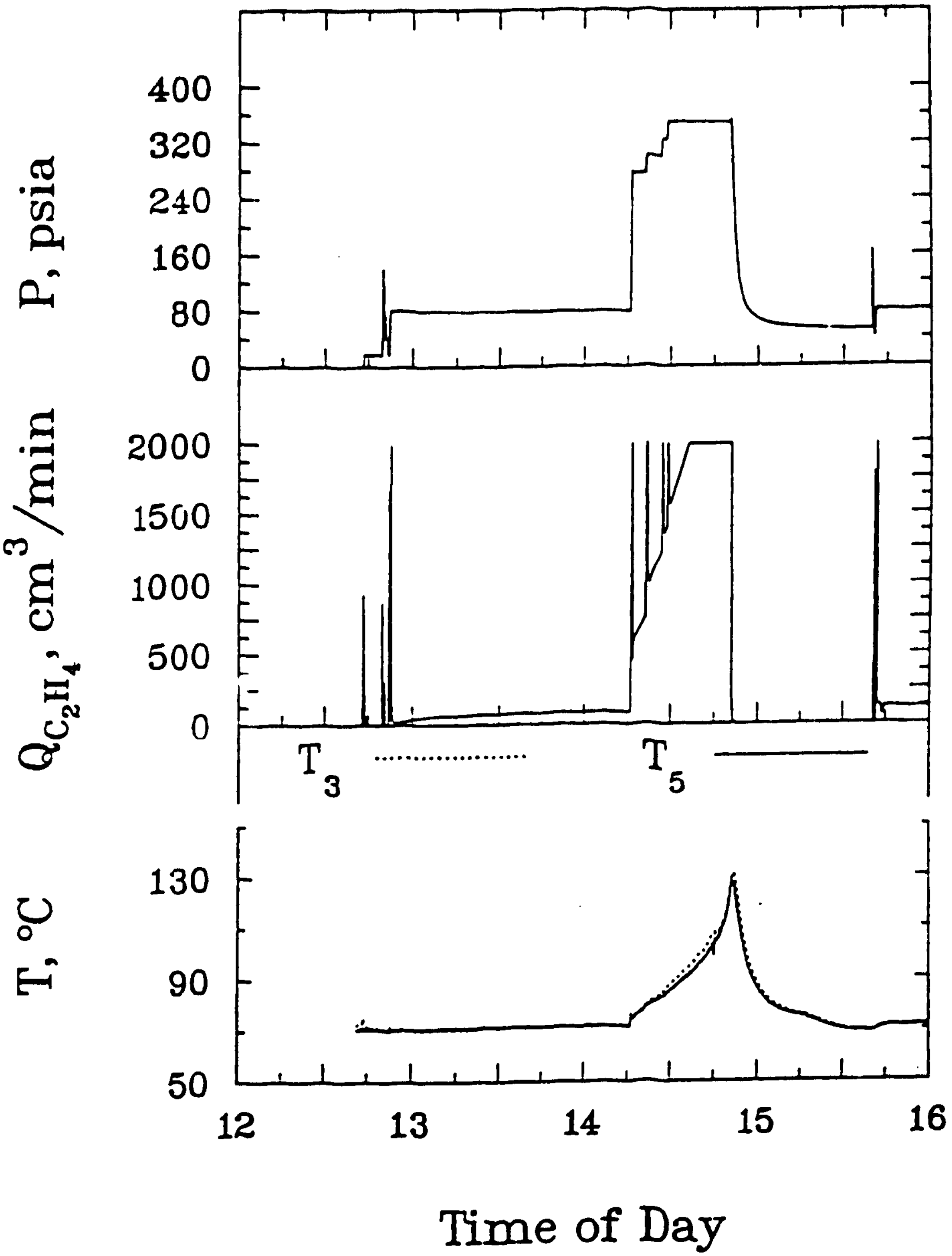
22 JANUARY 1992 25 g NOVA PE GAS9203

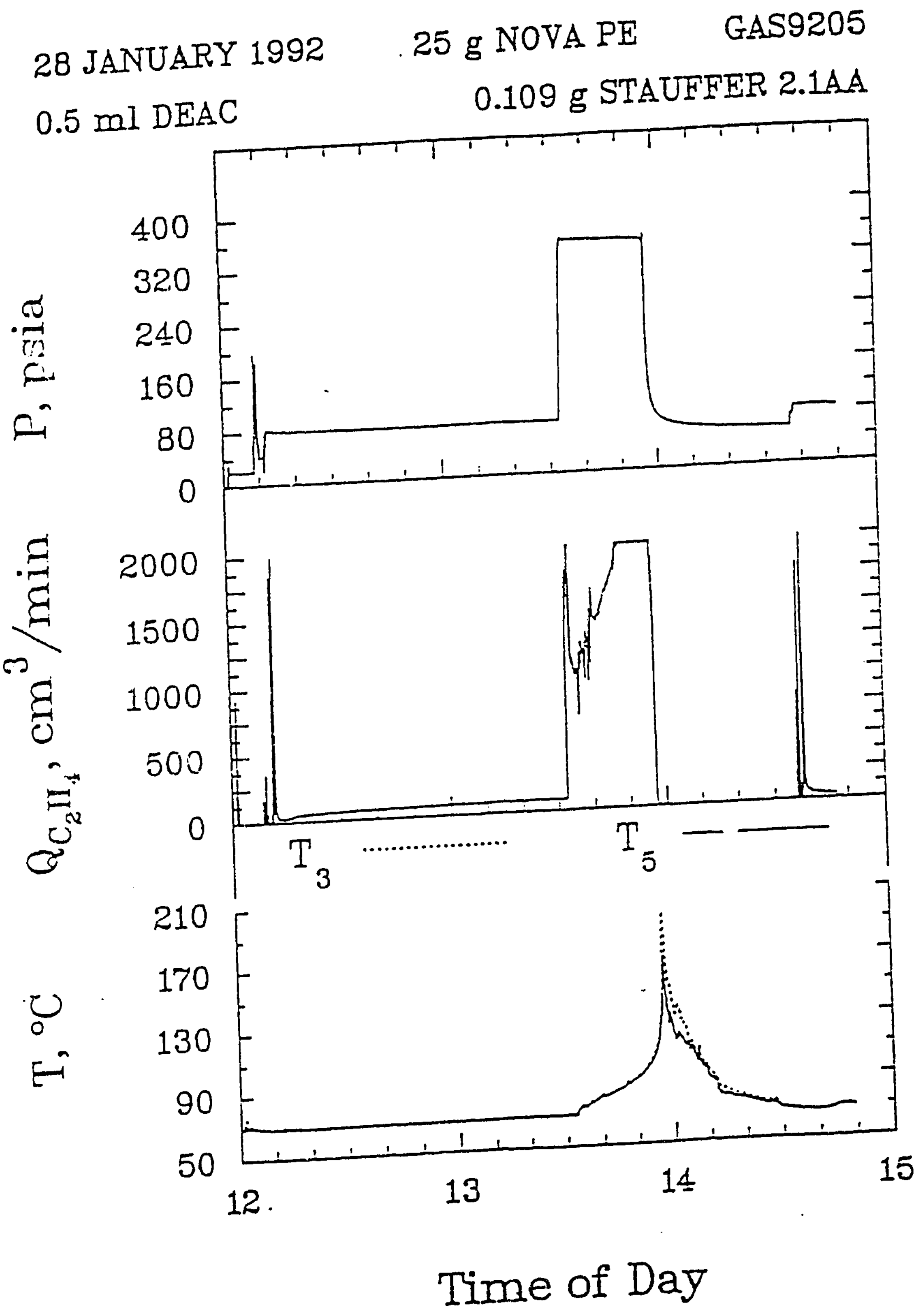
0.5 ml DEAC 0.103 g STAUFFER 2.1AA

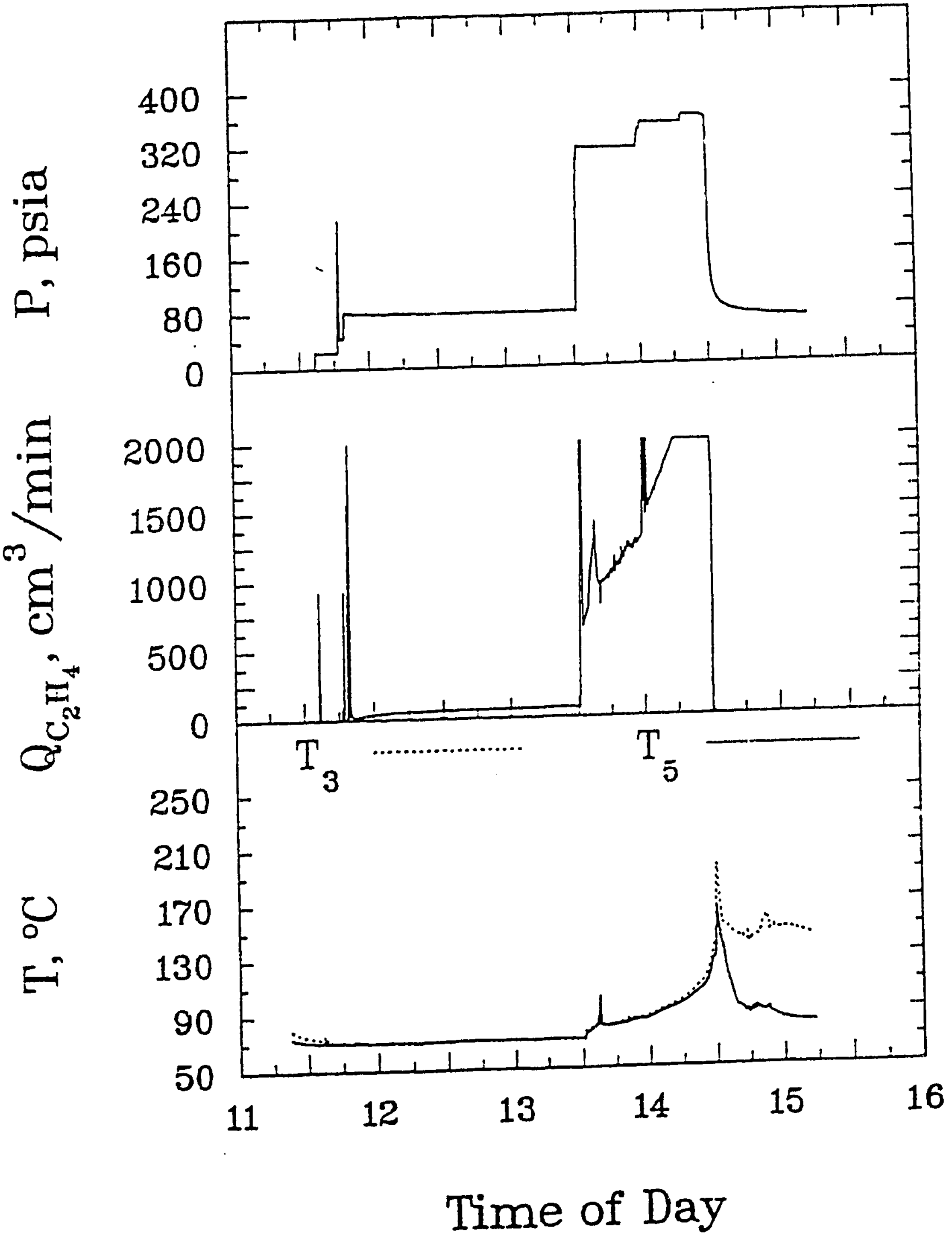


24 JANUARY 1992 25 g NOVA PE GAS9204

0.5 ml DEAC 0.104 g STAUFFER 2.1AA



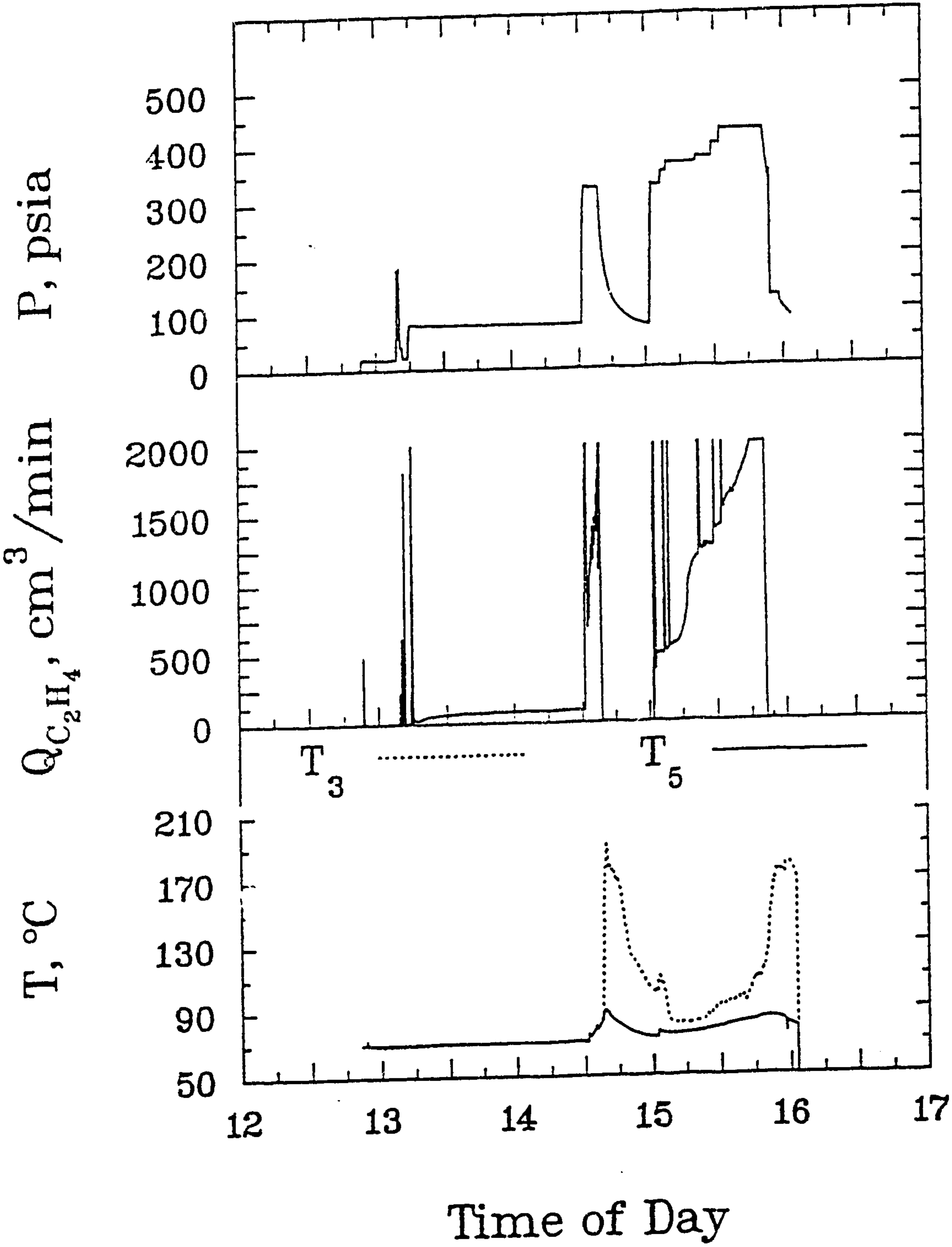

28 JANUARY 1992
25 g NOVA PE
GAS9205
0.5 ml DEAC
0.109 g STAUFFER 2.1AA
P, psia
400
320
240
160
80
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
210
170
130
90
50
12
13
14
15
Time of Day



30 JANUARY 1992 25 g NOVA PE GAS9206
0.5 ml DEAC 0.99 g STAUFFER 2.1AA

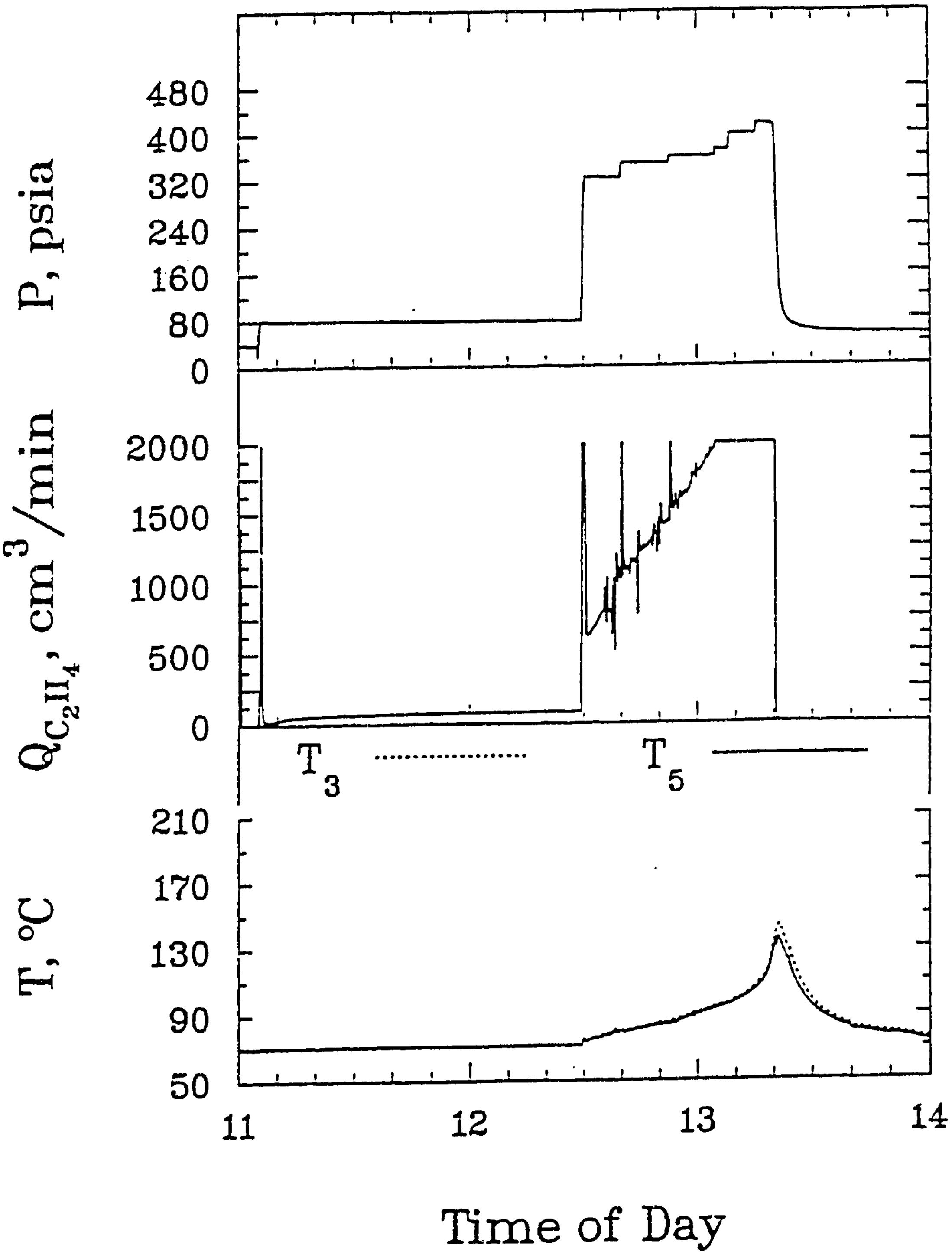
1 FEBRUARY 1992 25 g NOVA PE GAS9207

0.5 ml DEAC 0.106 g STAUFFER 2.1AA



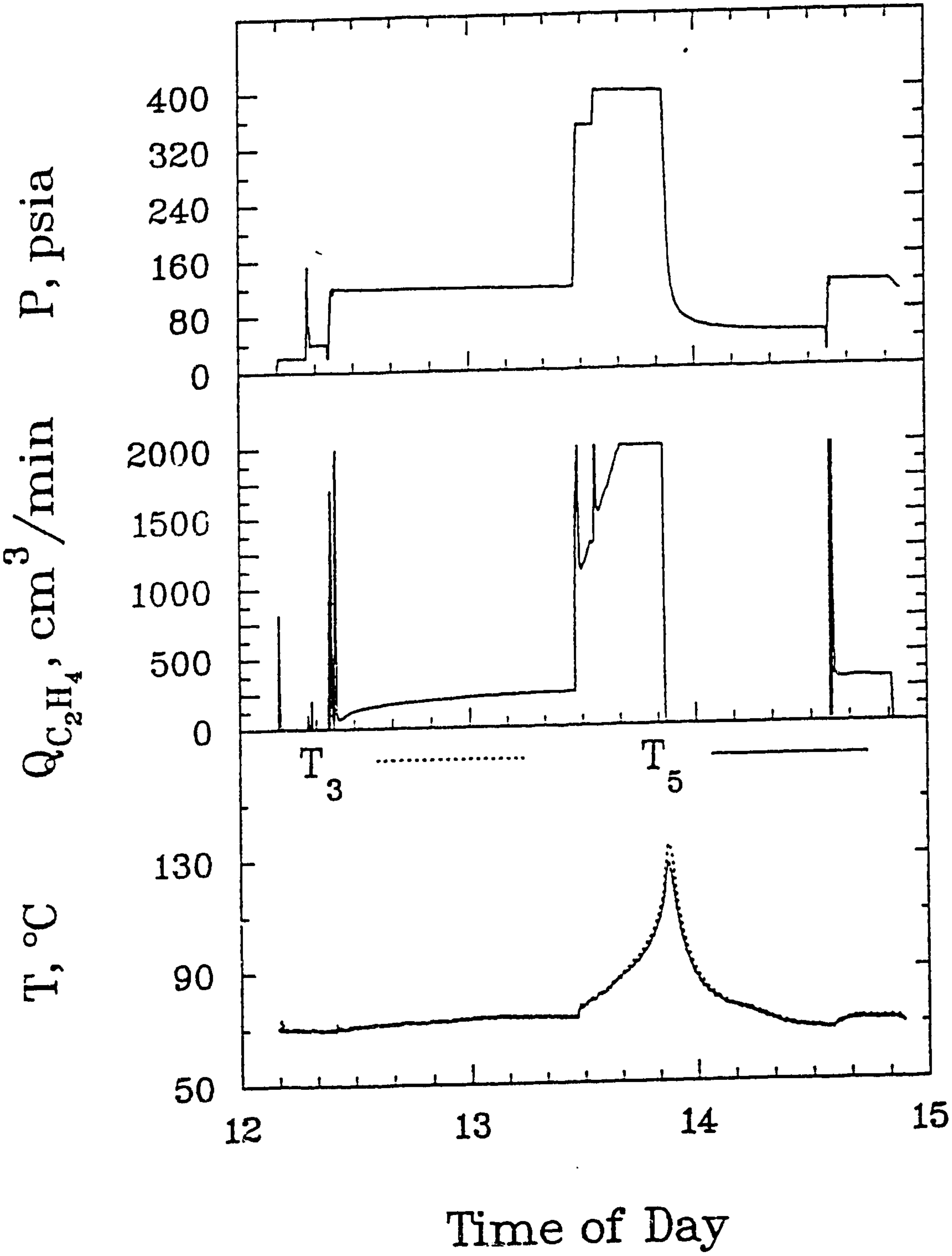
5 FEBRUARY 1992 25 g NOVA PE GAS9208

0.5 ml DEAC 0.104 g STAUFFER 2.1AA



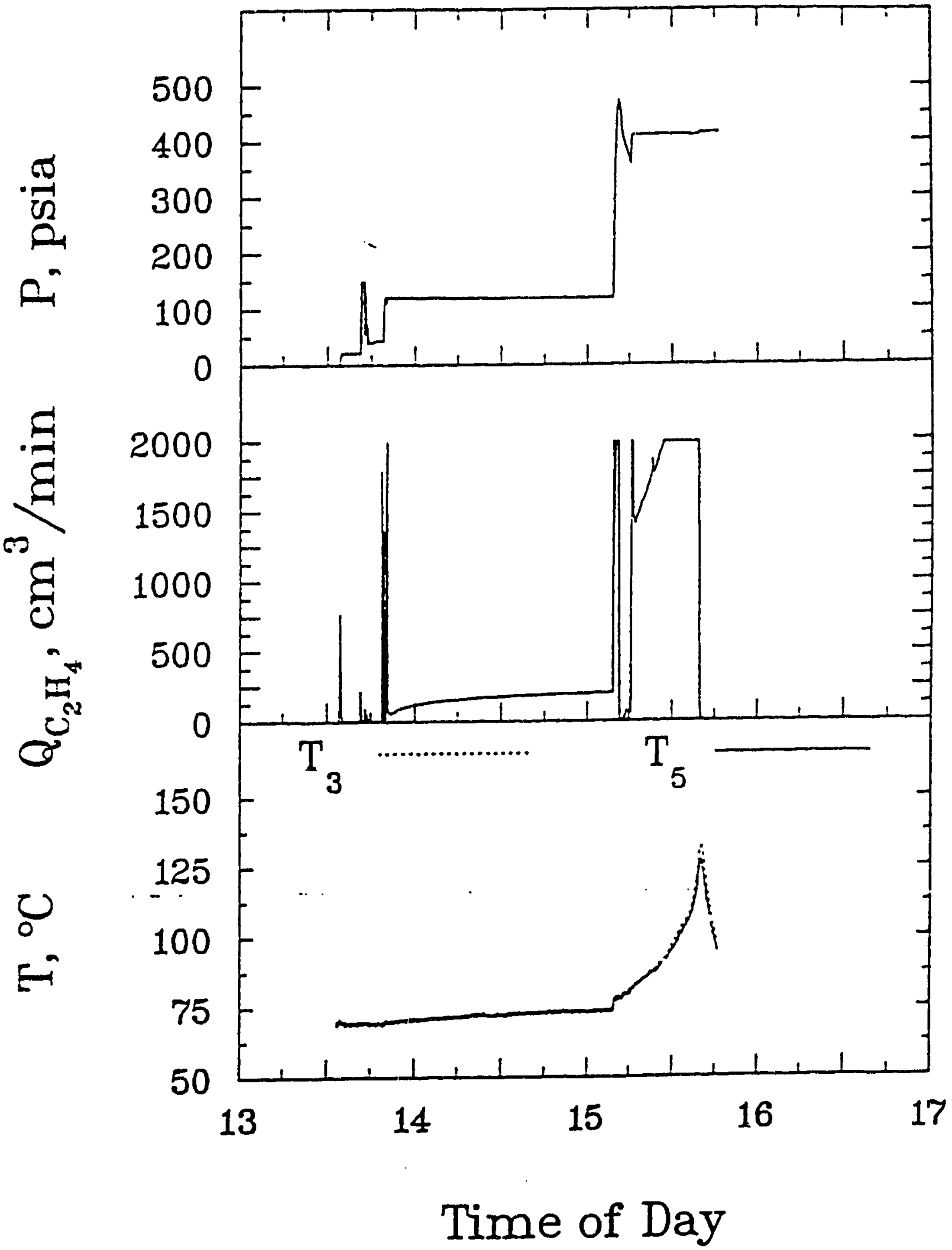
7 FEBRUARY 1992 25 g NOVA PE GAS9209

0.5 ml DEAC 0.110 g STAUFFER 2.1AA



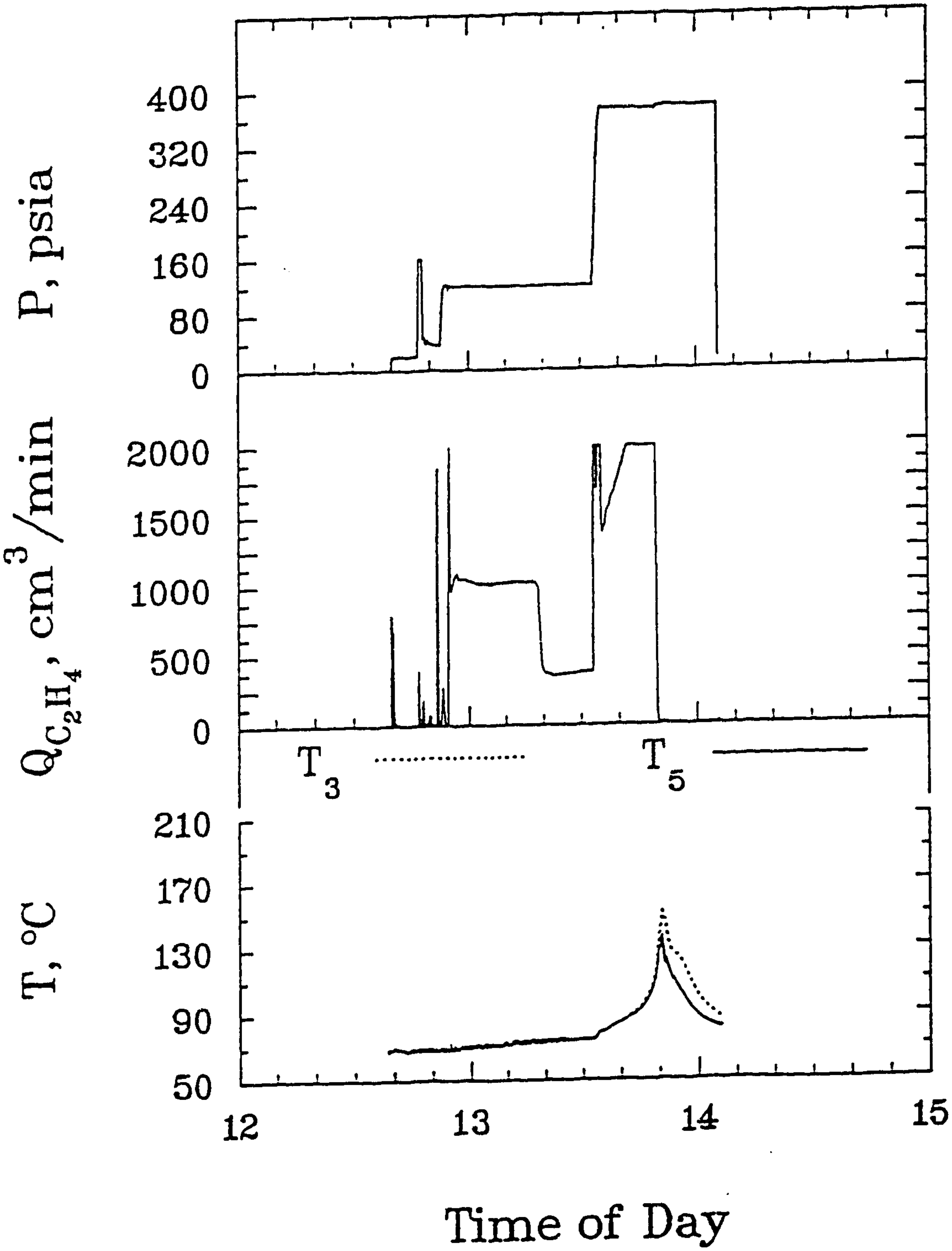
11 FEBRUARY 1992 25 g NOVA PE GAS9210

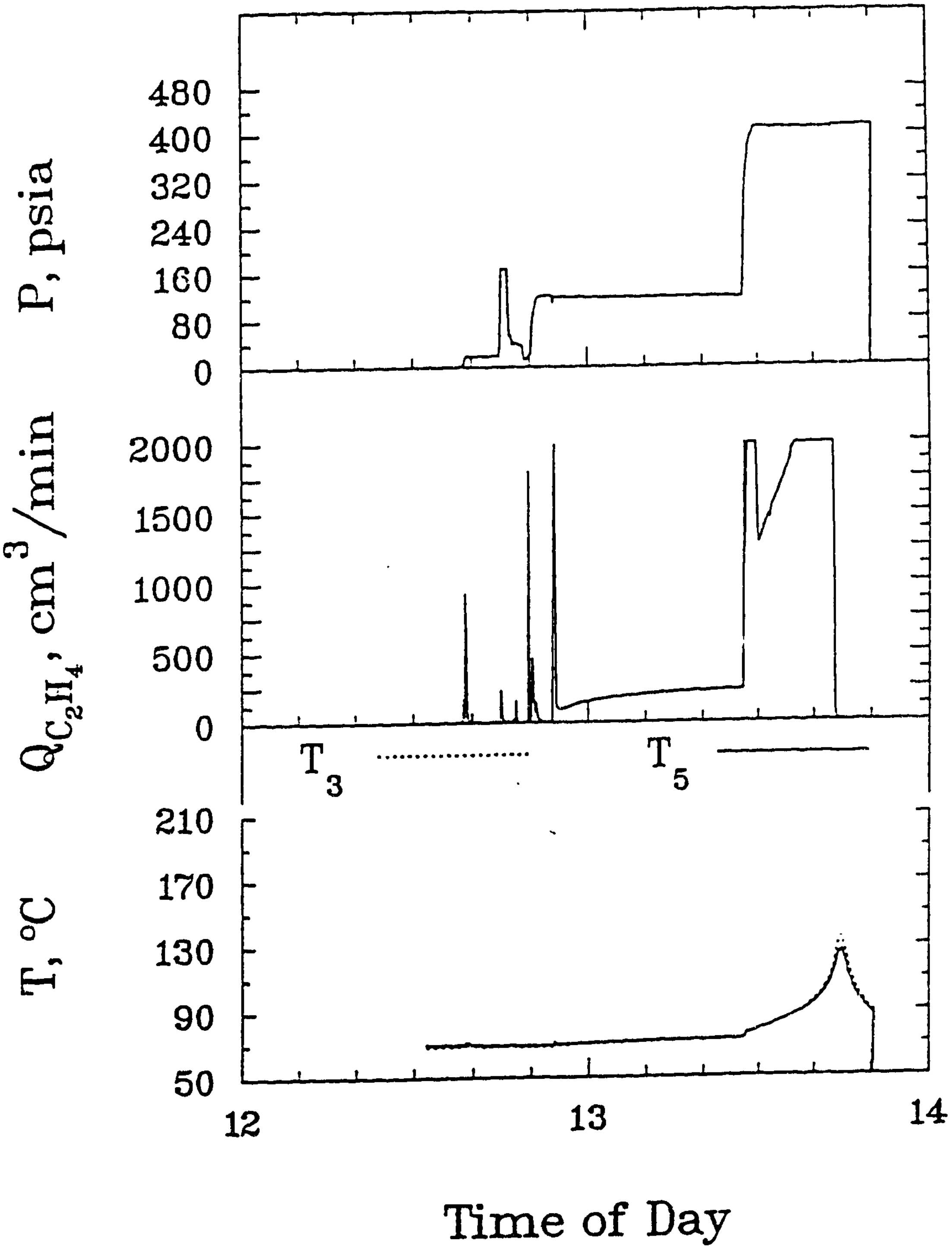
0.5 ml DEAC 0.108 g STAUFFER 2.1AA



13 FEBRUARY 1992 25 g NOVA PE GAS9211

0.5 ml DEAC 0.108 g STAUFFER 2.1AA



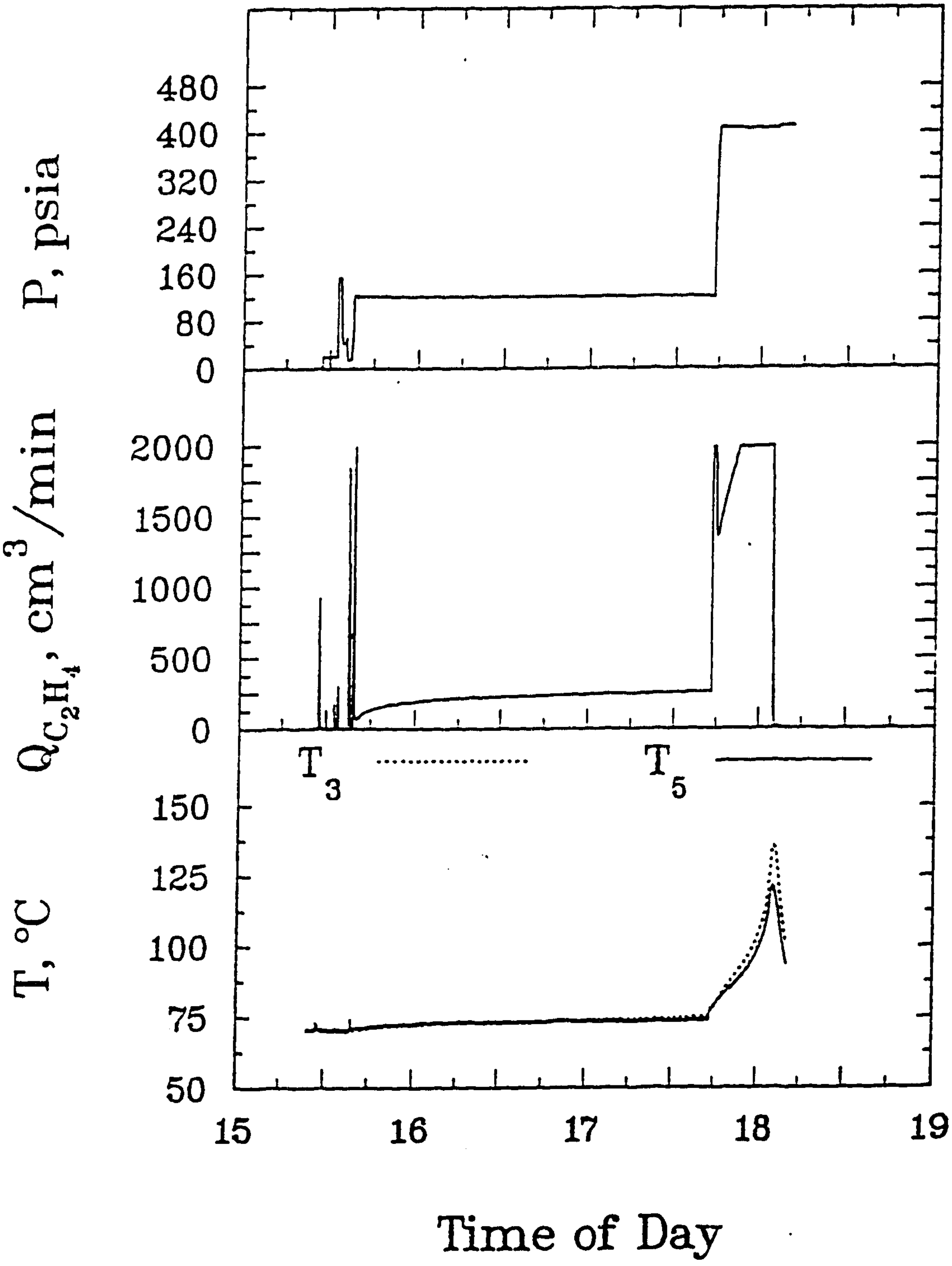


15 FEBRUARY 1992 25 g NOVA PE GAS9212

0.5 ml DEAC 0.108 g STAUFFER 2.1AA

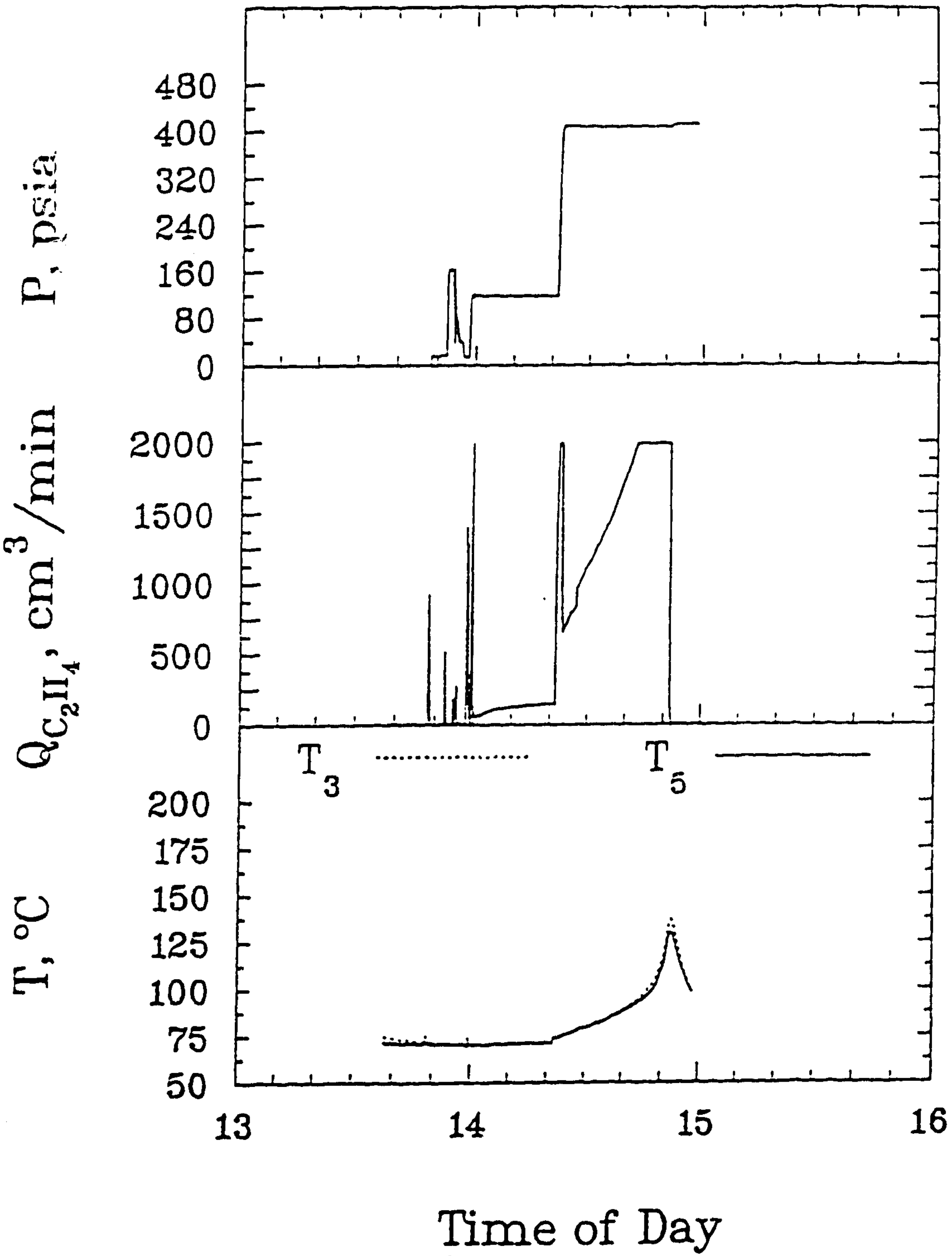
19 FEBRUARY 1992 25 g NOVA PE GAS9213

0.5 ml DEAC 0.104 g STAUFFER 2.1AA



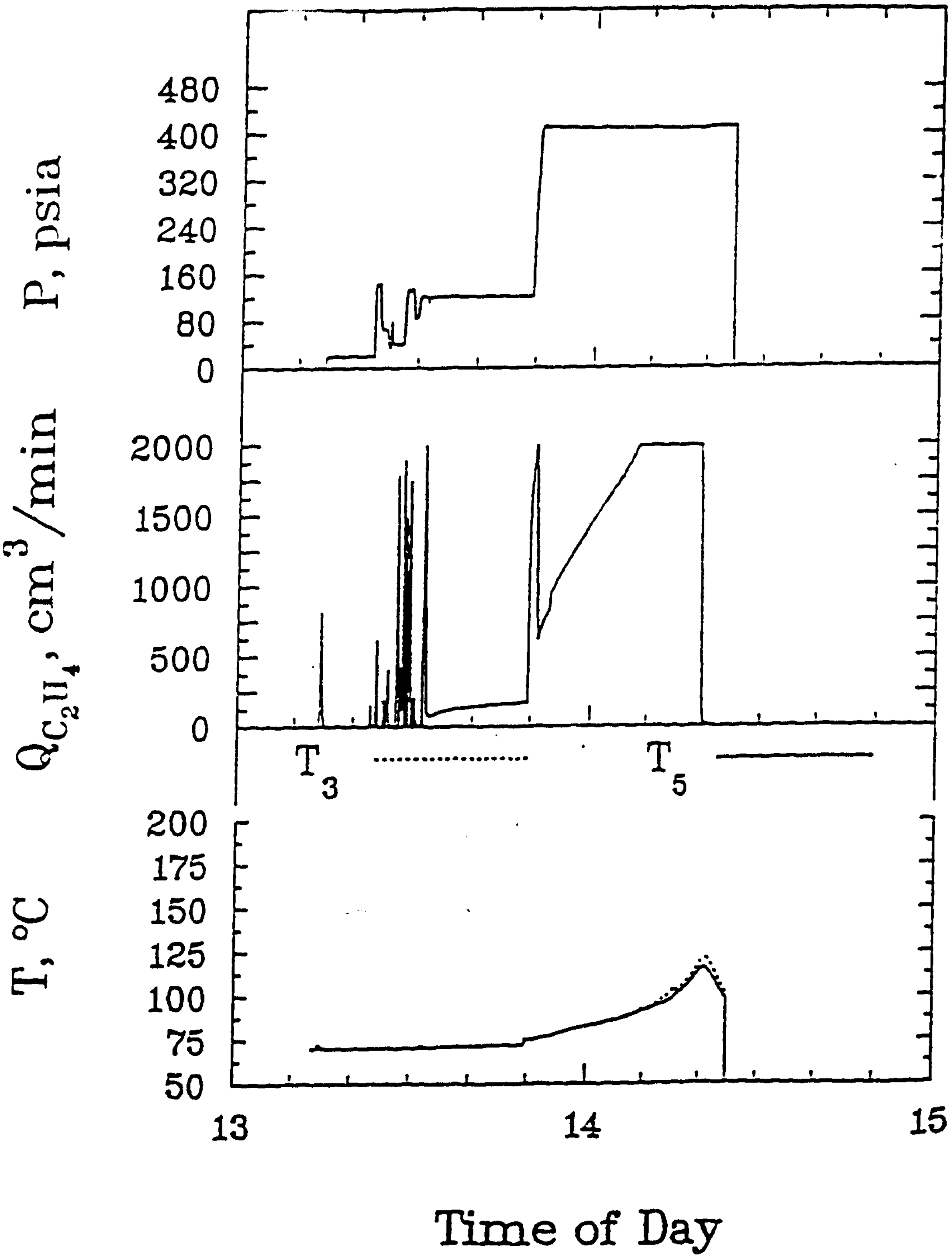
22 FEBRUARY 1992 25 g NOVA PE GAS9214

0.5 ml DEAC 0.108 g STAUFFER 2.1AA



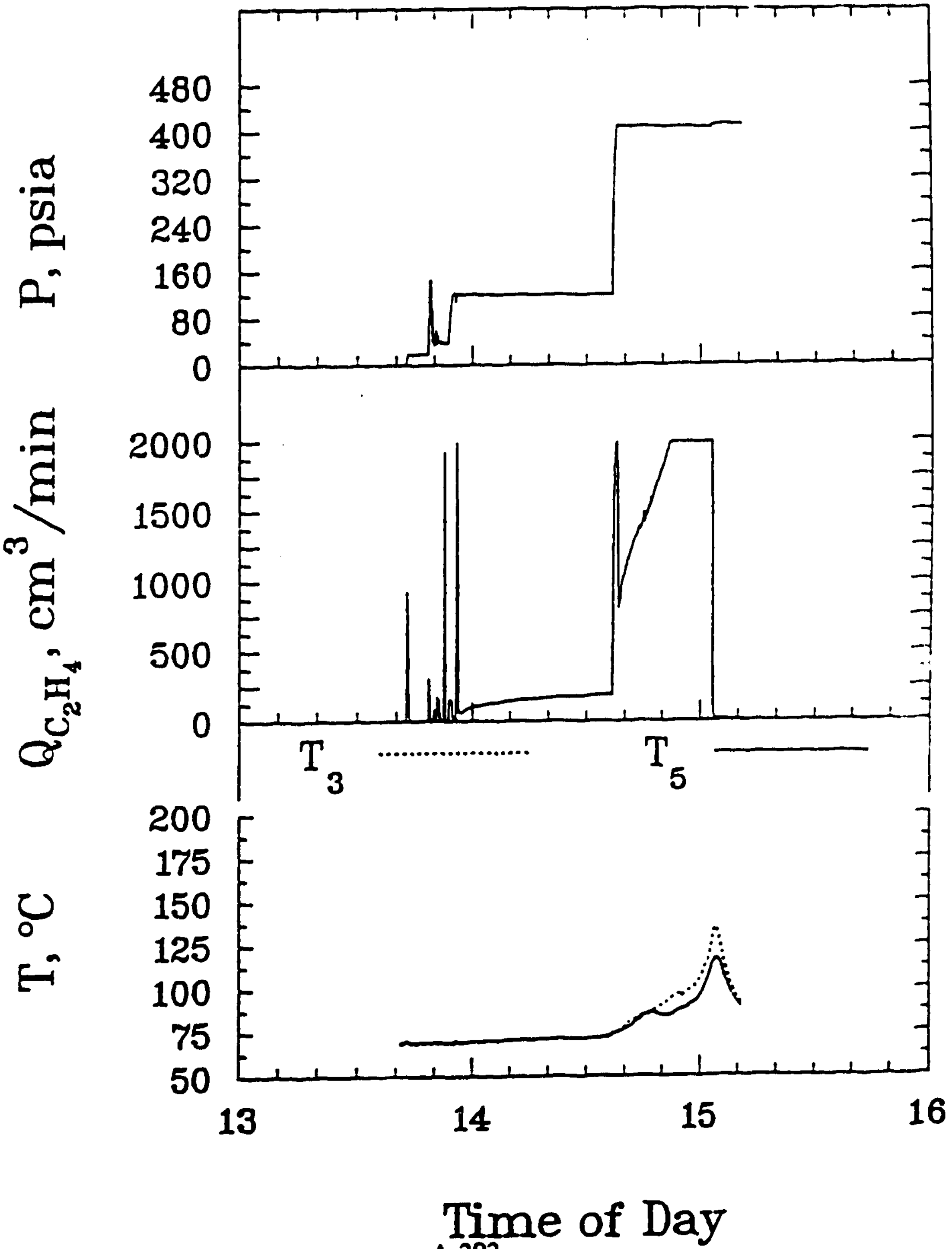
26 FEBRUARY 1992 25 g NOVA PE GAS9215

0.5 ml DEA 0.103 g STAUFFER 2.1AA



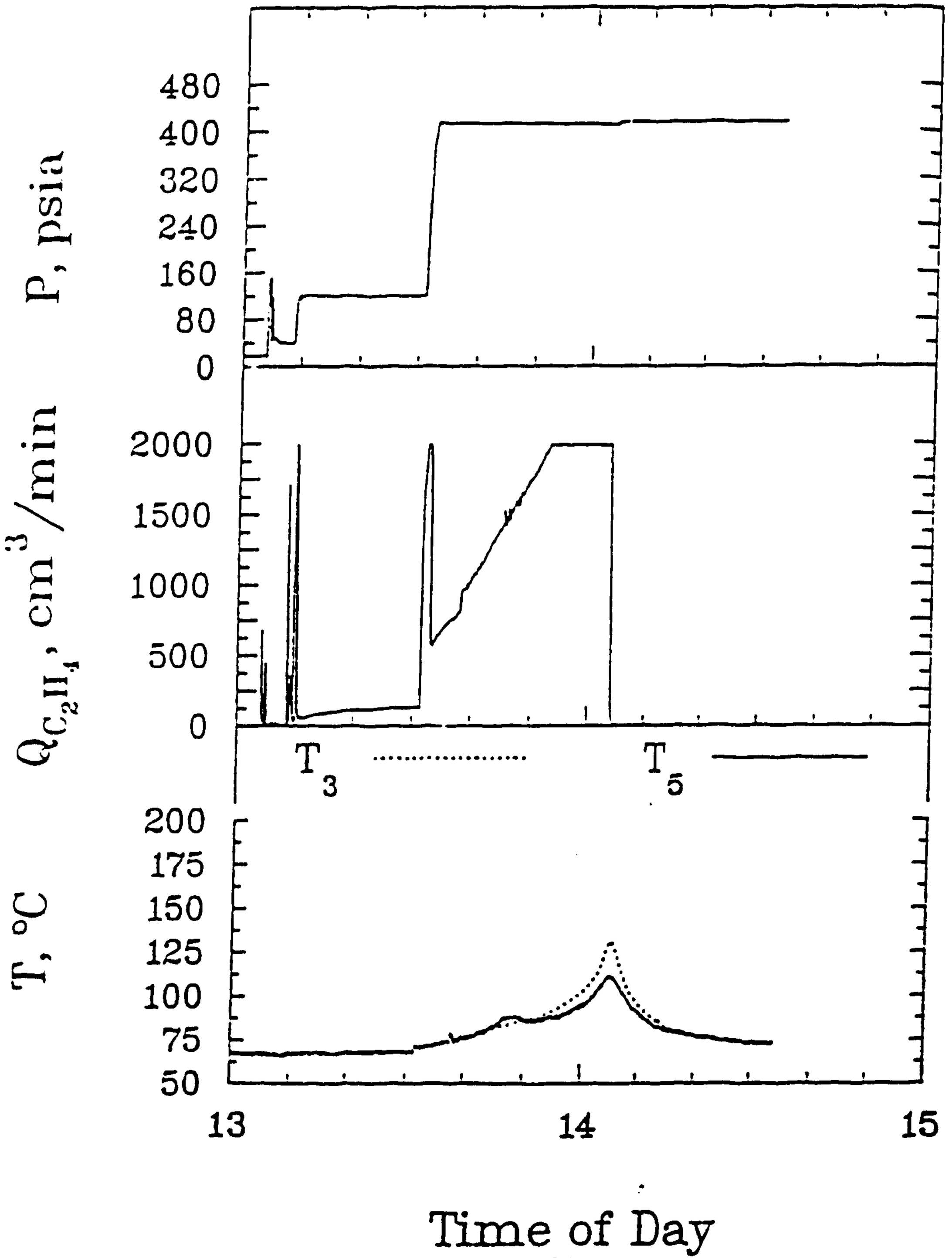
29 FEBRUARY 1992 25 g NOVA PE GAS9216

0.5 ml DEAC 0.110 g STAUFFER 2.1AA



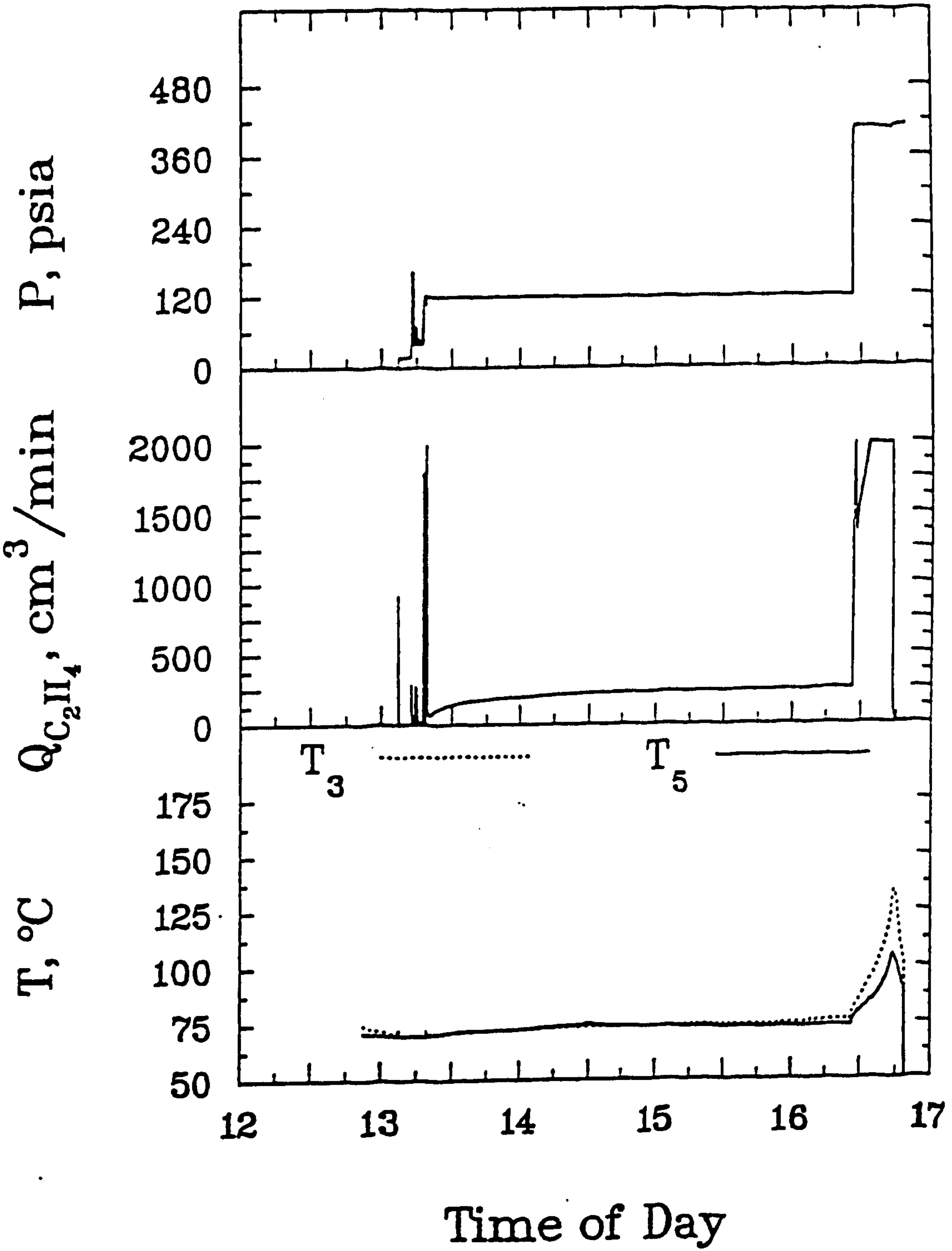
3 MARCH 1992 25 g NOVA PE GAS9217

0.5 ml DEAC 0.109 g STAUFFER 2.1AA



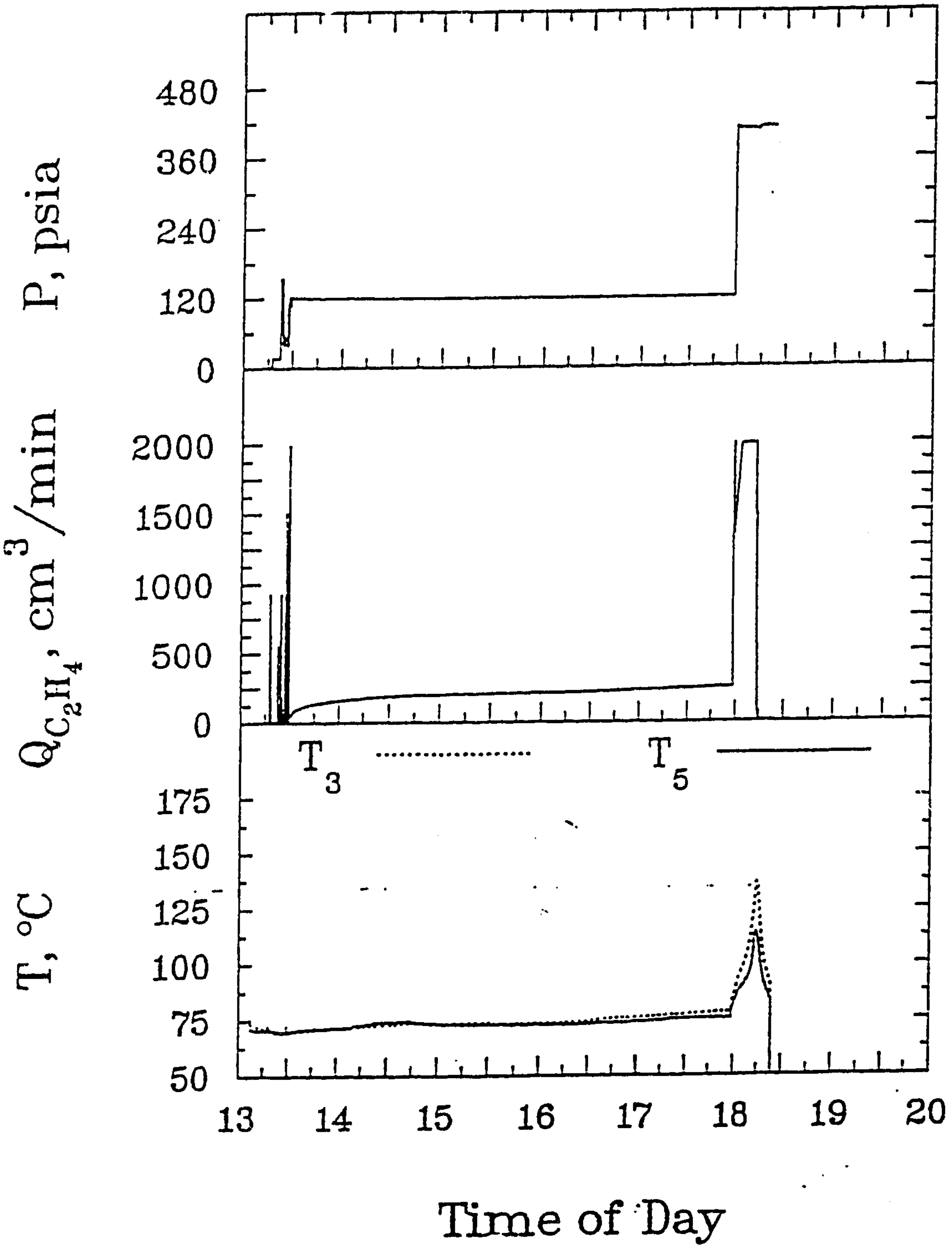
6 MARCH 1992 25 g NOVA PE GAS9218

0.5 ml DEAC 0.109 g STAUFFER 2.1AA

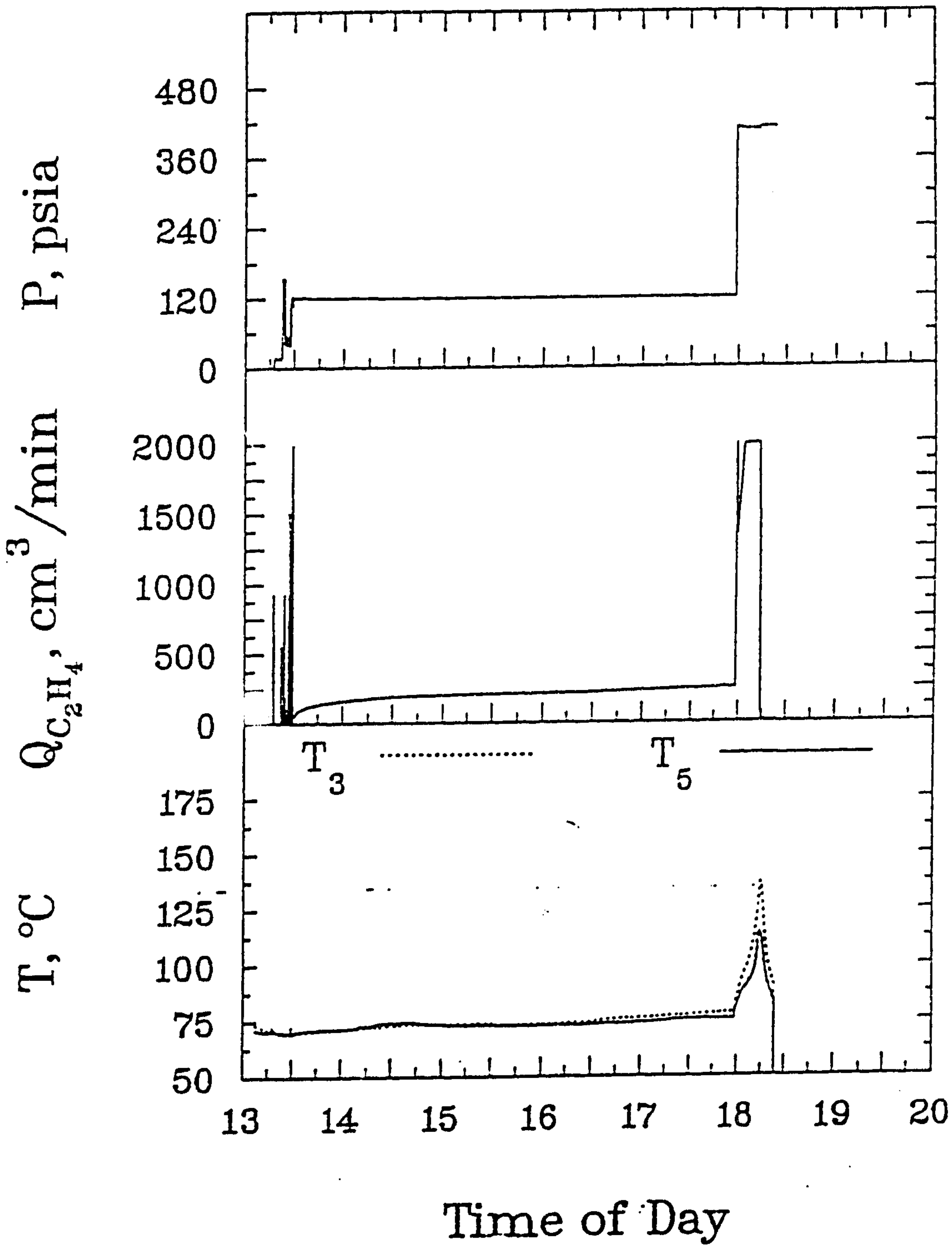


10 MARCH 1992 25 g NOVA PE GAS9219

0.5 ml DEAC 0.110 g STAUFFER 2.1AA

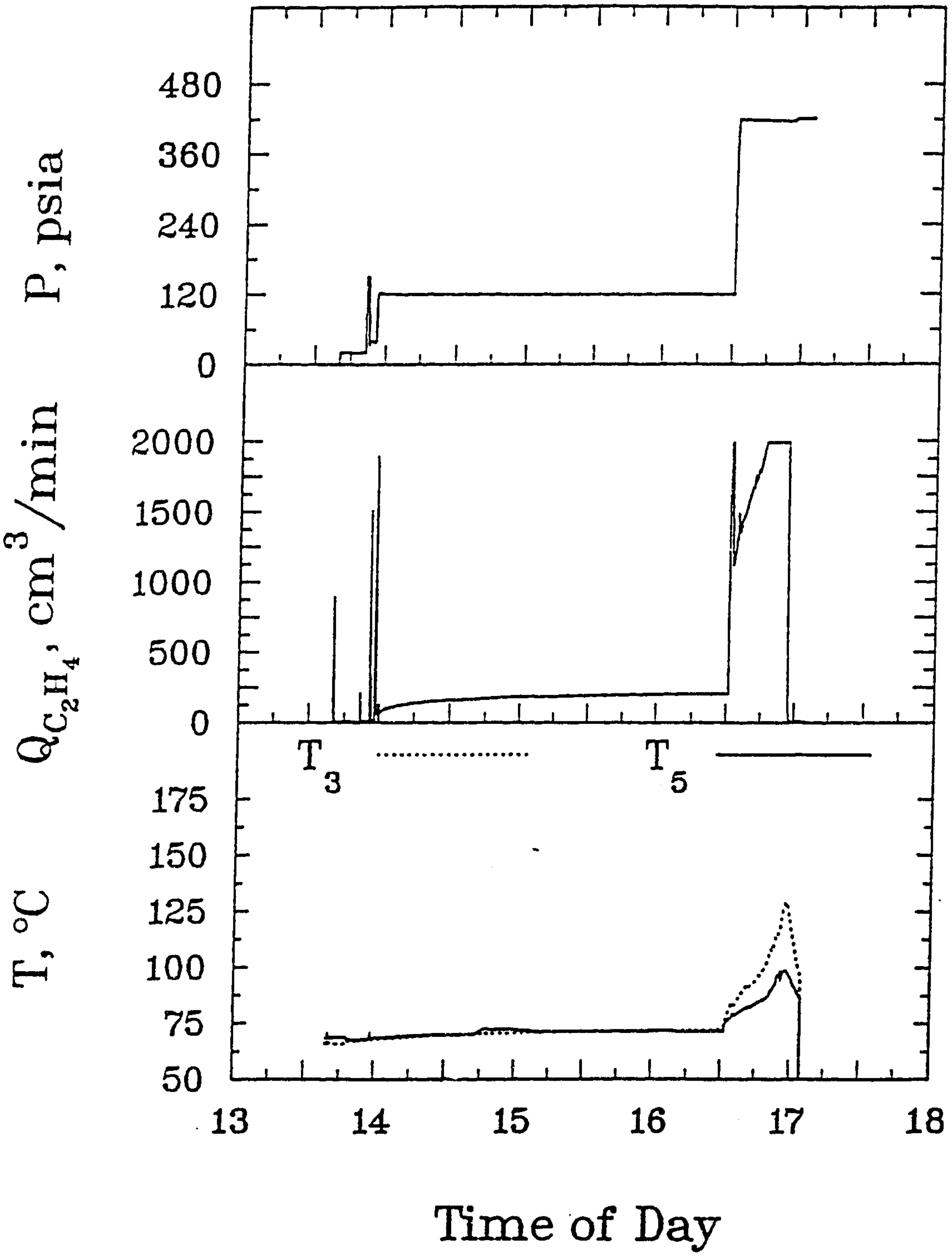


10 MARCH 1992 25 g NOVA PE GAS9219
0.5 ml DEAC 0.110 g STAUFFER 2.1AA



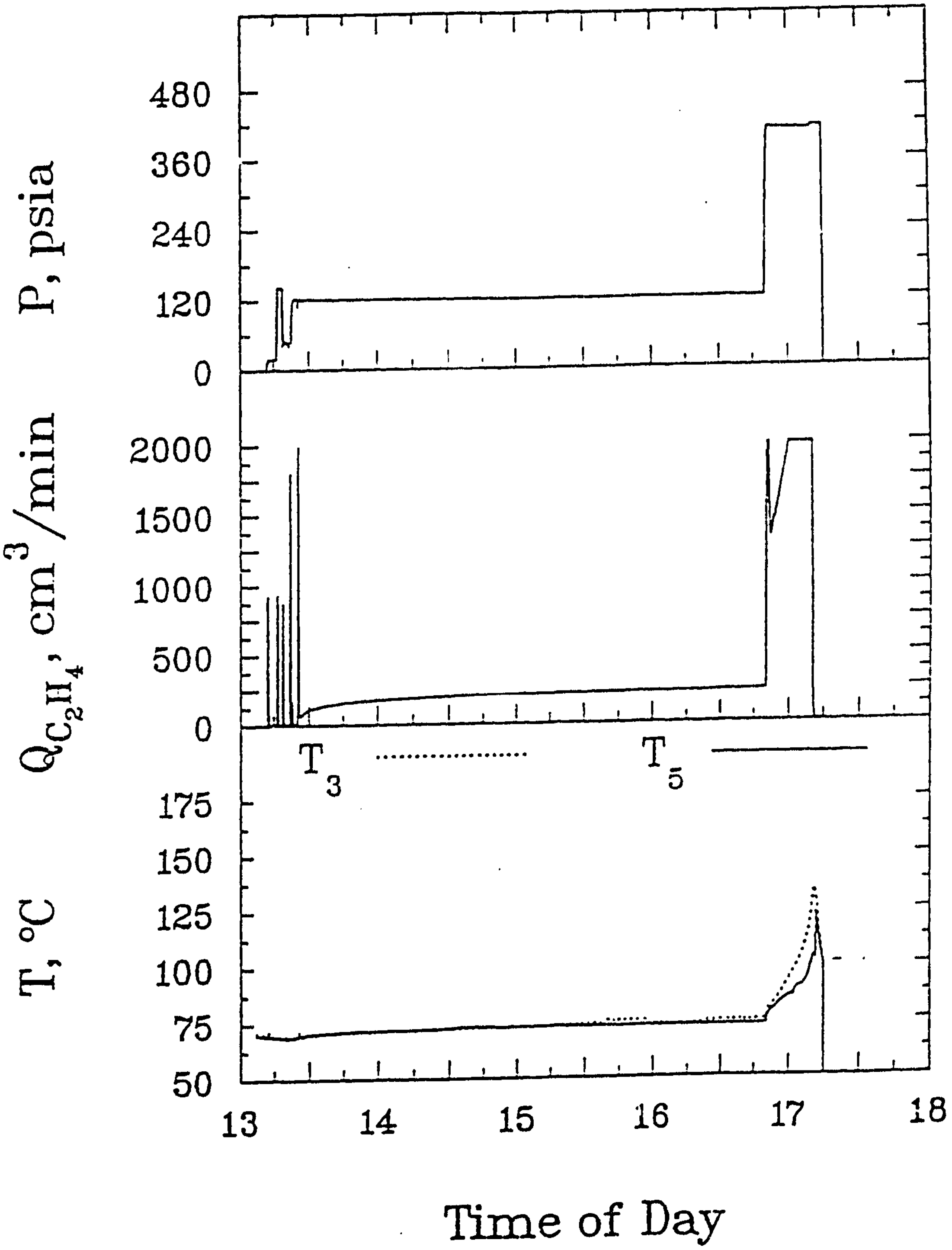
17 MARCH 1992 25 g NOVA PE GAS9221

0.5 ml DEAC 0.113 g STAUFFER 2.1AA



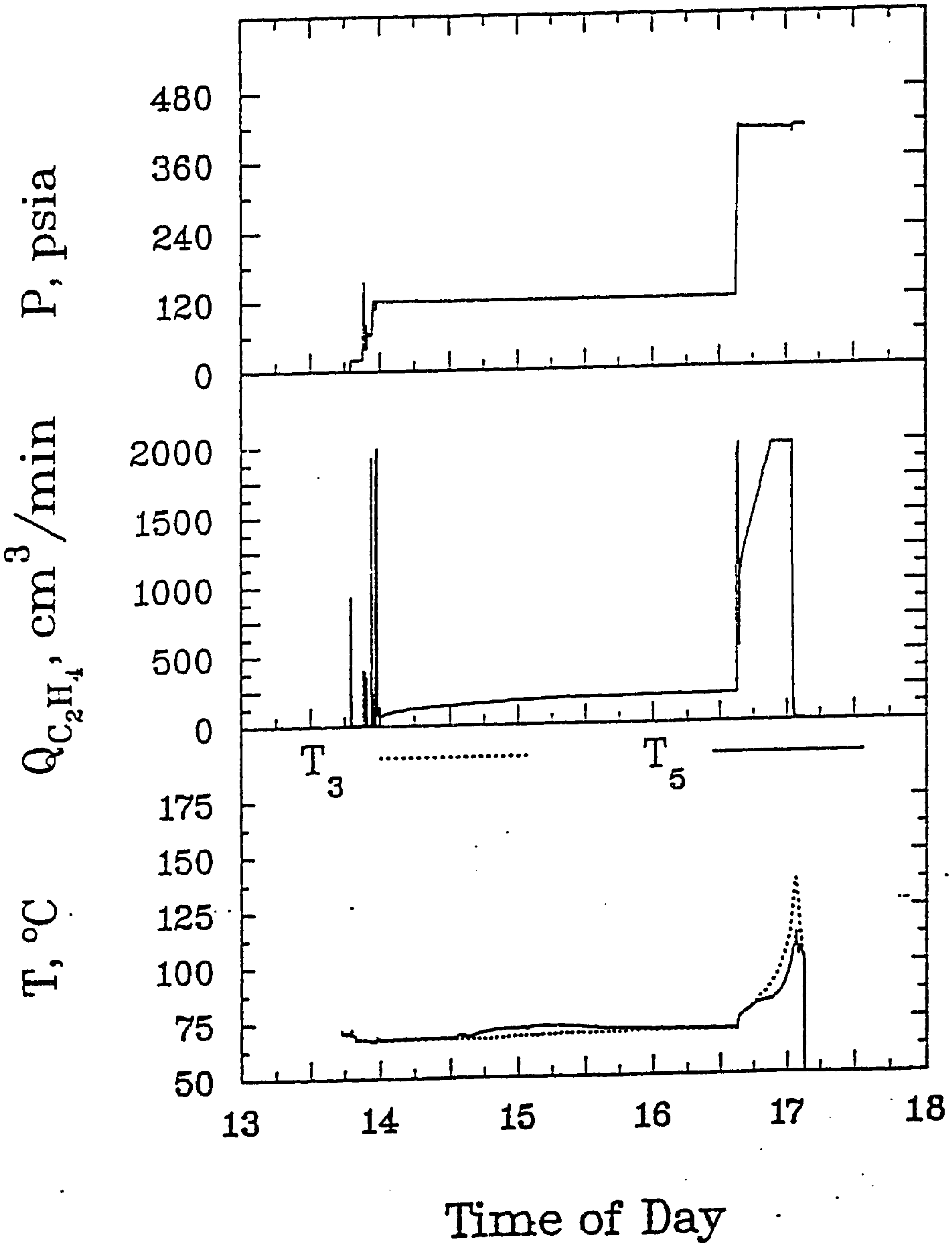
19 MARCH 1992 25 g NOVA PE GAS9222

0.5 ml DEAC 0.109 g STAUFFER 2.1AA



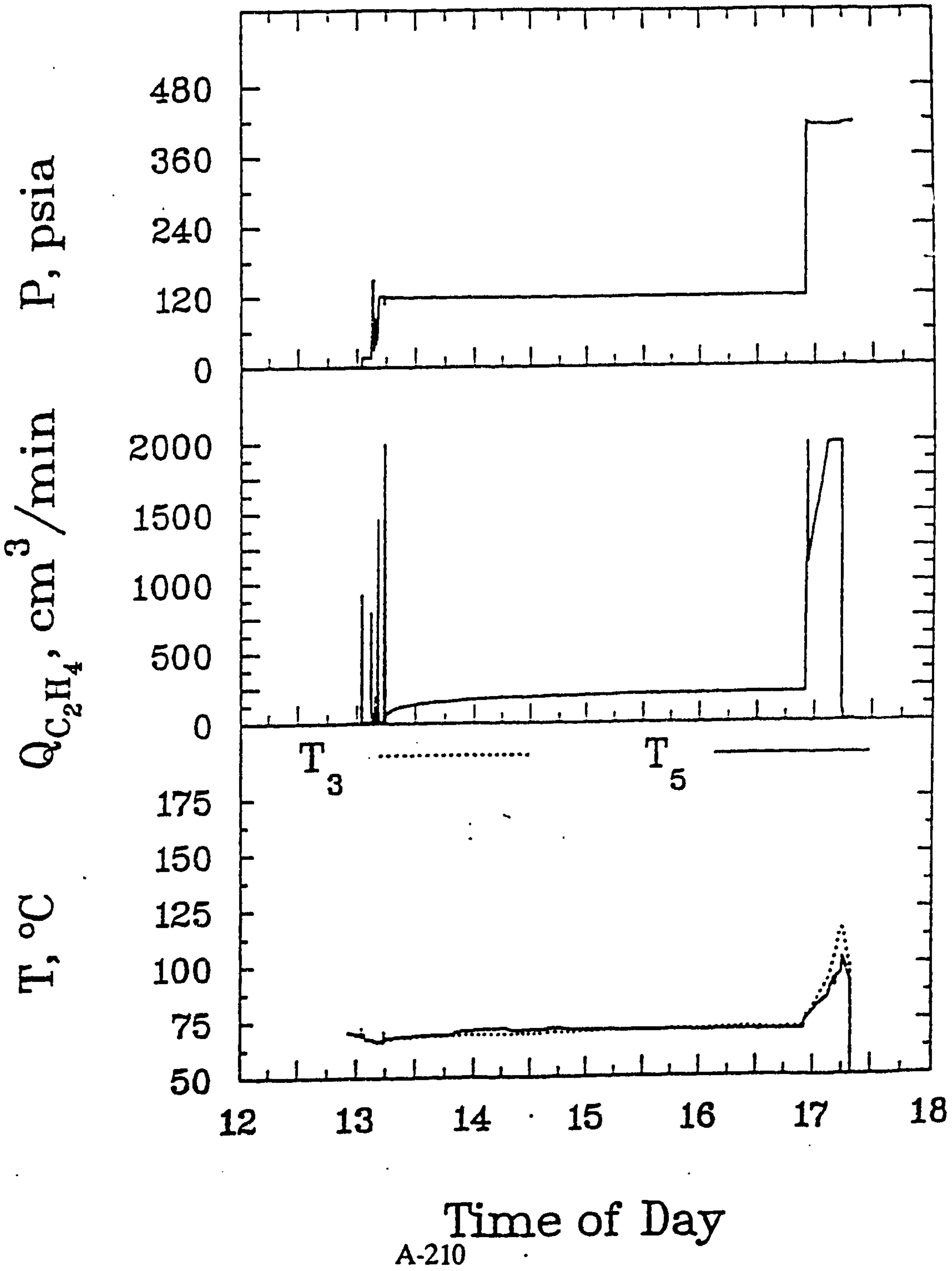
25 MARCH 1992 45 g NOVA PE GAS9223

0.5 ml DEAC 0.113 g STAUFFER 2.1AA



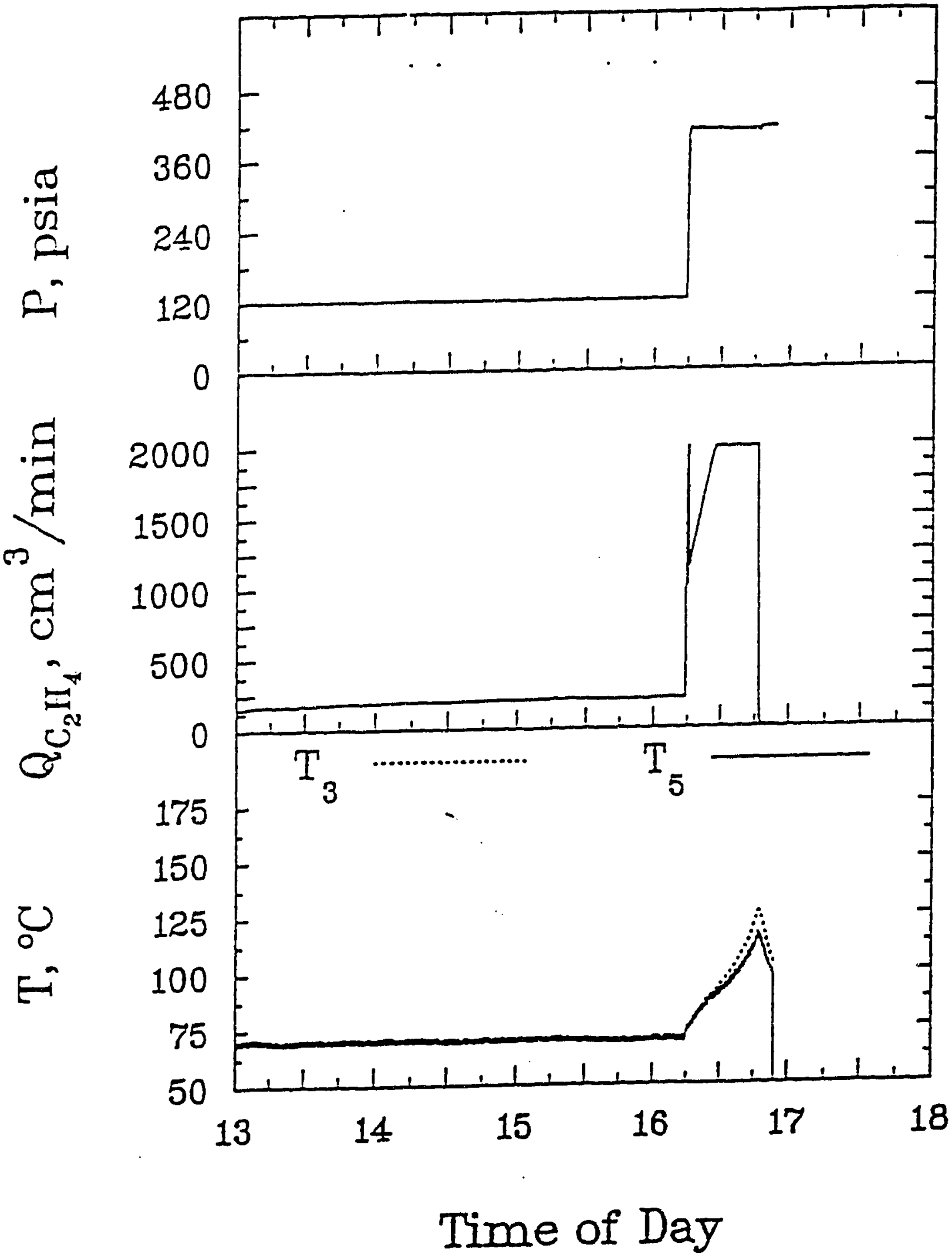
26 MARCH 1992 25 g NOVA PE GAS9224

0.5 ml DEAC 0.110 g STAUFFER 2.1AA



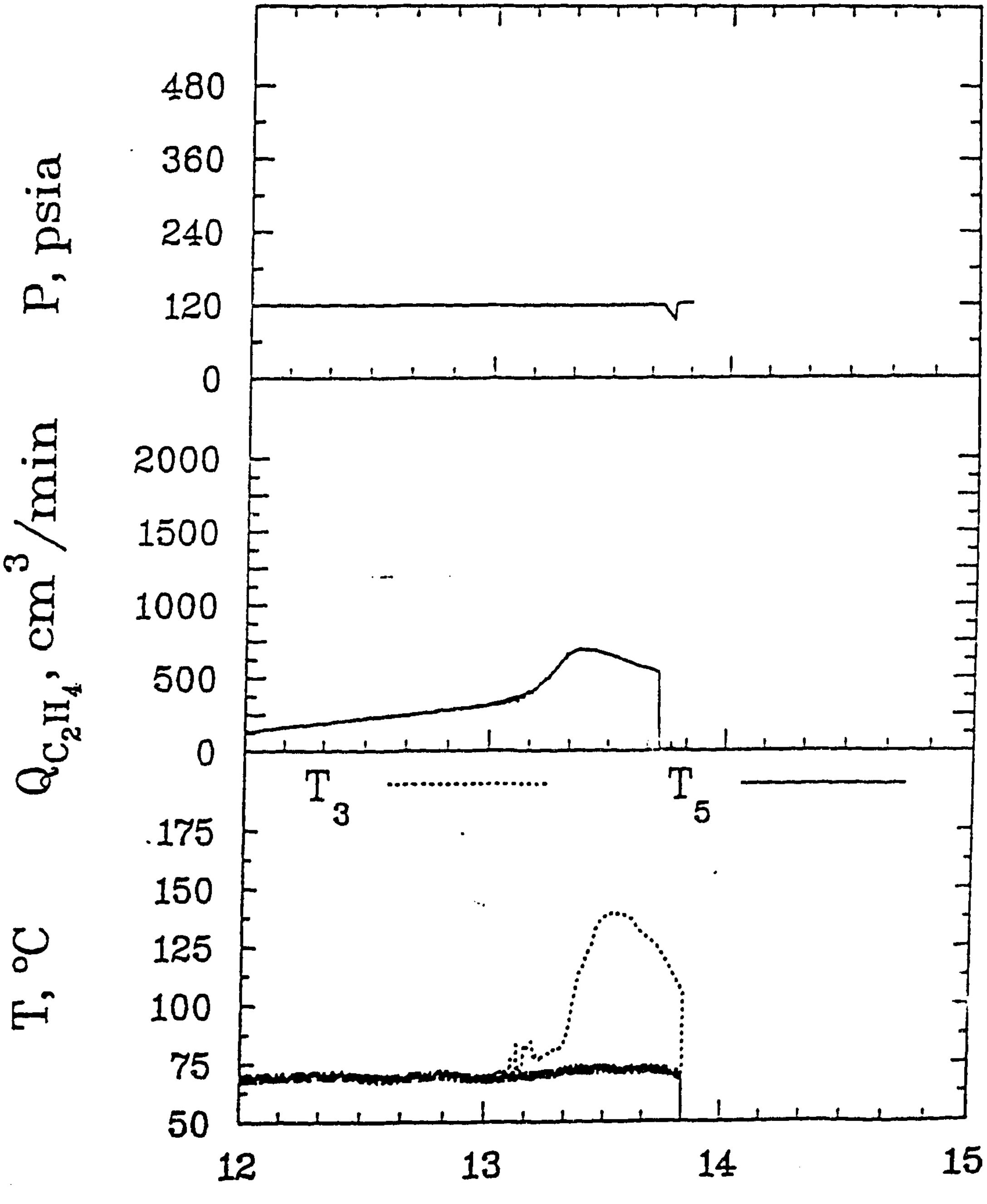
29 APRIL 1992 25 g NOVA PE GAS9235

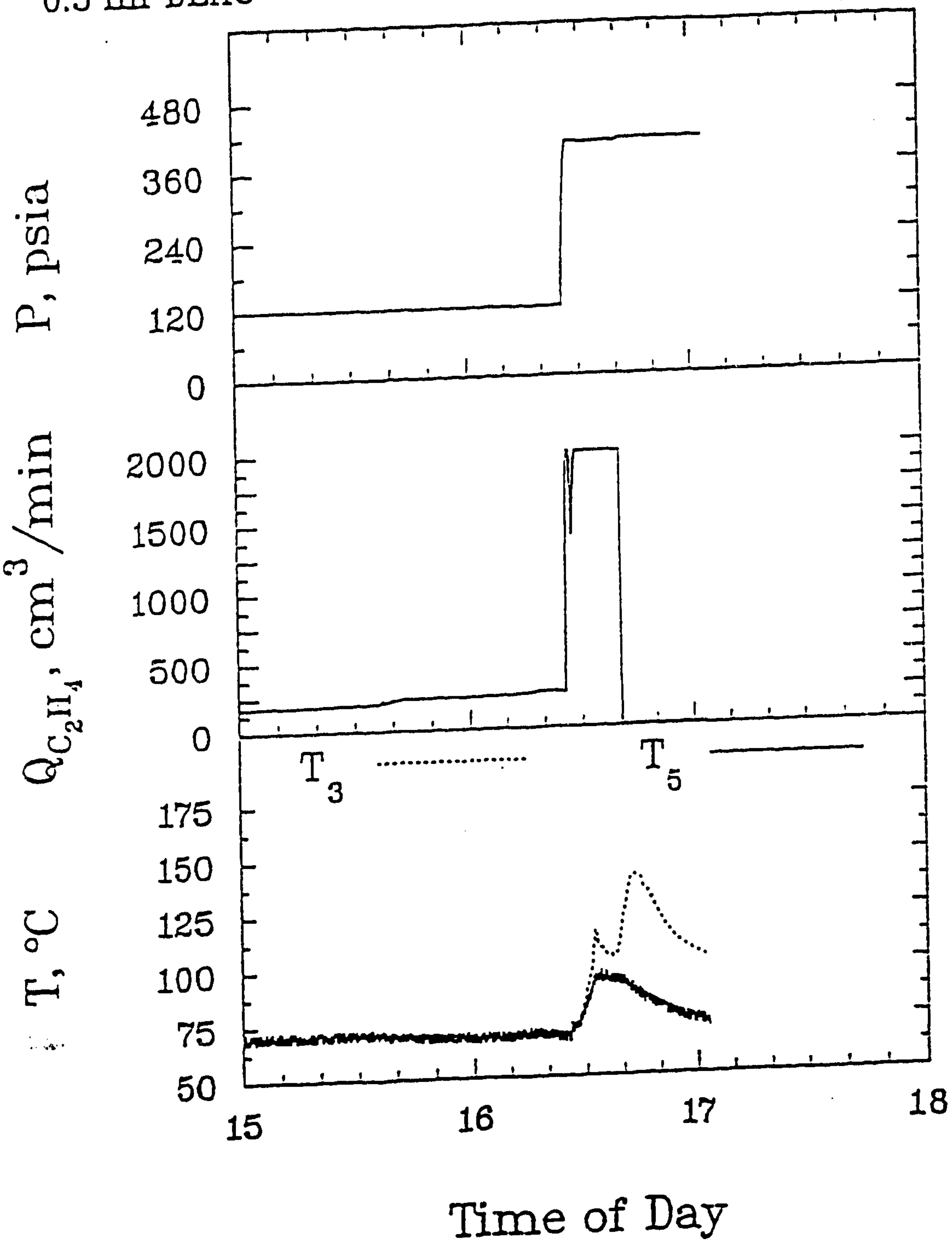
0.5 ml DEAC 0.114 g STAUFFER 2.1AA



1 MAY 1992 25 g NOVA PE GAS9236

0.5 ml DEAC 0.113 g STAUFFER 2.1AA





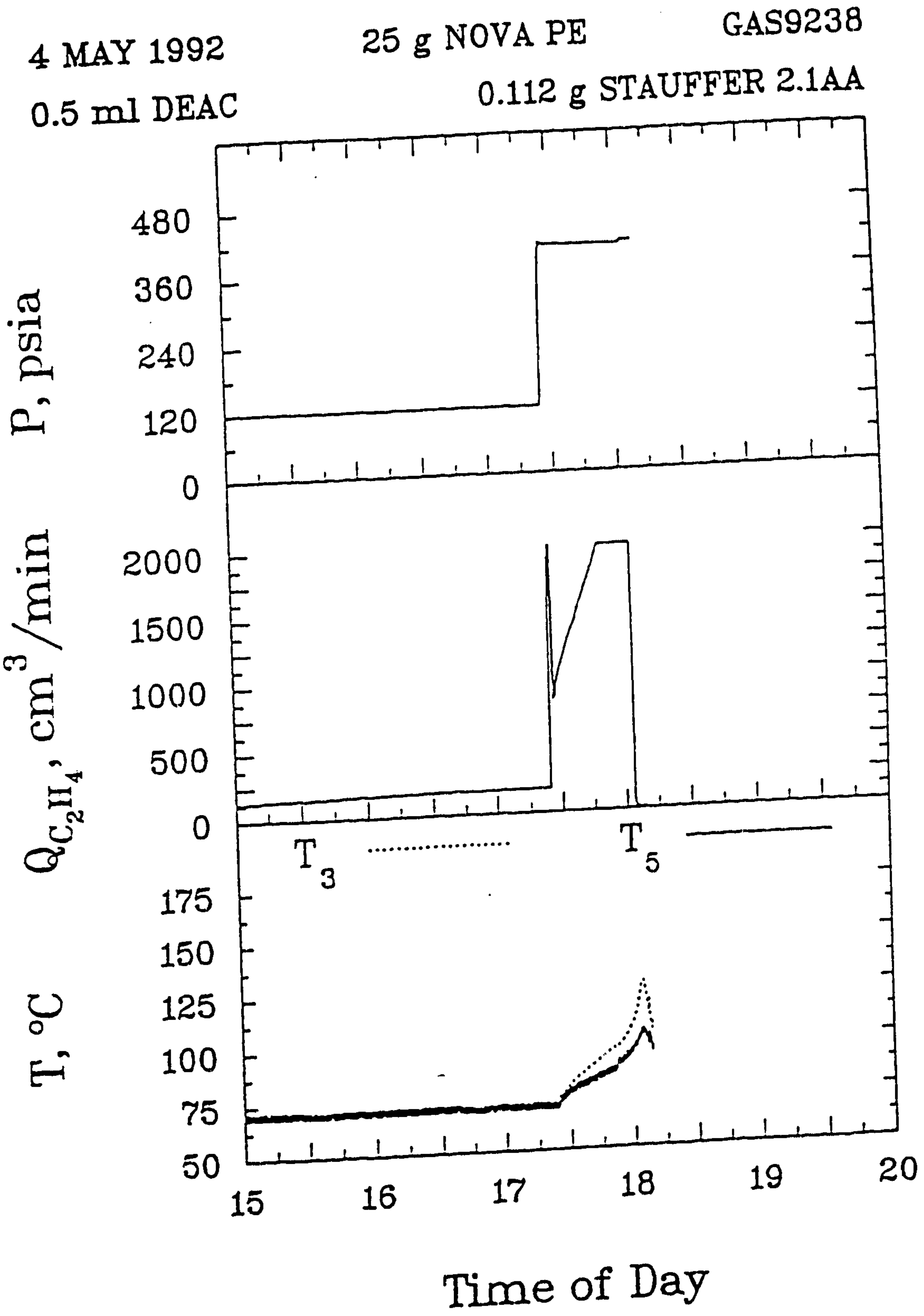
3 MAY 1992

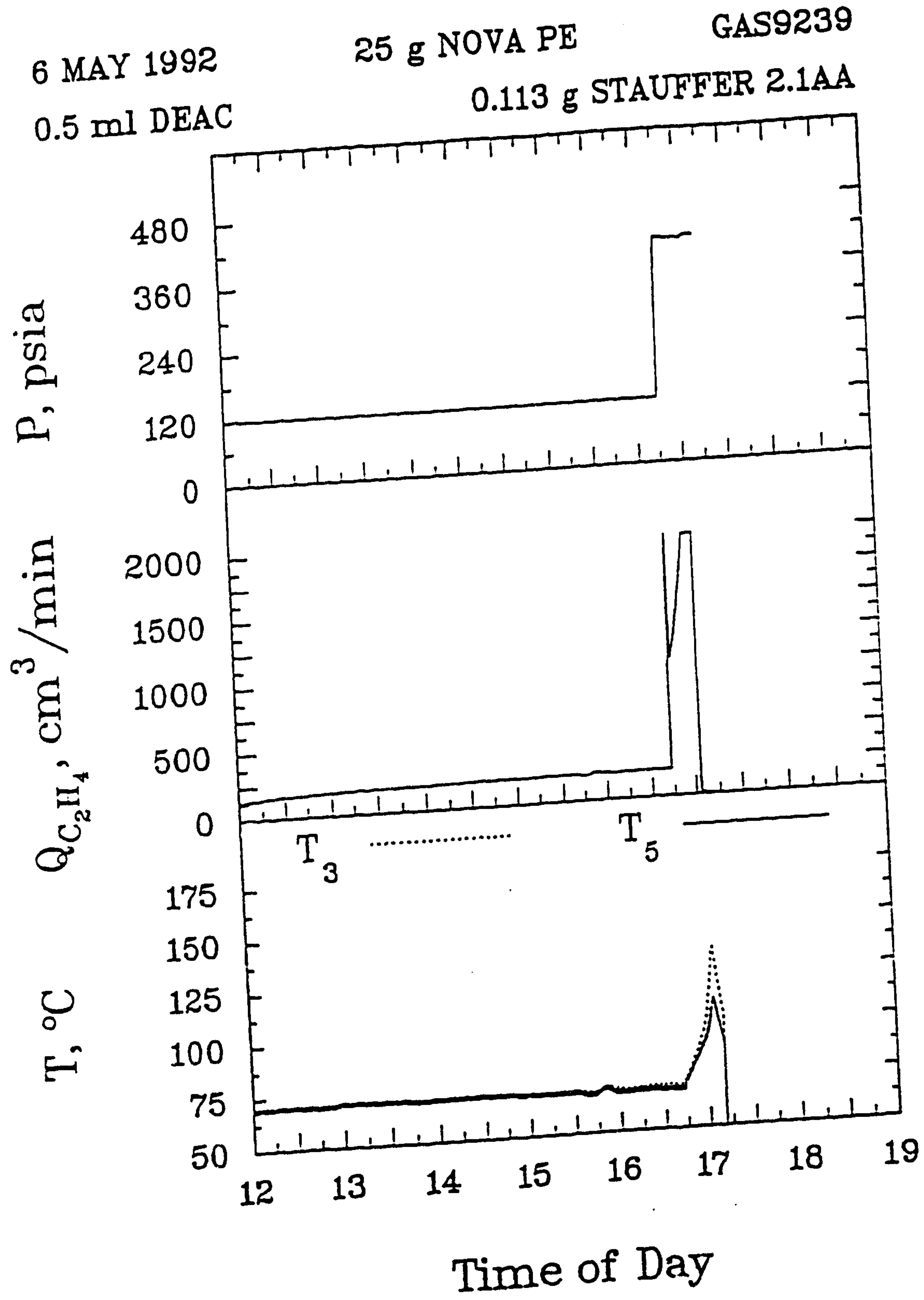
25 g NOVA PE

GAS9237

0.5 ml DEAC

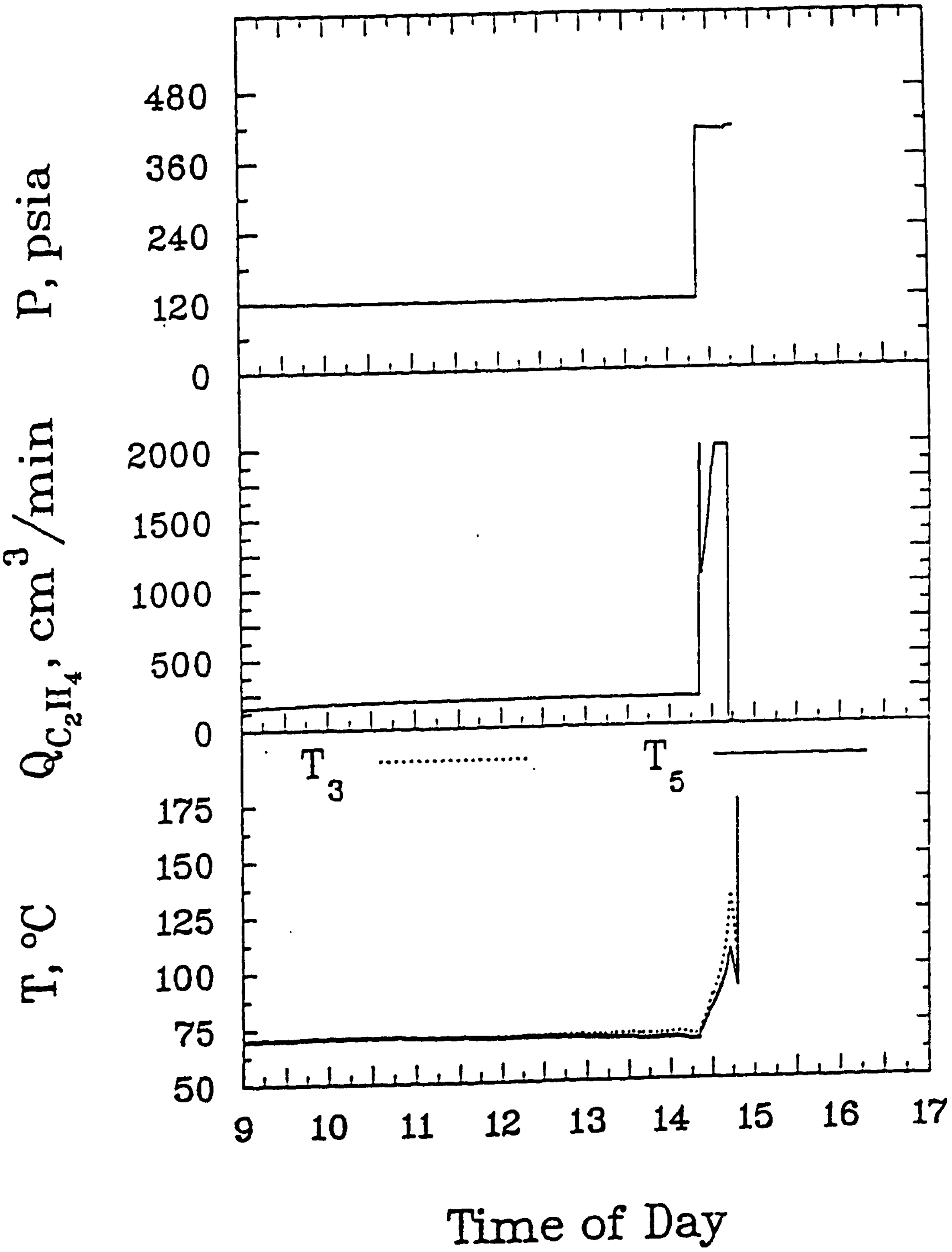
0.112 g STAUFFER 2.1AA

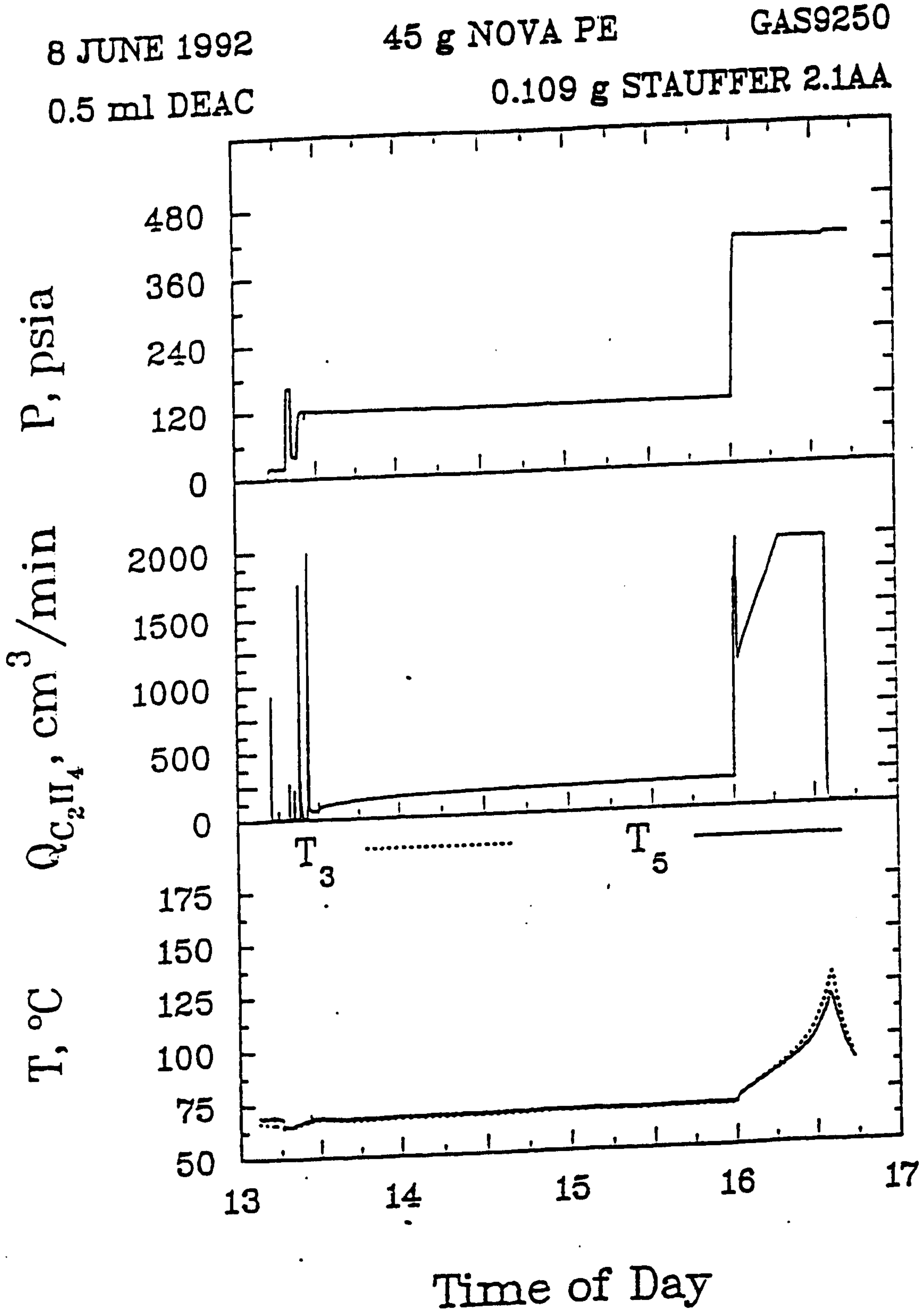

4 MAY 1992
25 g NOVA PE
GAS9238
0.5 ml DEAC
0.112 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T$_3$
T$_5$
T, °C
175
150
125
100
75
50
15
16
17
18
19
20
Time of Day


6 MAY 1992
0.5 ml DEAC
25 g NOVA PE
GAS9239
0.113 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
12
13
14
15
16
17
18
19
Time of Day

8 MAY 1992 25 g NOVA PE GAS9240

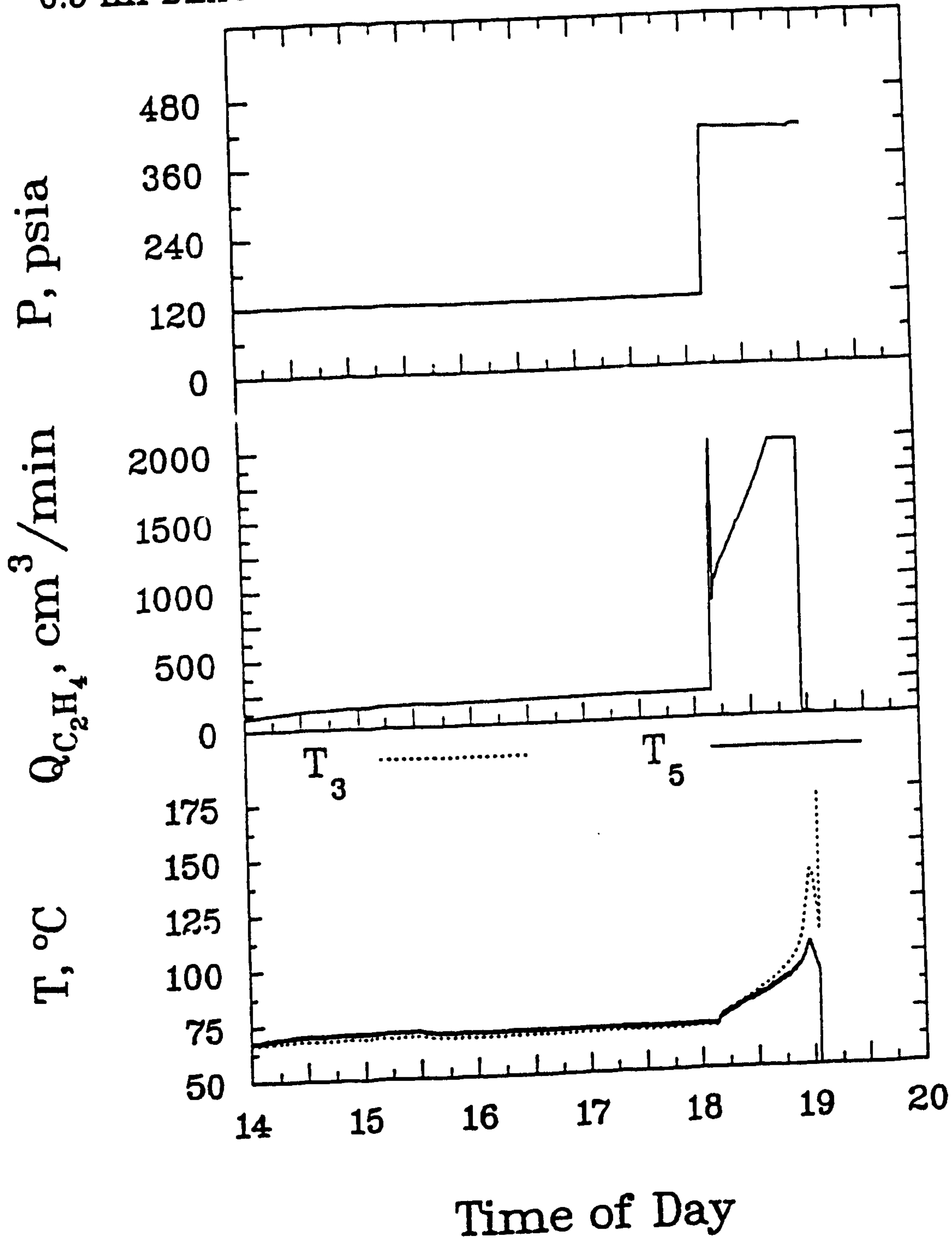
0.5 ml DEAC 0.113 g STAUFFER 2.1AA

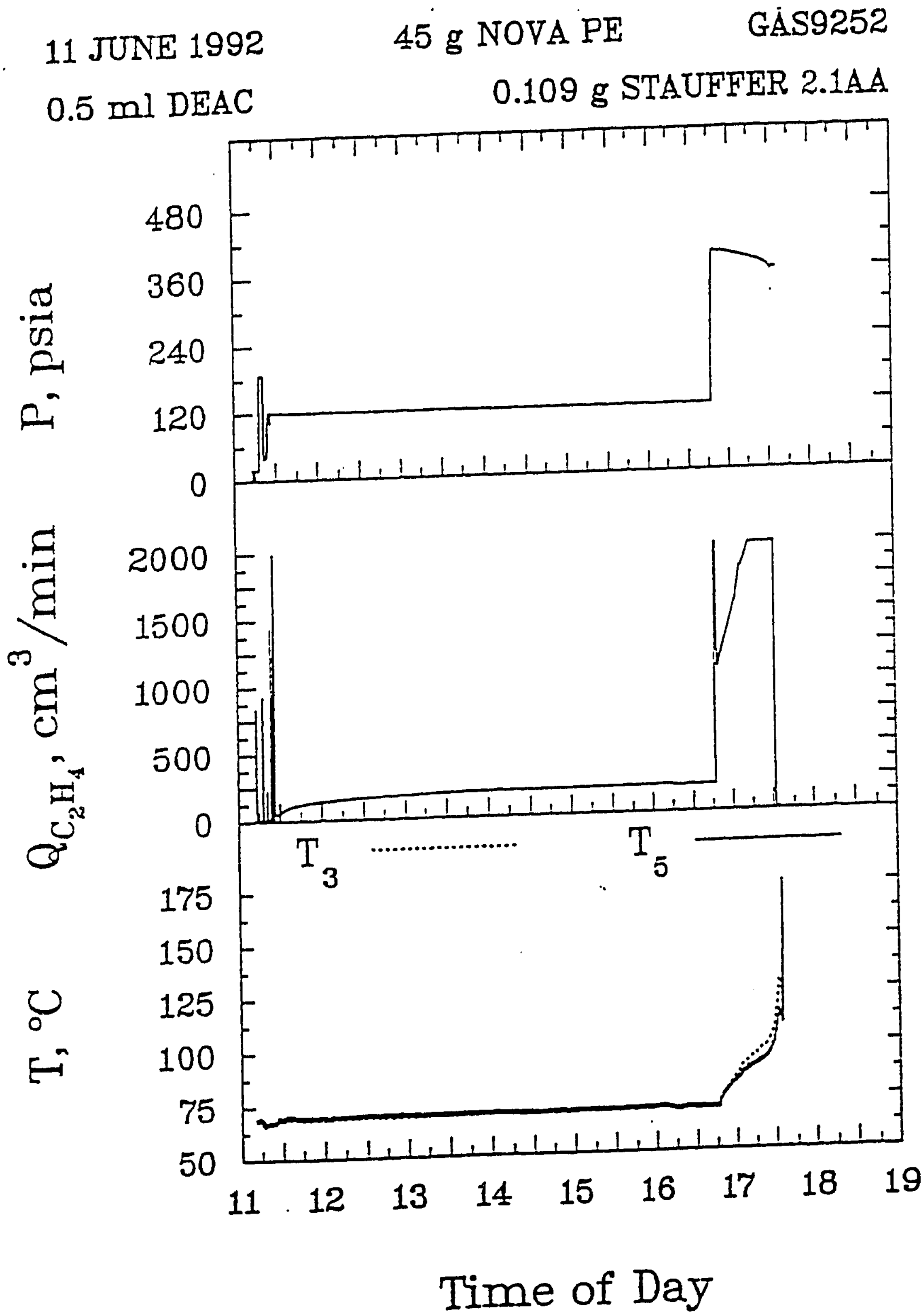



8 JUNE 1992
45 g NOVA PE
GAS9250
0.5 ml DEAC
0.109 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
13
14
15
16
17
Time of Day

9 JUNE 1992 45 g NOVA PE GAS9251

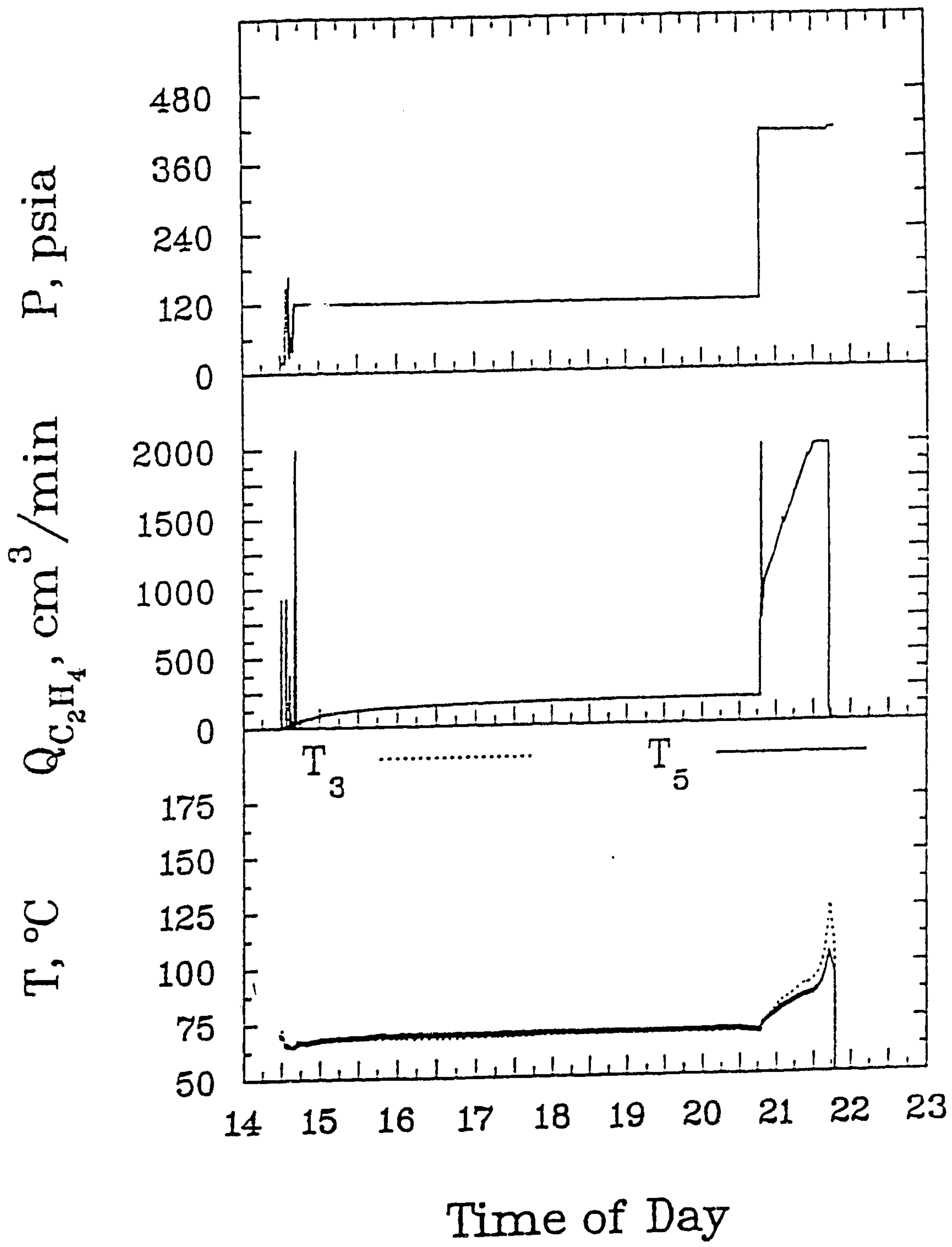
0.5 ml DEAC 0.109 g STAUFFER 2.1AA





11 JUNE 1992 45 g NOVA PE GAS9252

0.5 ml DEAC 0.109 g STAUFFER 2.1AA

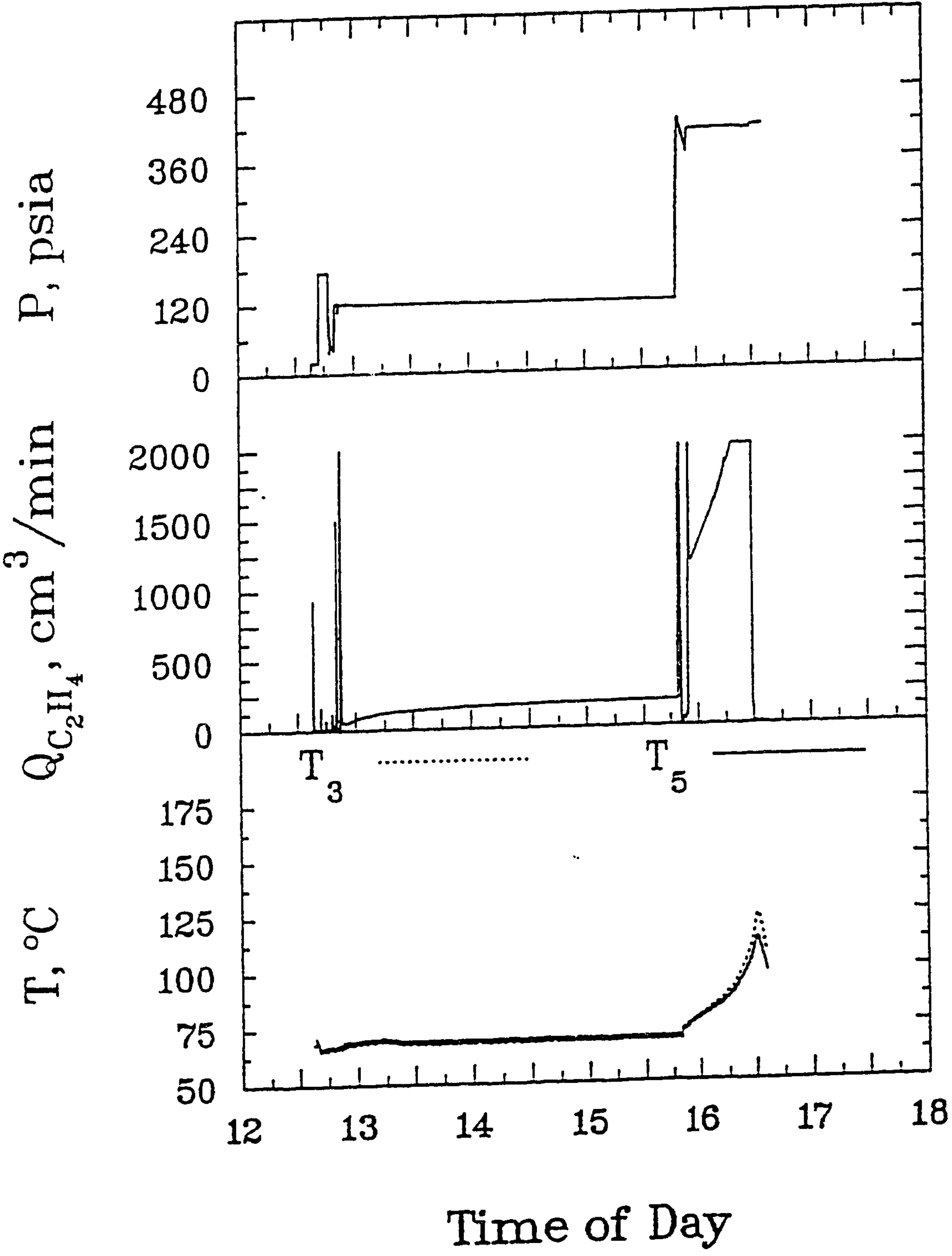


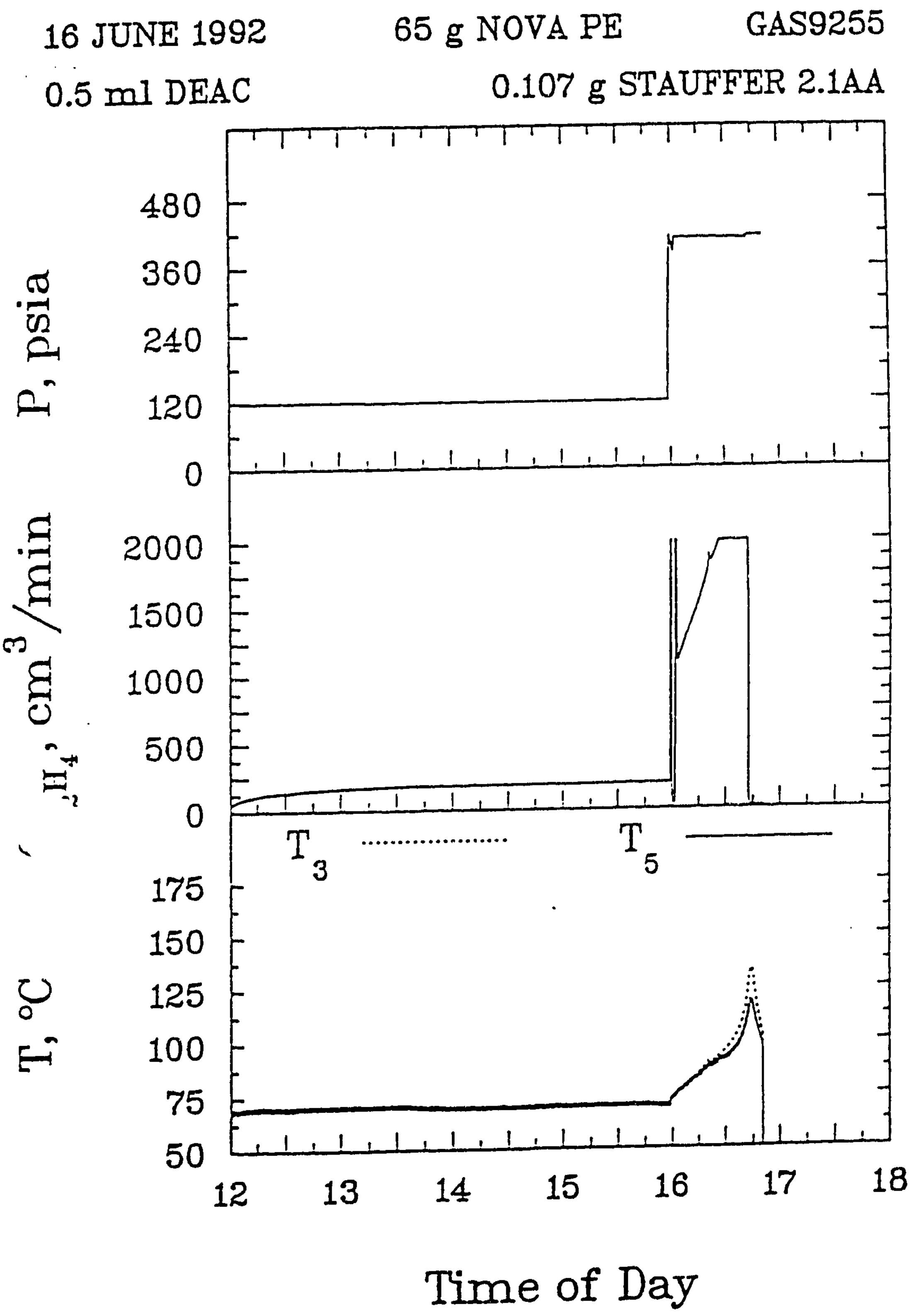
12 JUNE 1992 45 g NOVA PE GAS9253

0.5 ml DEAC 0.111 g STAUFFER 2.1AA

15 JUNE 1992 65 g NOVA PE GAS9254

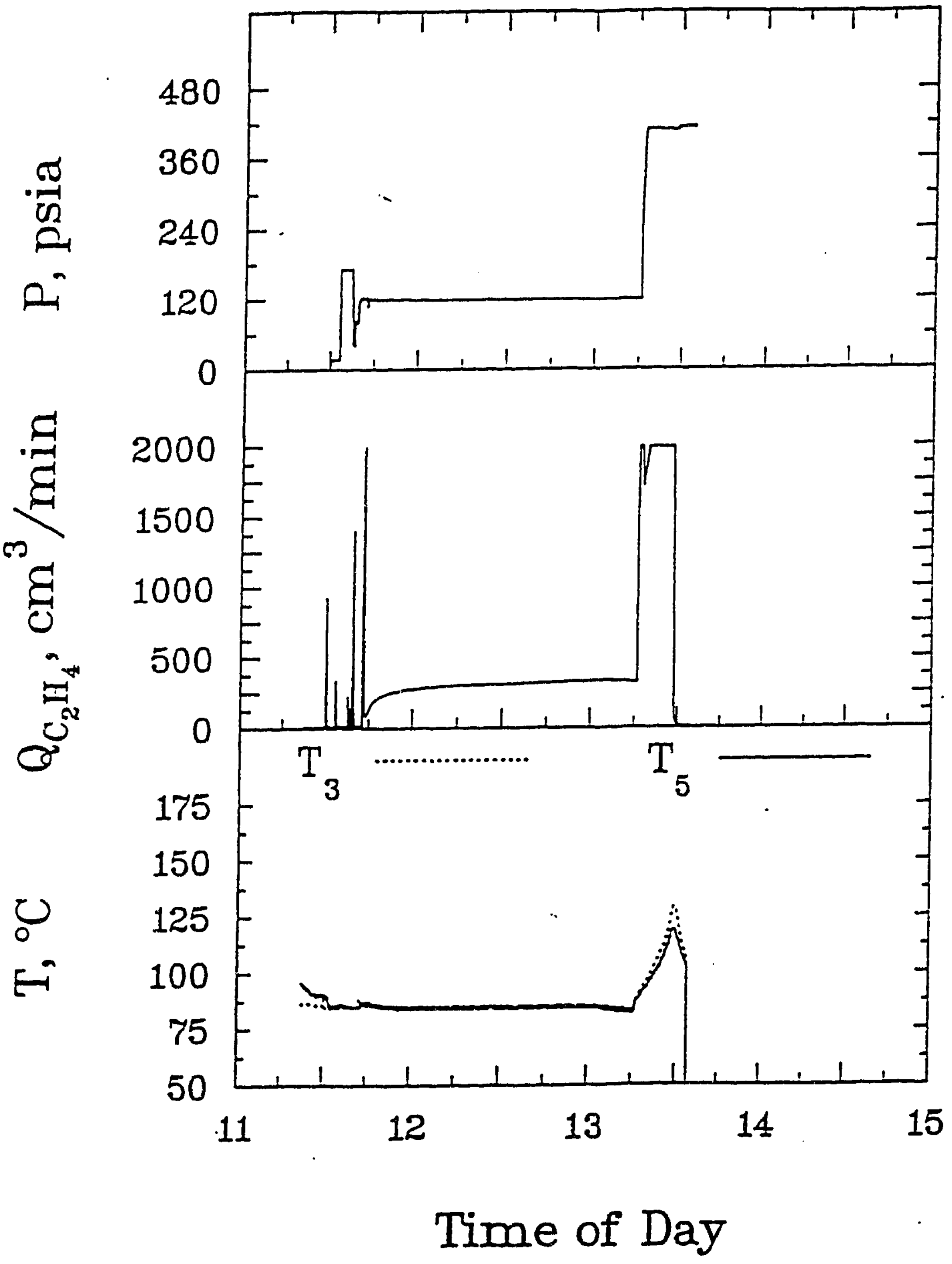
0.5 ml DEAC 0.107 g STAUFFER 2.1AA

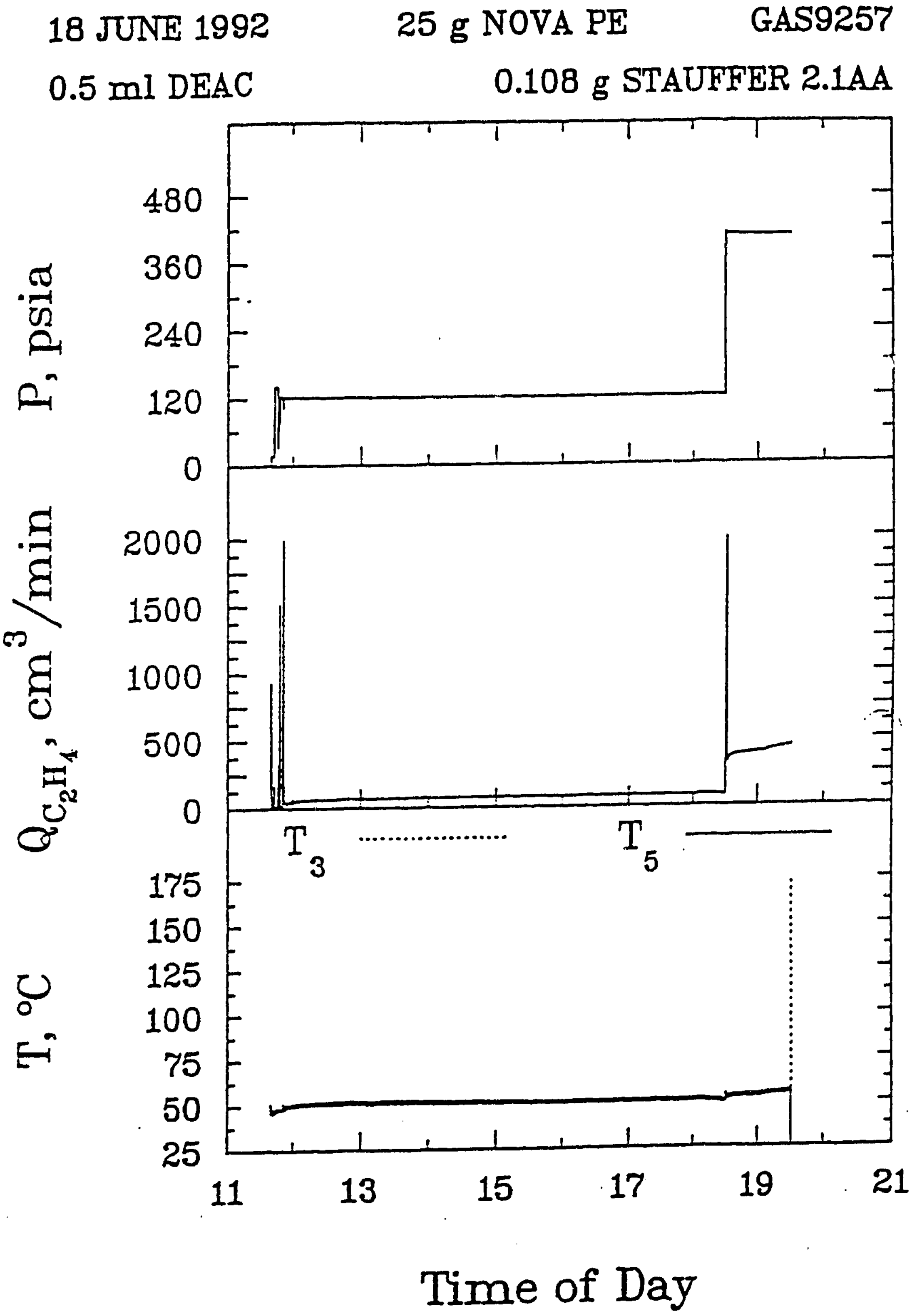



16 JUNE 1992
65 g NOVA PE
GAS9255
0.5 ml DEAC
0.107 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
C2H4, cm3/min
2000
1500
1000
500
0
T3
T5
T, °C
175
150
125
100
75
50
12
13
14
15
16
17
18
Time of Day

17 JUNE 1992 25 g NOVA PE GAS9256

0.5 ml DEAC 0.110 g STAUFFER 2.1AA

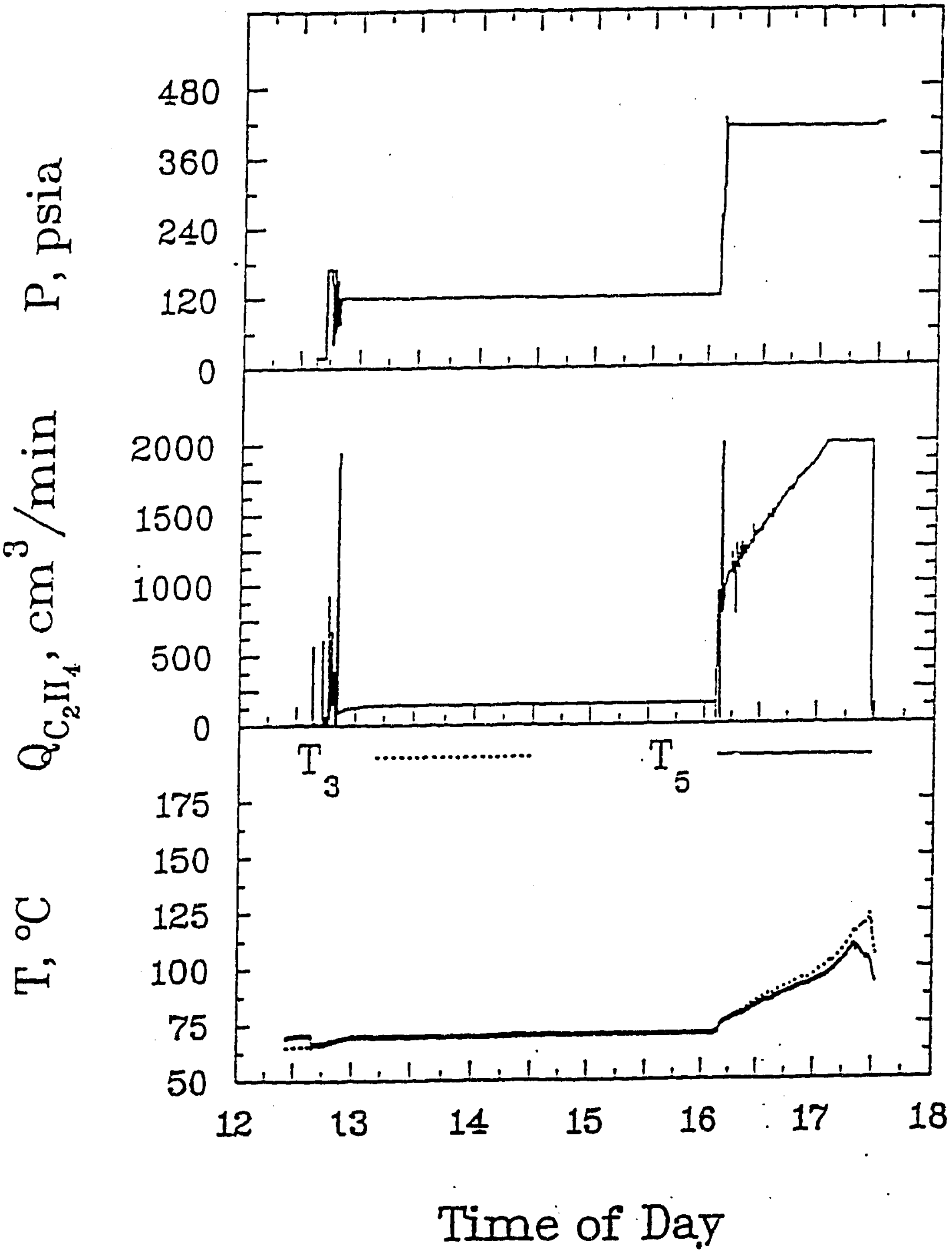


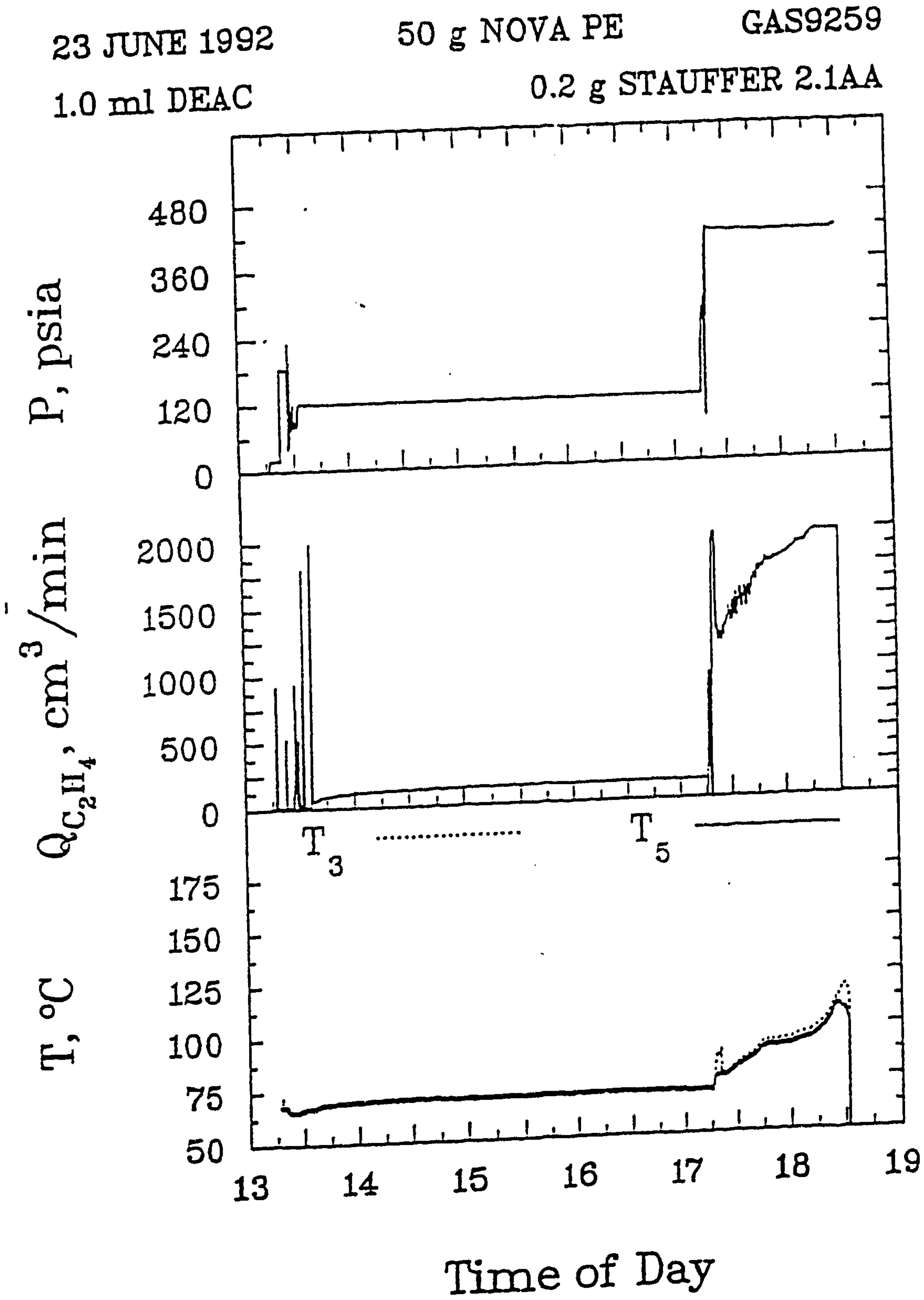


18 JUNE 1992
25 g NOVA PE
GAS9257
0.5 ml DEAC
0.108 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
25
11
13
15
17
19
21
Time of Day

22 JUNE 1992 25 g NOVA PE GAS9258

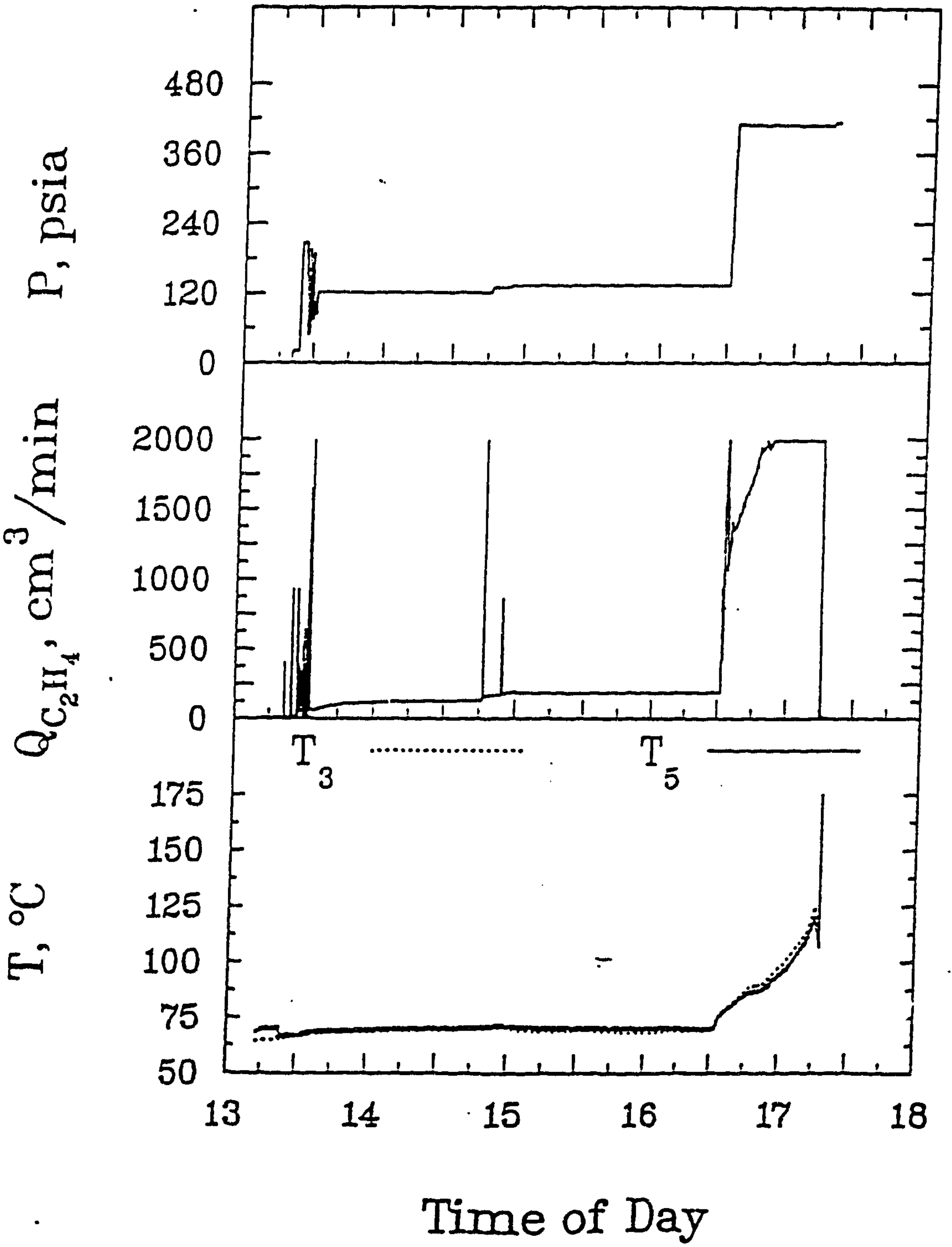
1.0 ml DEAC 0.2 g STAUFFER 2.1AA




23 JUNE 1992
50 g NOVA PE
GAS9259
1.0 ml DEAC
0.2 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
13
14
15
16
17
18
19
Time of Day

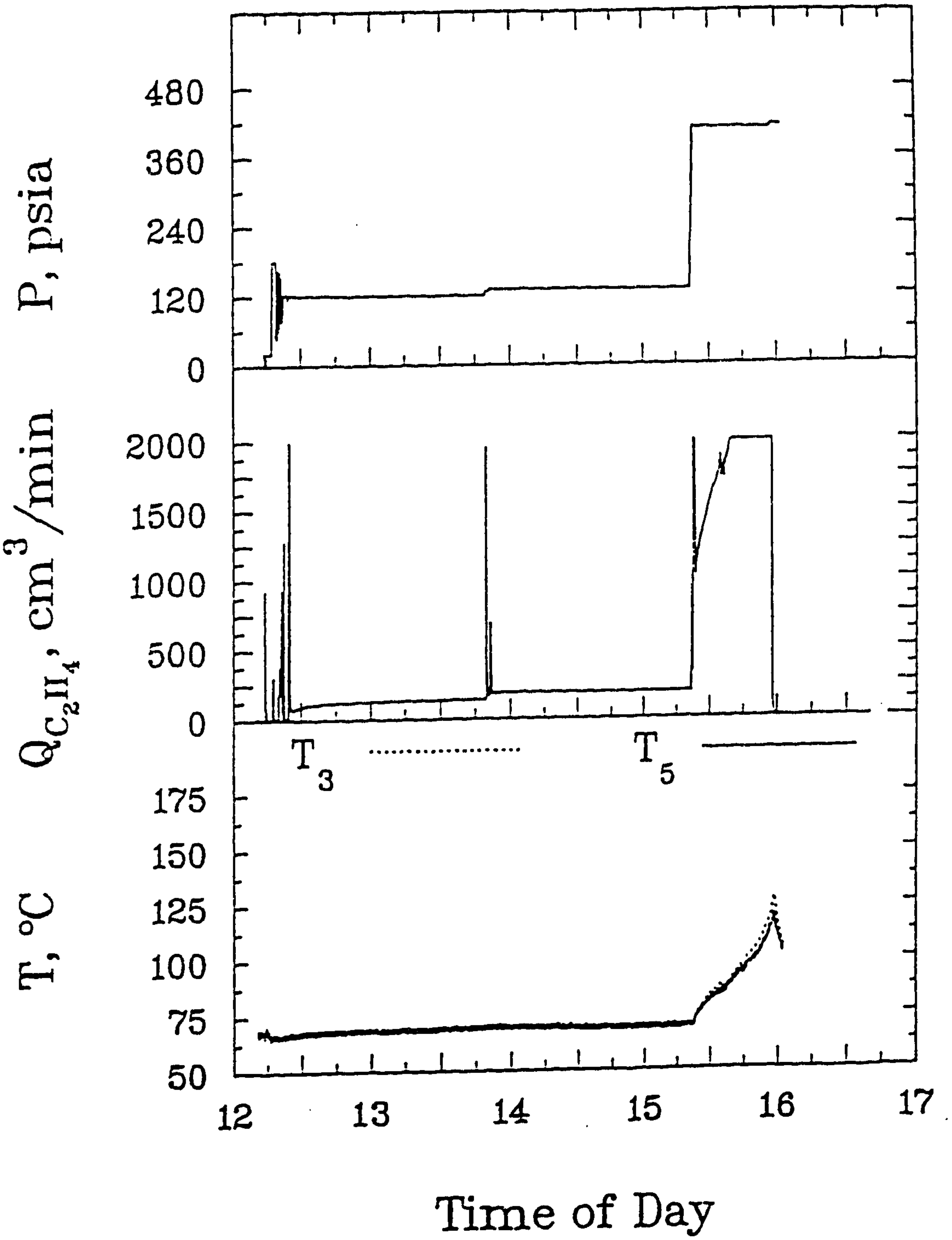
26 JUNE 1992 25 g NOVA PE GAS9260

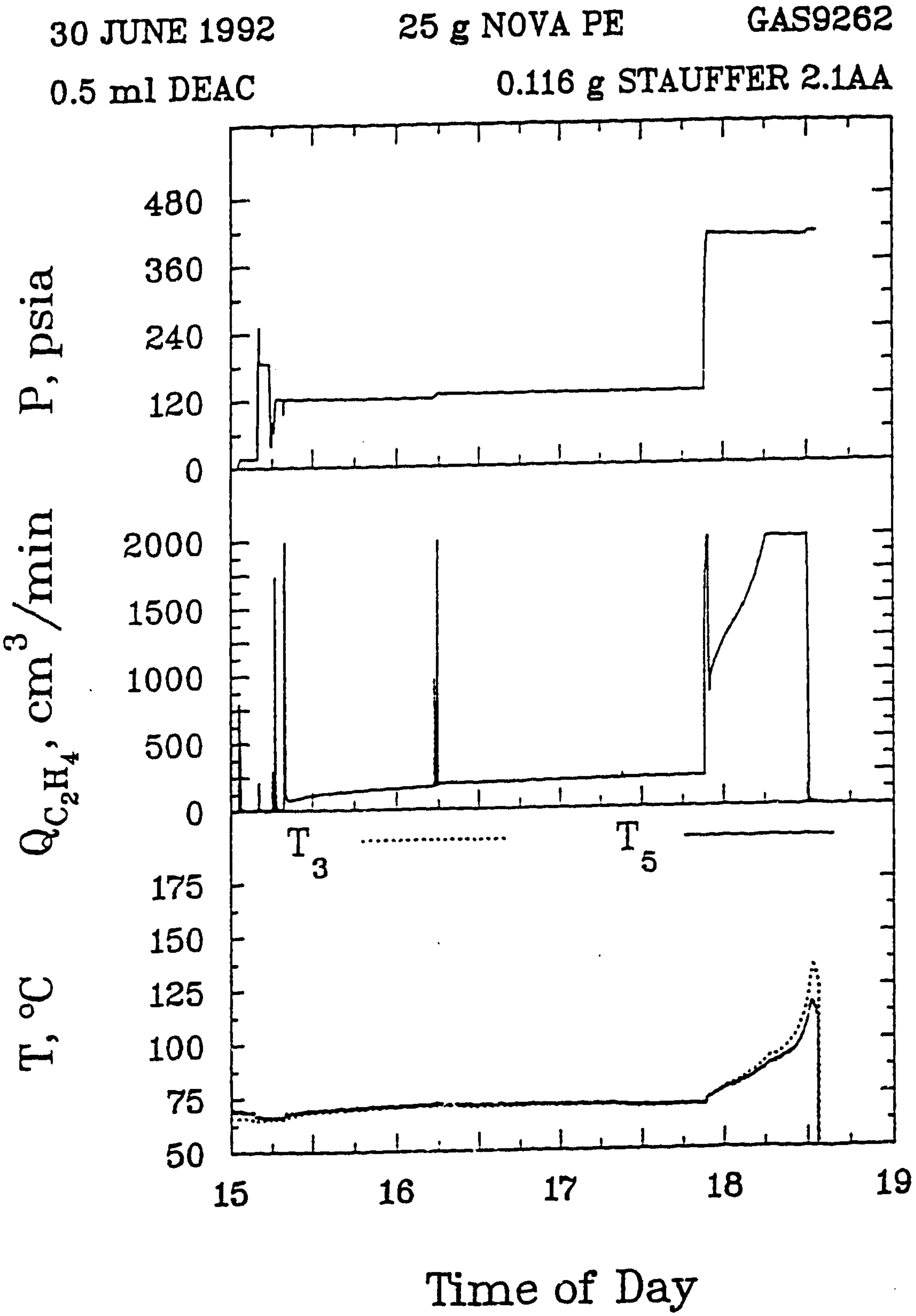
1.0 ml DEAC 0.218 g STAUFFER 2.1AA



29 JUNE 1992 50 g NOVA PE GAS9261

1.0 ml DEAC 0.22 g STAUFFER 2.1AA



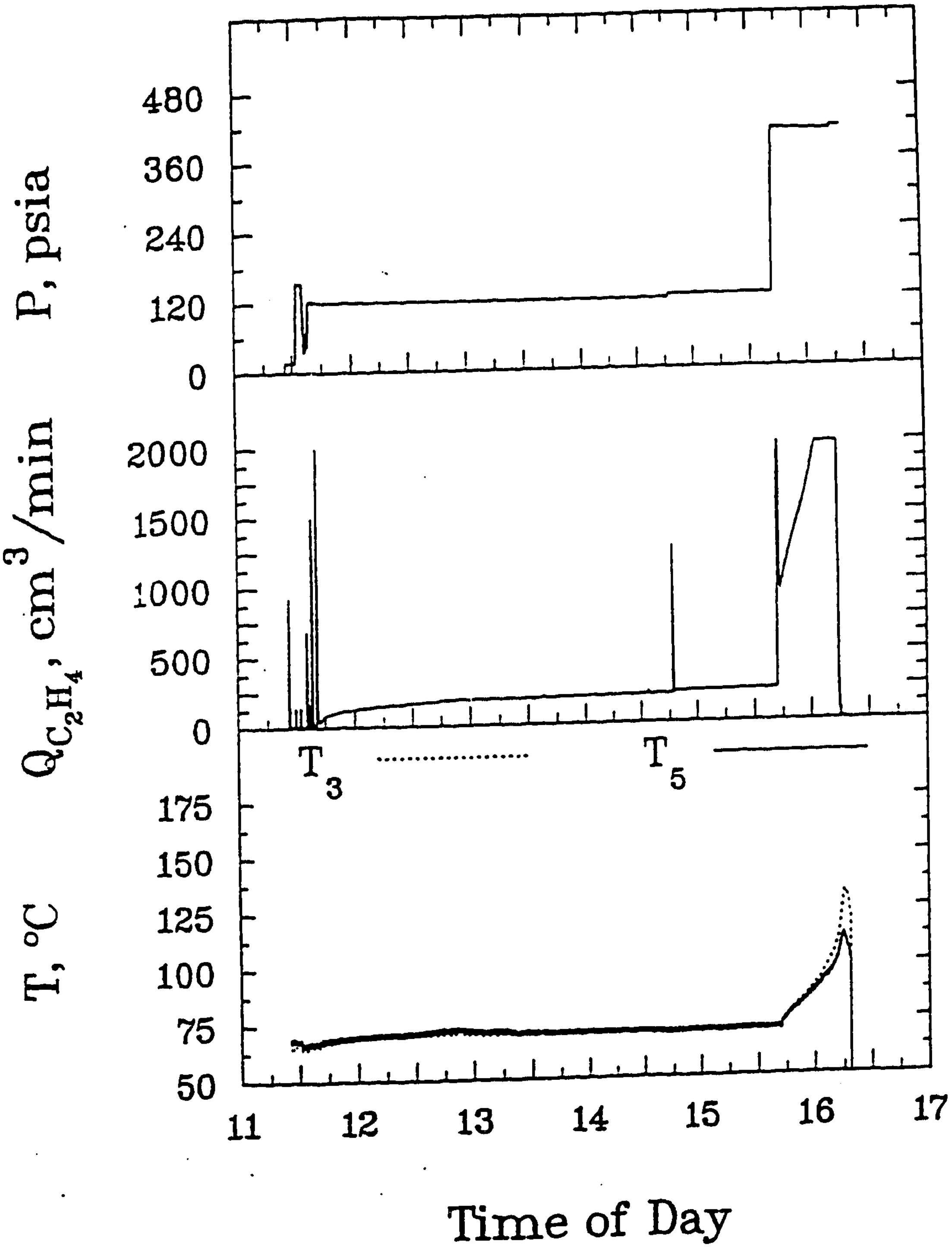


30 JUNE 1992 25 g NOVA PE GAS9262

0.5 ml DEAC 0.116 g STAUFFER 2.1AA

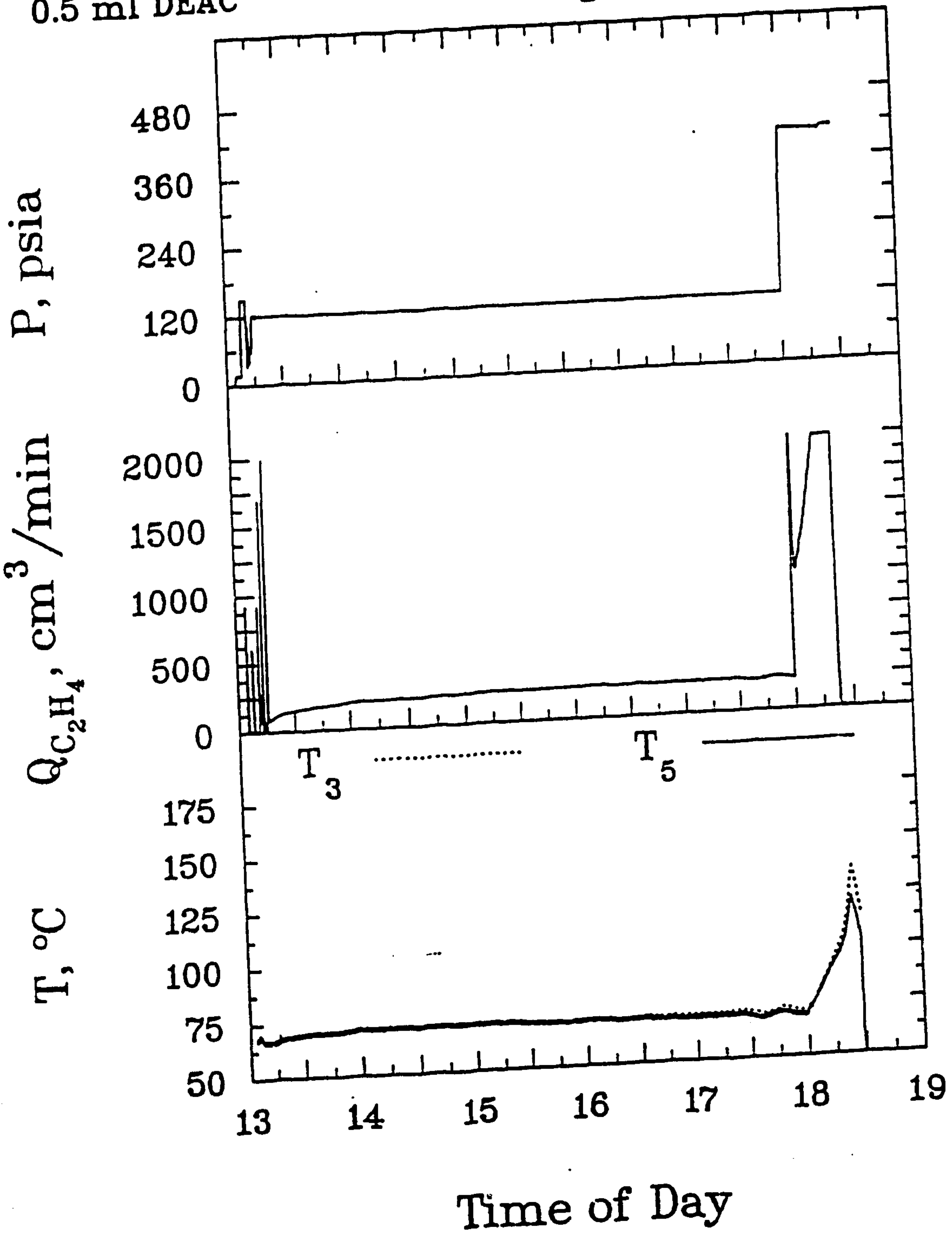
2 JULY 1992 25 g NOVA PE GAS9263

0.5 ml DEAC 0.109 g STAUFFER 2.1AA



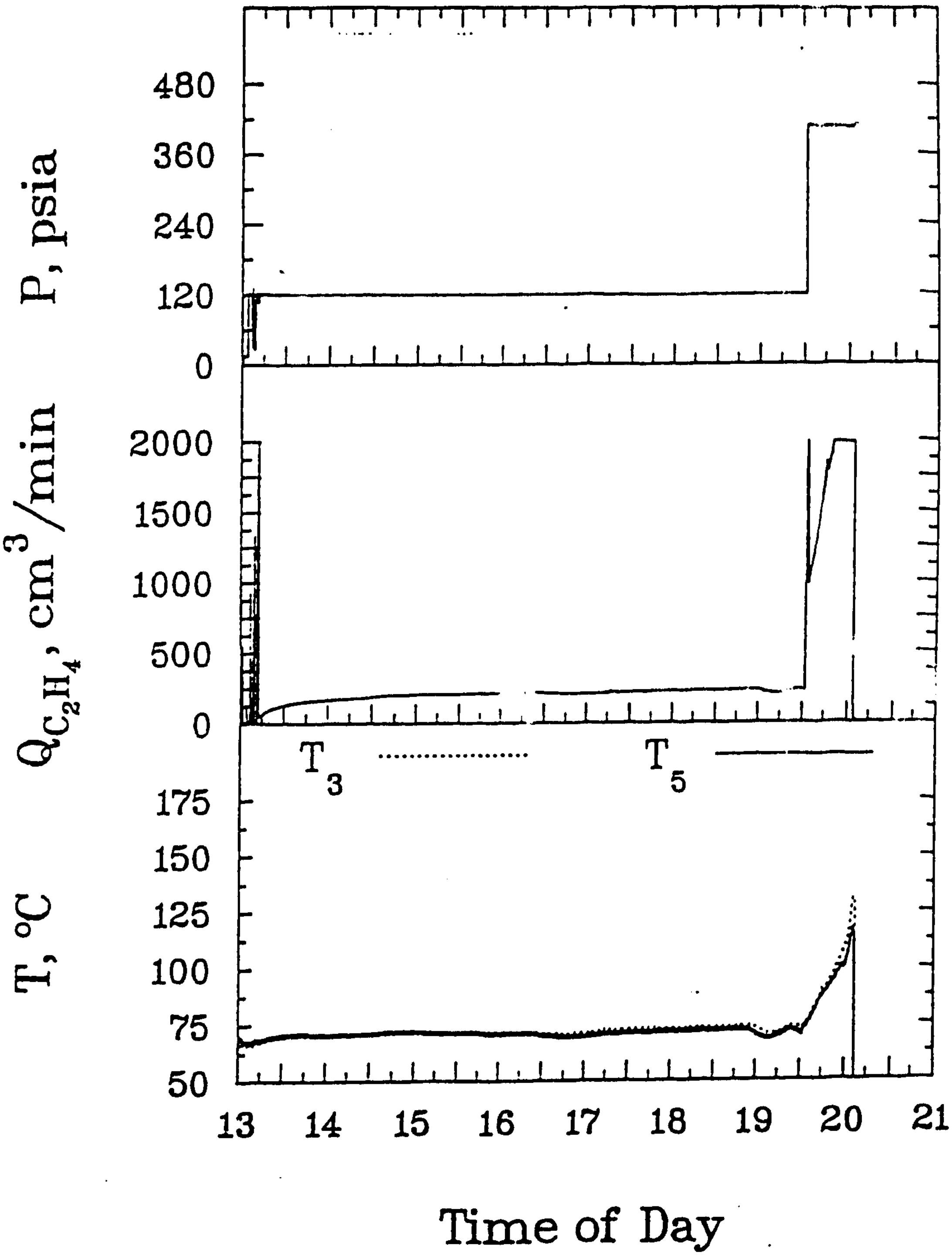
3 JULY 1992 25 g NOVA PE GAS9264

0.5 ml DEAC 0.108 g STAUFFER 2.1AA



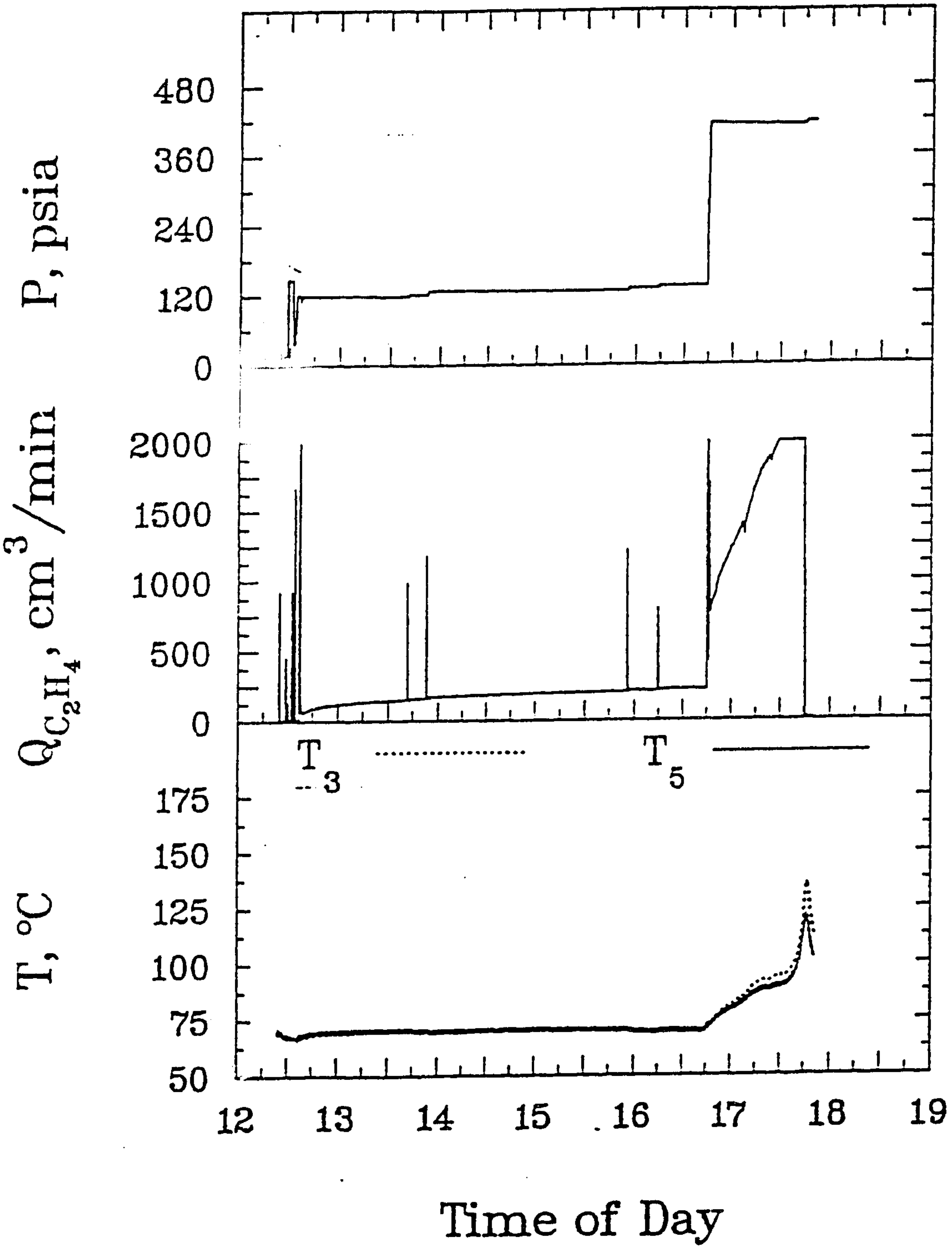
6 JULY 1992 25 g NOVA PE GAS9265

0.5 ml DEAC 0.109 g STAUFFER 2.1AA



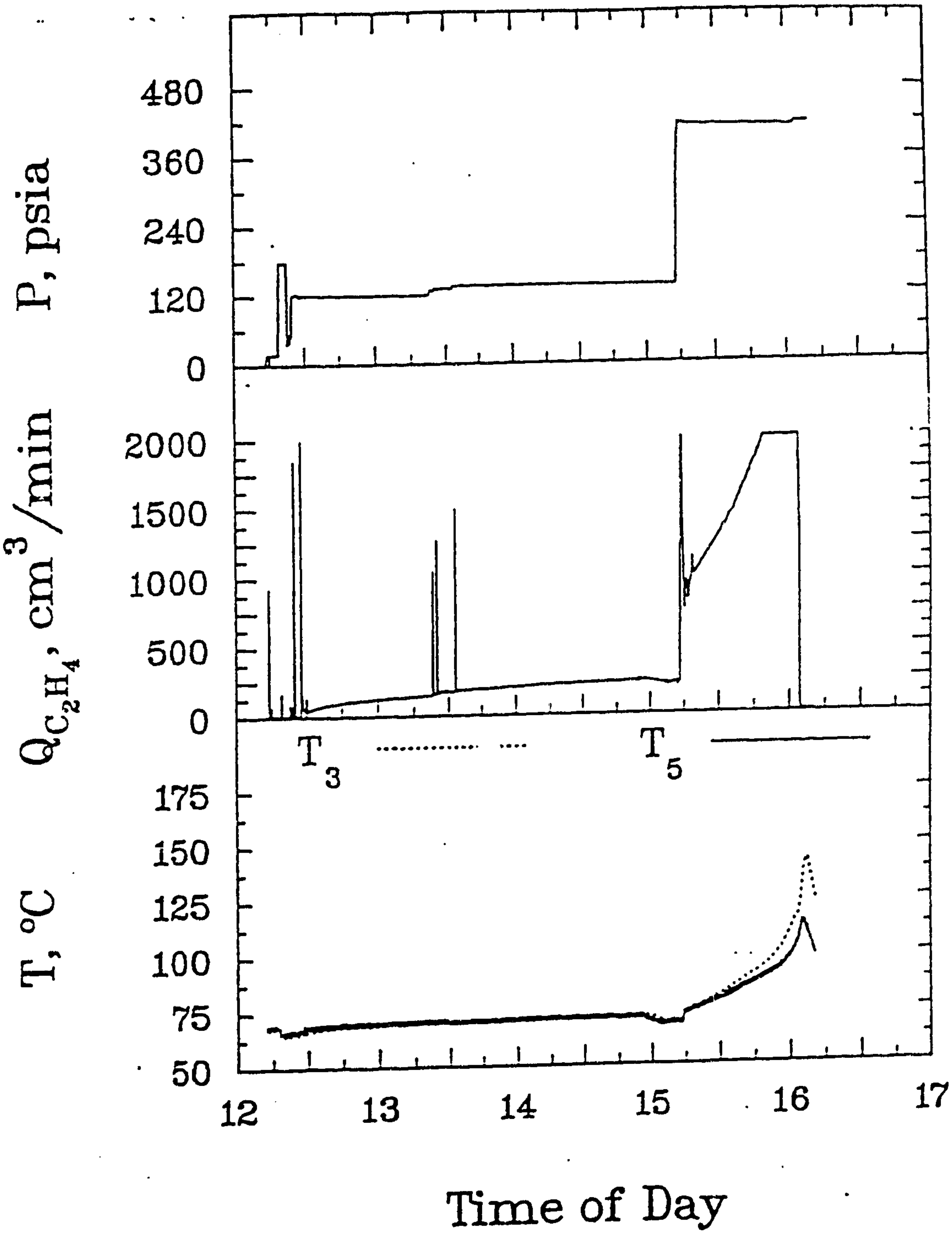
7 JULY 1992 45 g NOVA PE GAS9266

0.5 ml DEAC 0.108 g STAUFFER 2.1AA



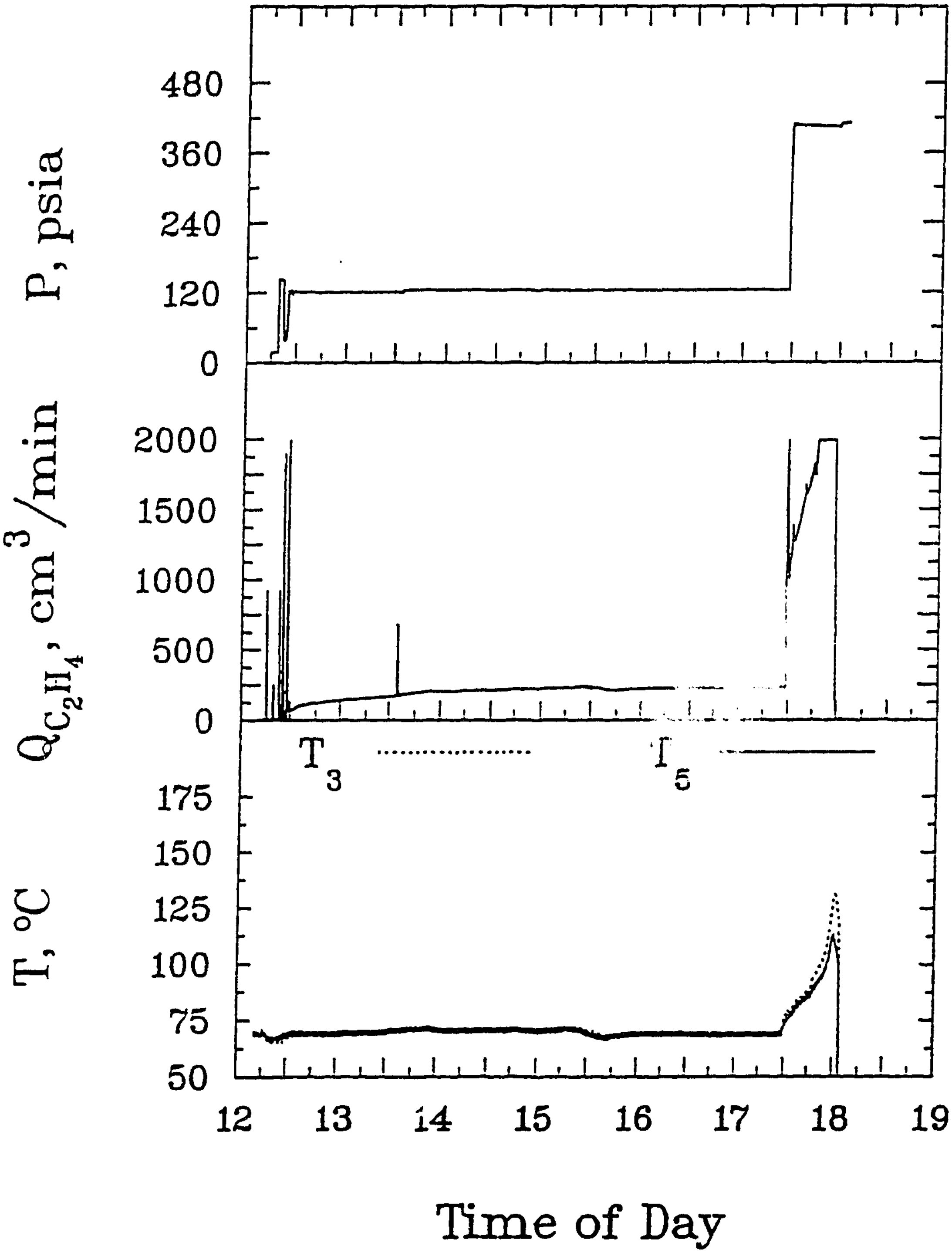
8 JULY 1992 45 g NOVA PE GAS9267

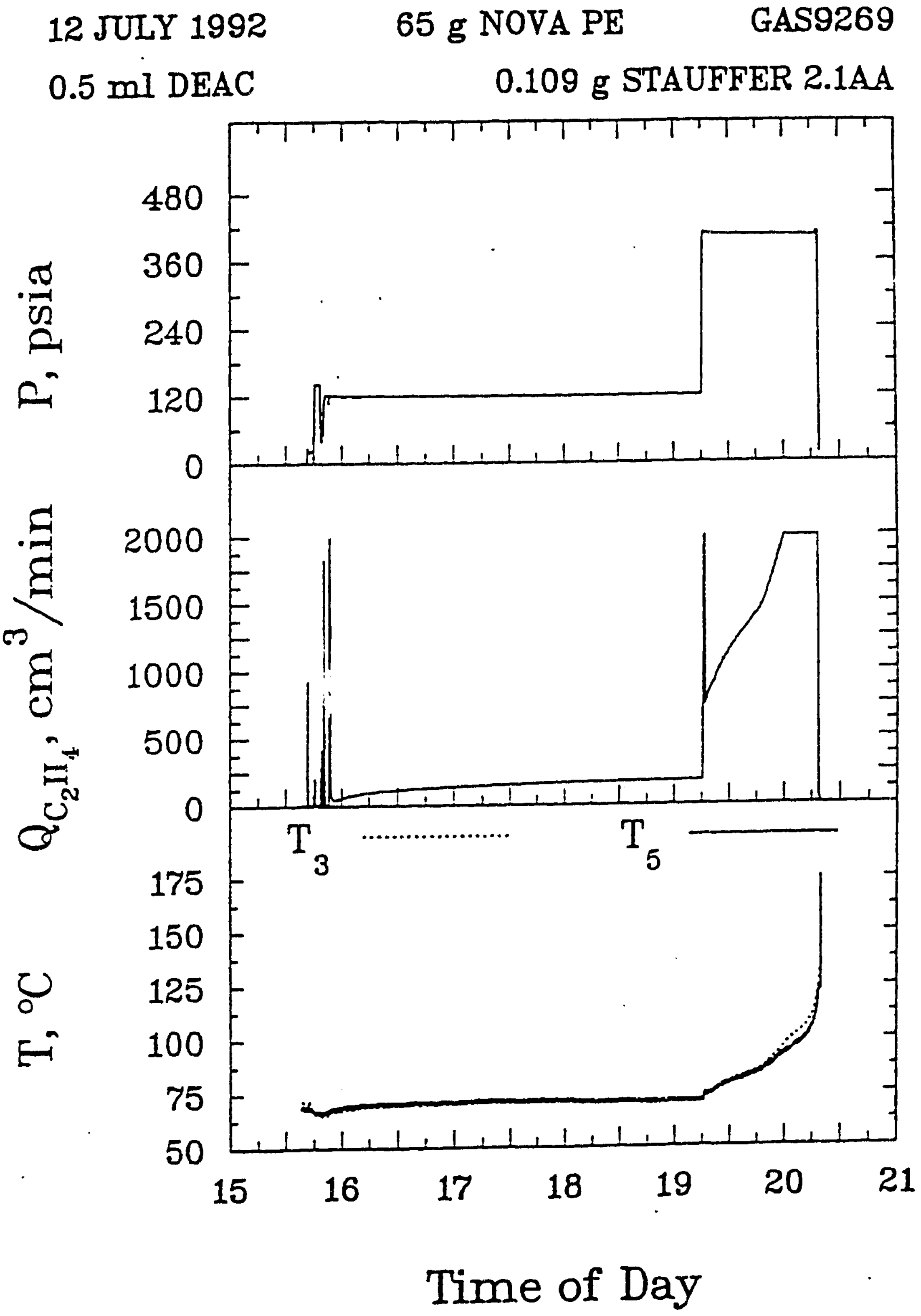
0.5 ml DEAC 0.110 g STAUFFER 2.1AA



10 JULY 1992 45 g NOVA PE GAS9268

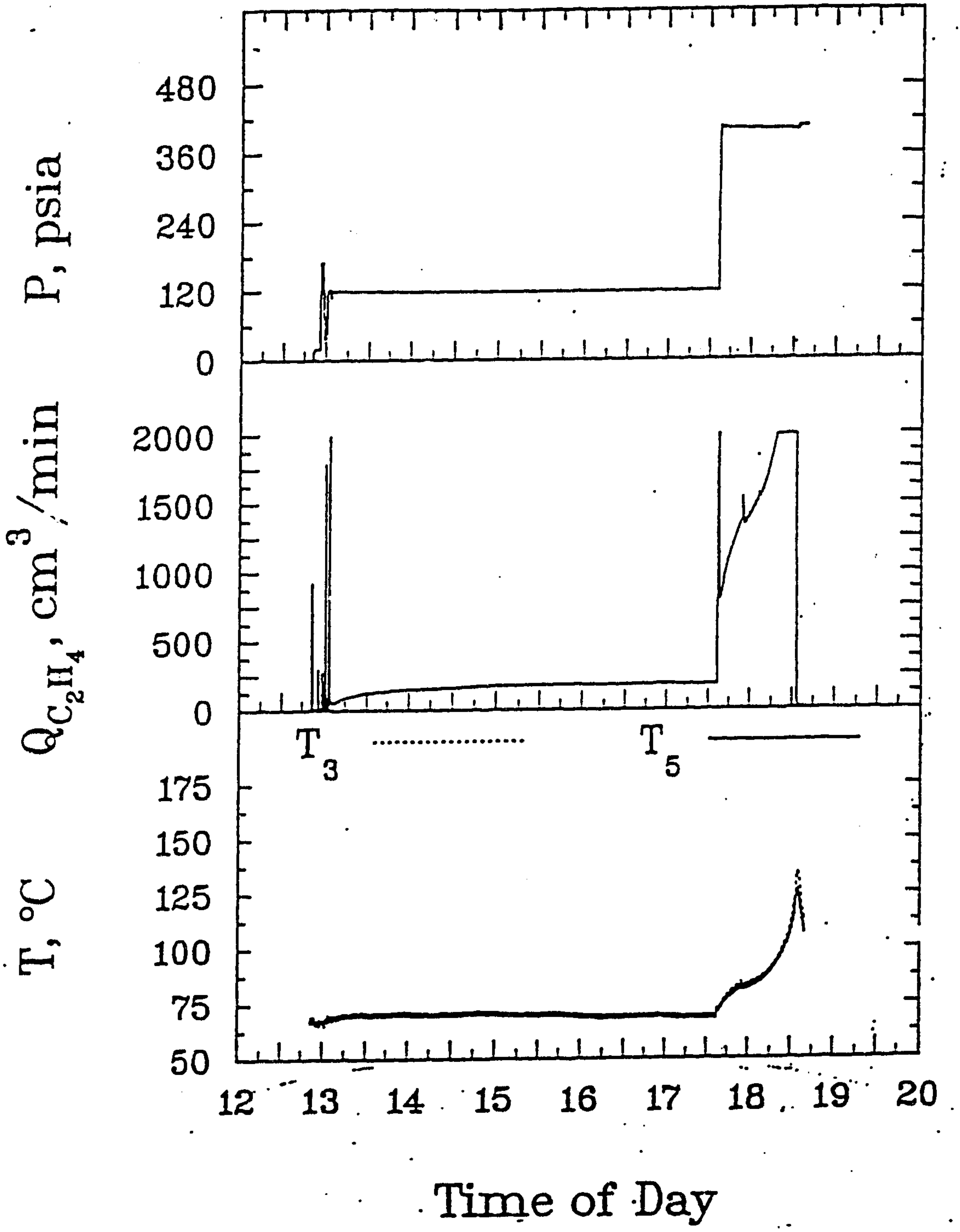
0.5 ml DEAC 0.110 g STAUFFER 2.1AA

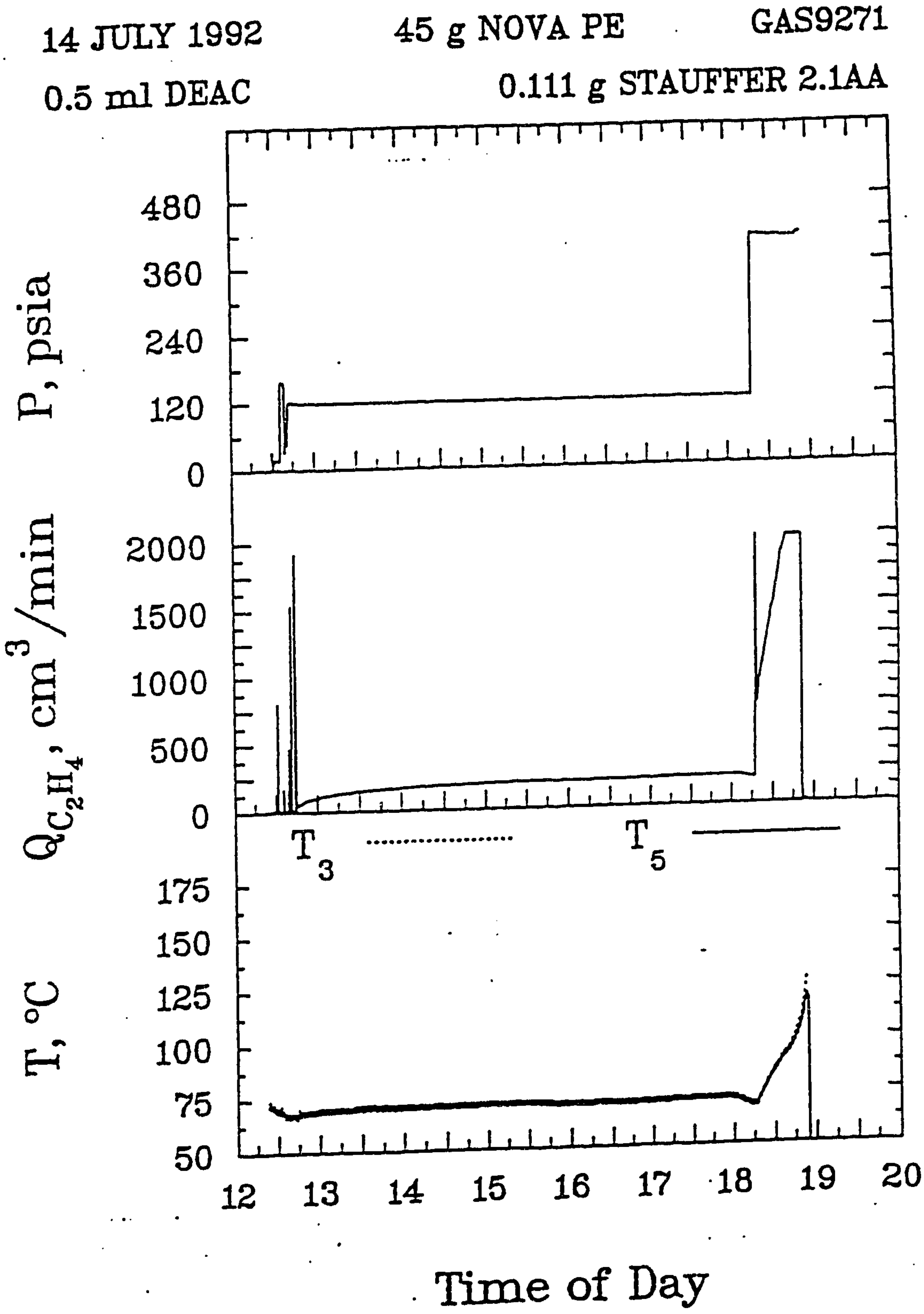


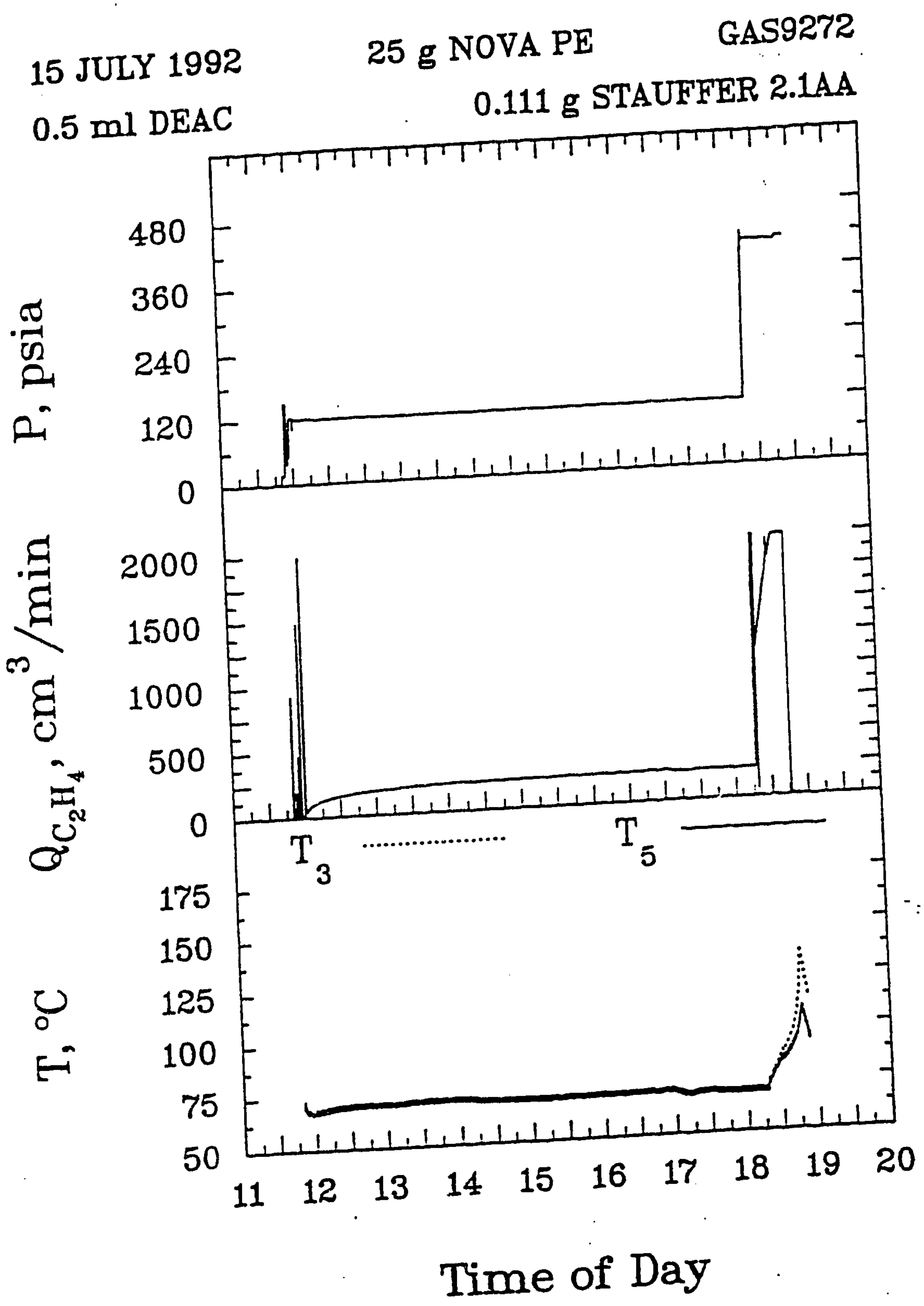

12 JULY 1992
65 g NOVA PE
GAS9269
0.5 ml DEAC
0.109 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
15
16
17
18
19
20
21
Time of Day

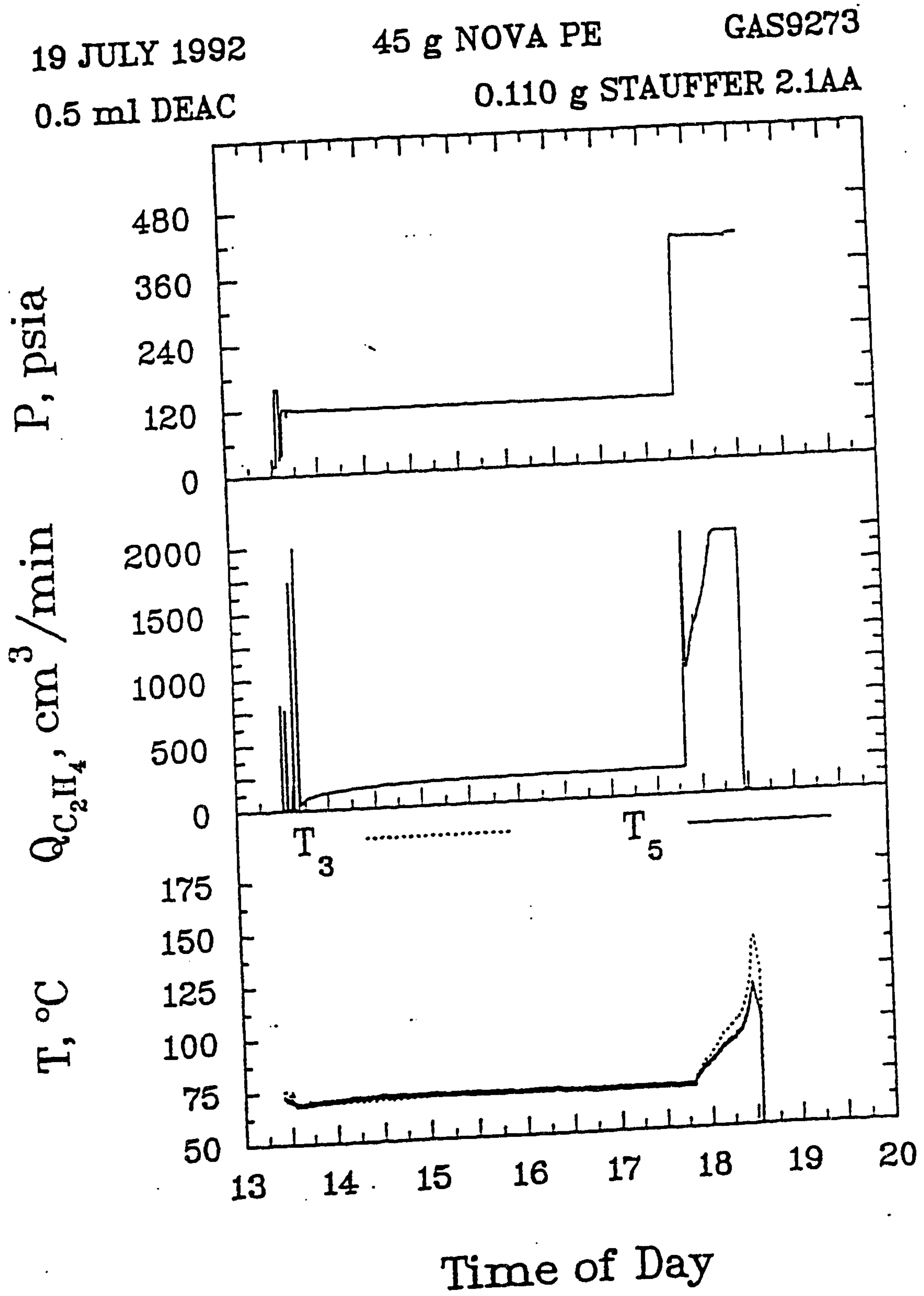
13 JULY 1992 65 g NOVA PE GAS9270

0.5 ml DEAC 0.110 g STAUFFER 2.1AA




14 JULY 1992
45 g NOVA PE
GAS9271
0.5 ml DEAC
0.111 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
12
13
14
15
16
17
18
19
20
Time of Day


15 JULY 1992
25 g NOVA PE
GAS9272
0.5 ml DEAC
0.111 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
11
12
13
14
15
16
17
18
19
20
Time of Day


19 JULY 1992
45 g NOVA PE
GAS9273
0.5 ml DEAC
0.110 g STAUFFER 2.1AA
P, psia
480
360
240
120
0
$Q_{C_2H_4}$, cm^3/min
2000
1500
1000
500
0
T_3
T_5
T, °C
175
150
125
100
75
50
13
14
15
16
17
18
19
20
Time of Day

APPENDIX B

Temperature Profiles of Thermocouples at Locations 2 to 5 for all Gas-Phase Experiments

Temperature profiles of the thermocouples at locations 2 to 5, for the gas-phase experiments GAS9108 to GAS9111, and GAS9201 to GAS9273, are given in this appendix.

Figure B.1

Temperature profiles of locations 2 to 5

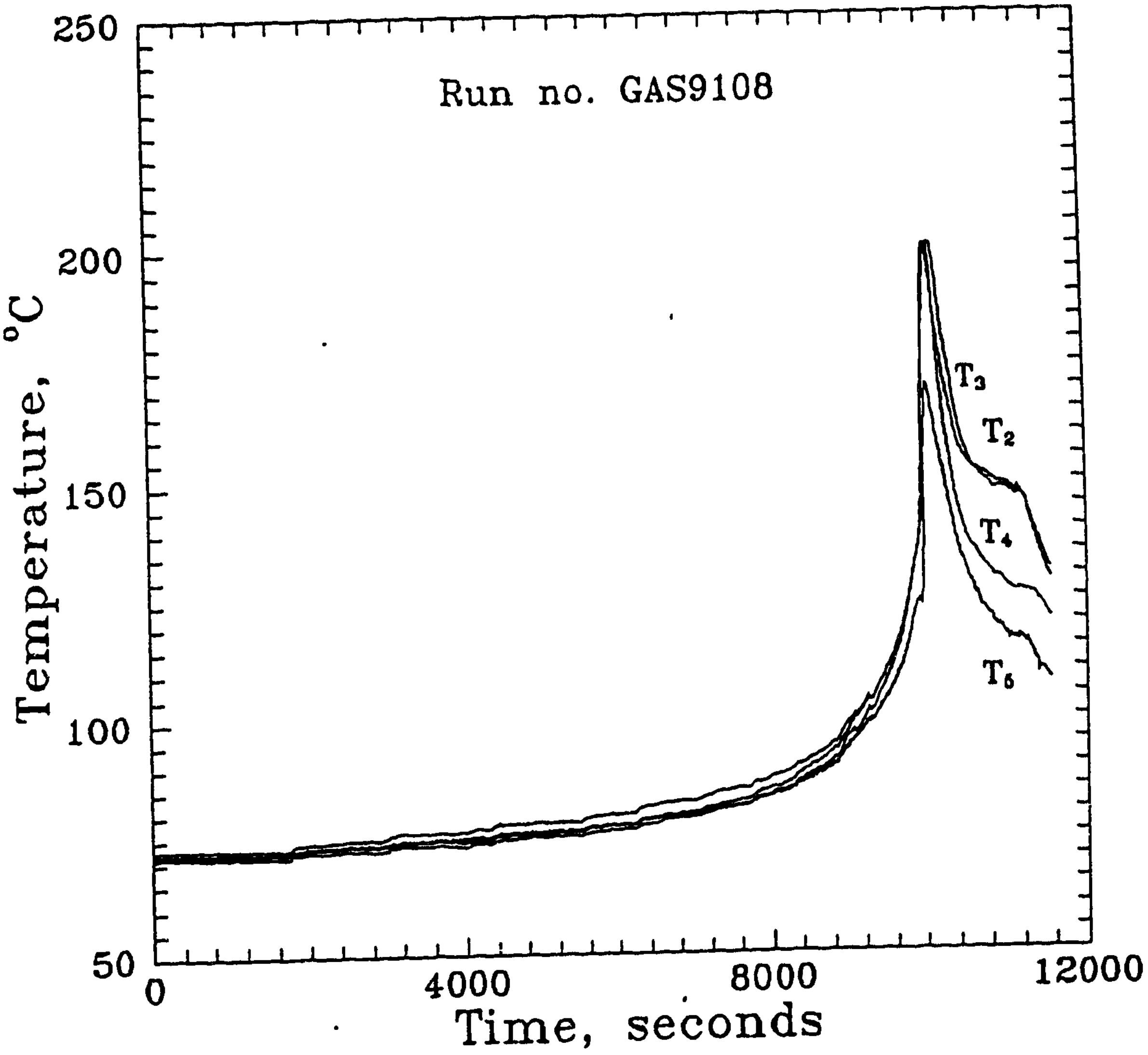


Figure B.2

Temperature profiles of locations 2 to 5

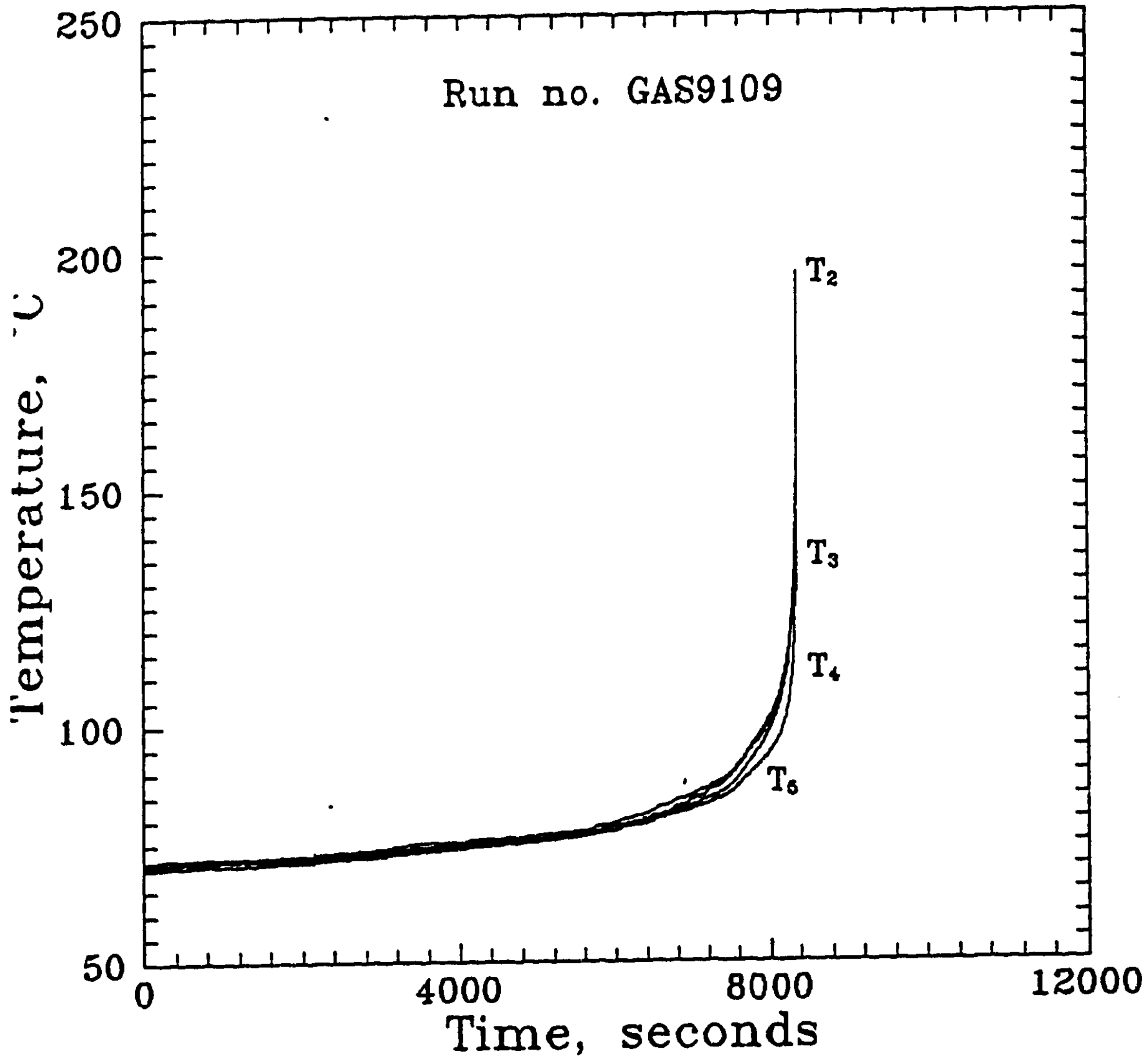


Figure B.3
Temperature profiles of locations 2 to 5

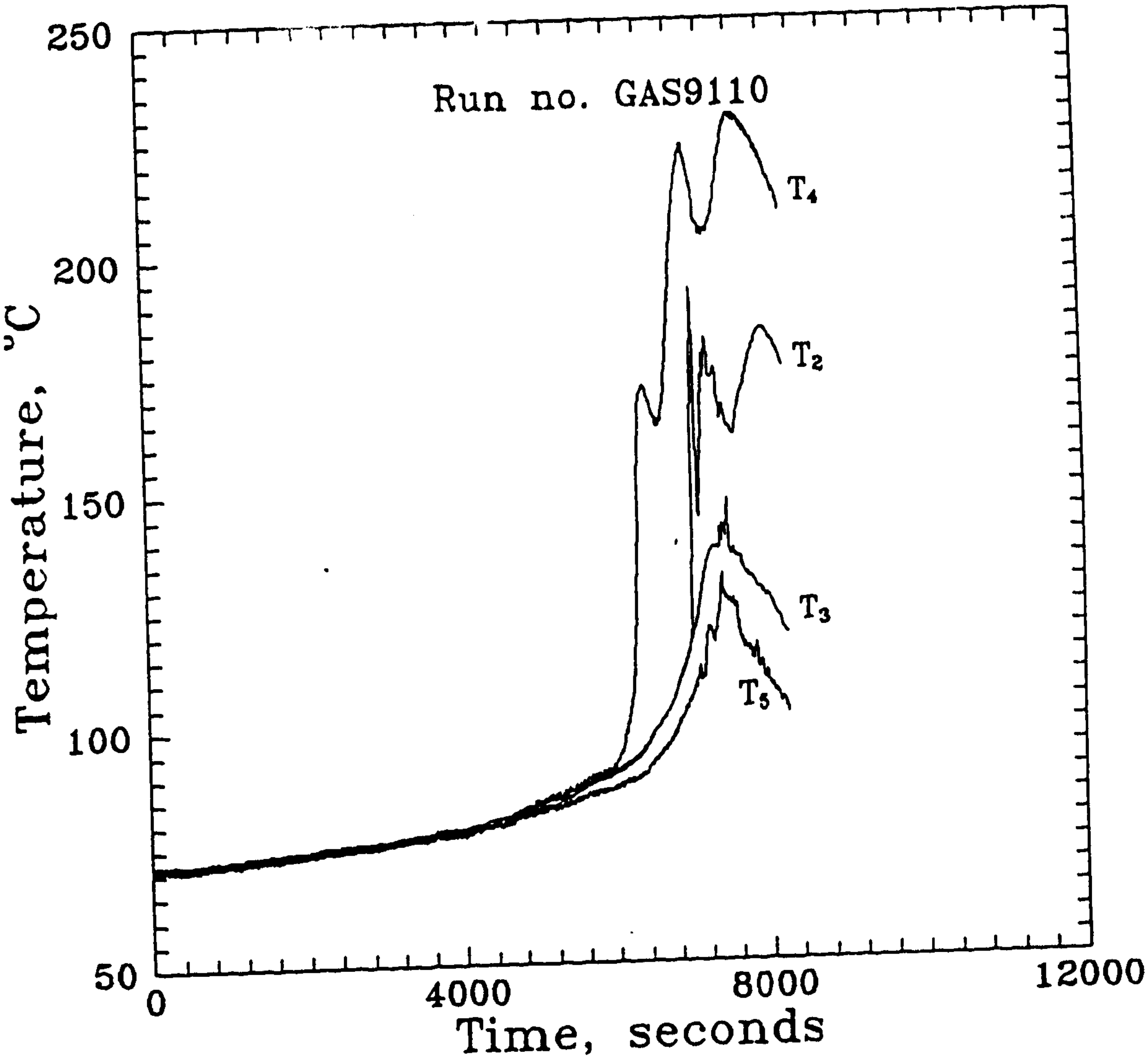


Figure B.4

Temperature profiles of locations 2 to 5

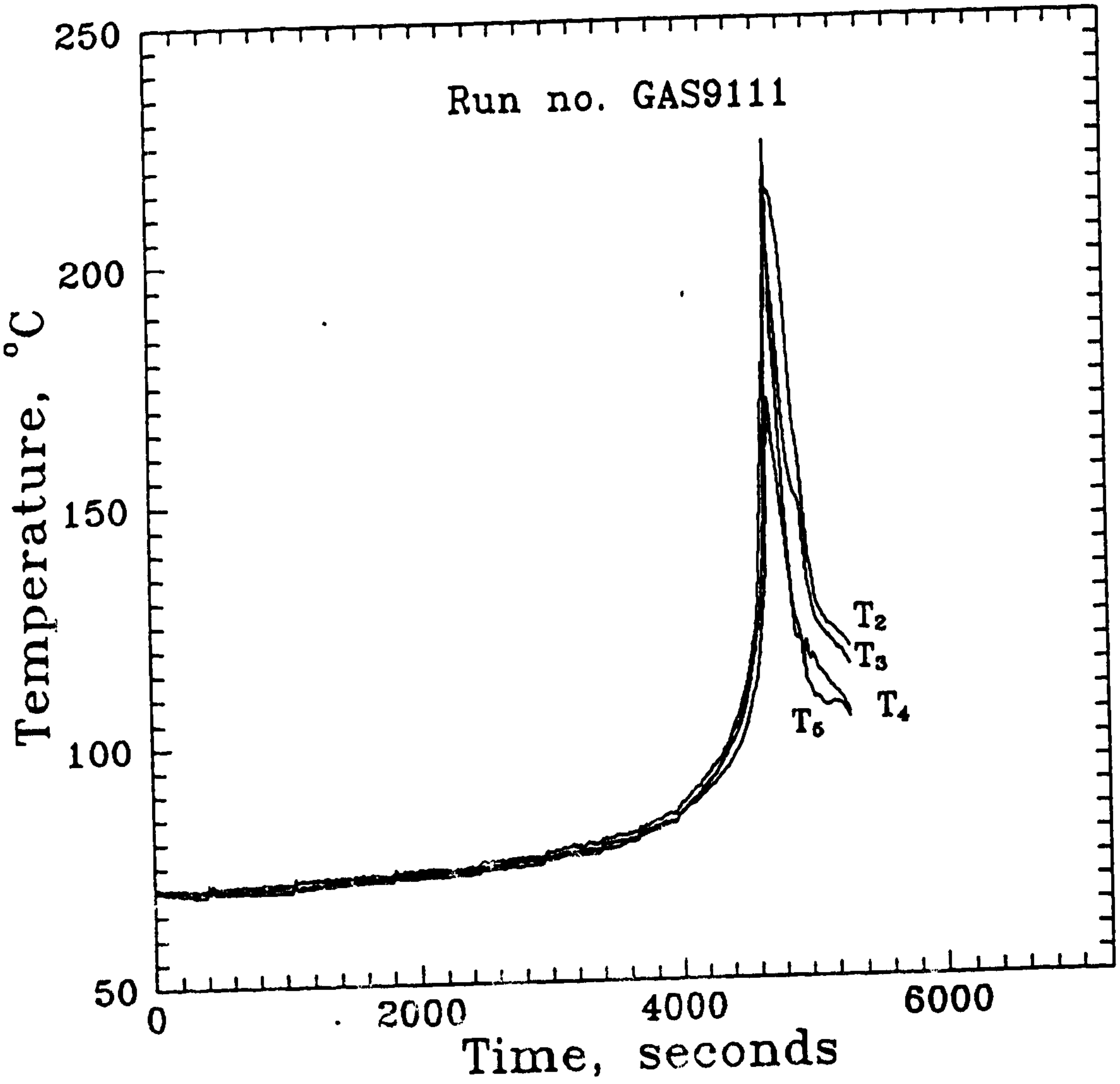


Figure B.5

Temperature profiles of locations 2 to 5

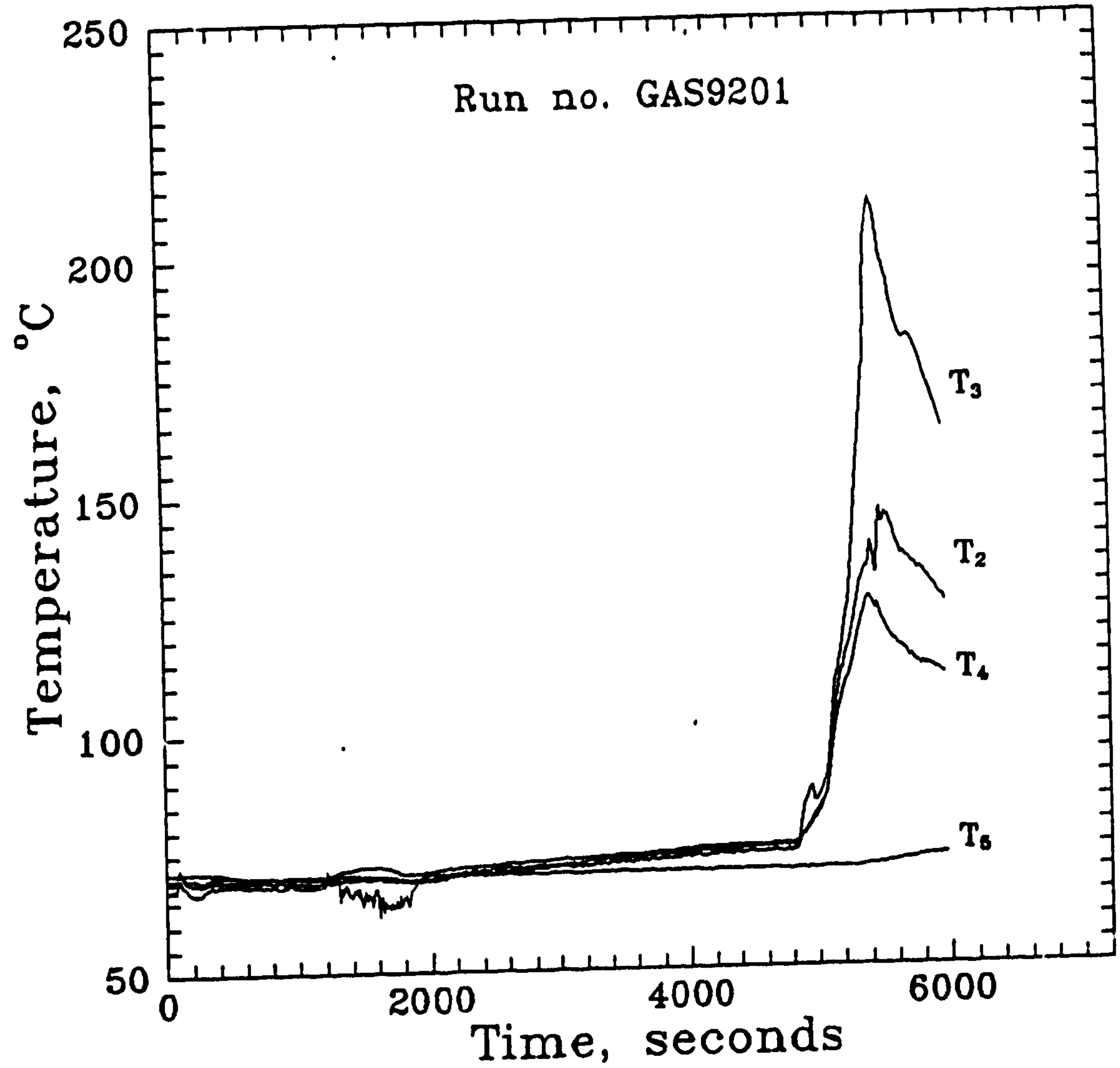


Figure B.6

Temperature profiles of locations 2 to 5

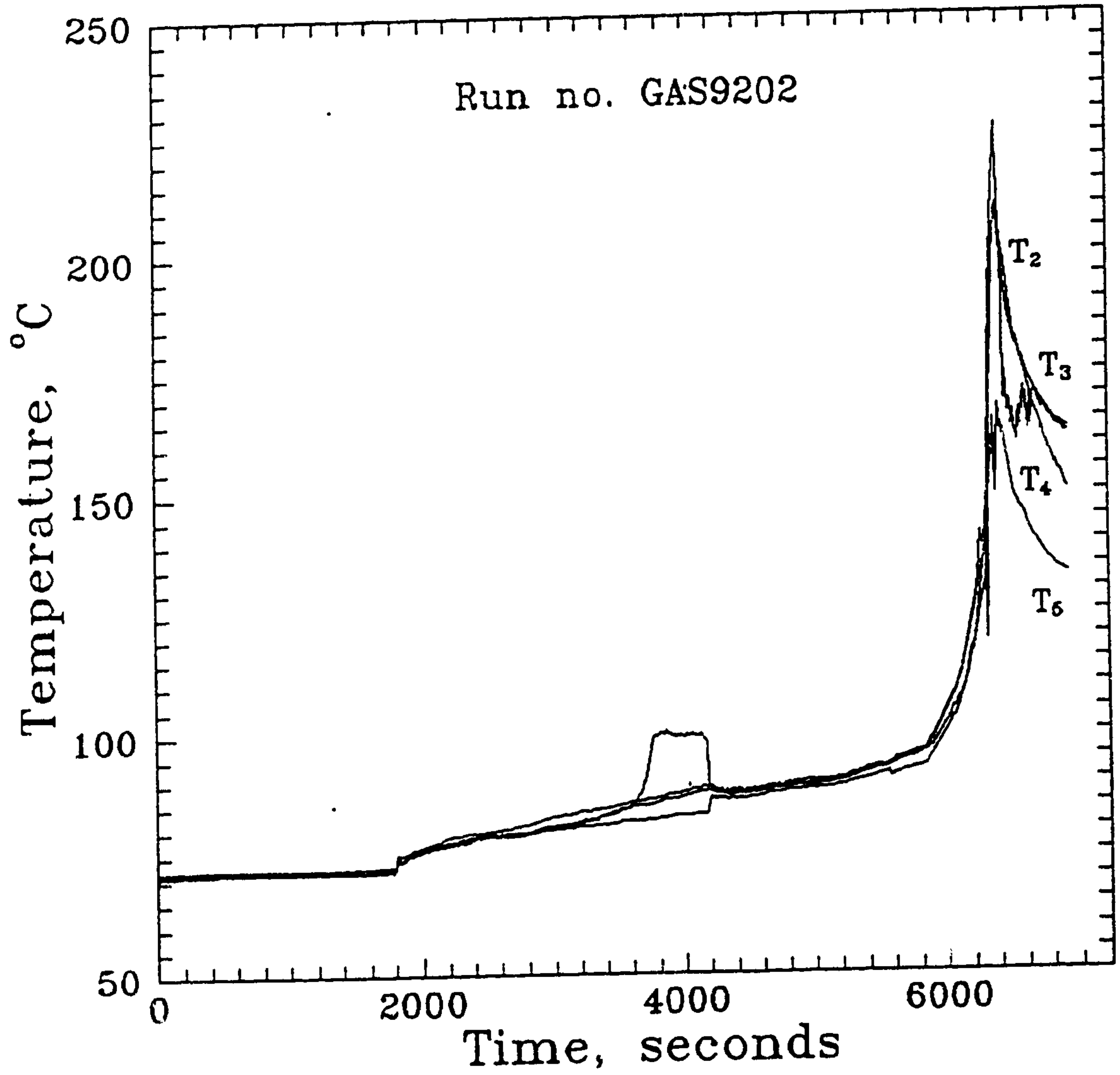


Figure B.7

Temperature profiles of locations 2 to 5

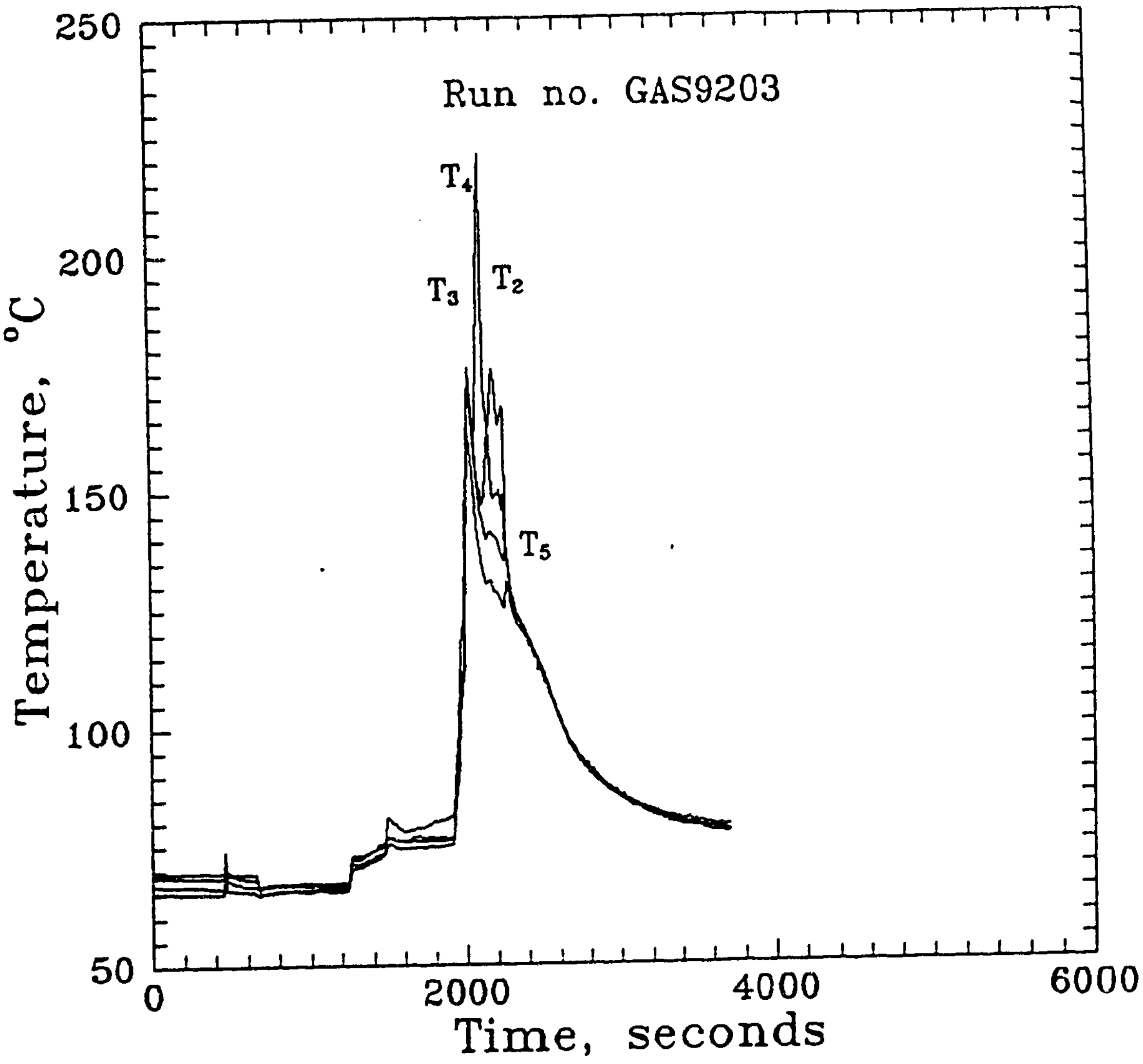


Figure B.8

Temperature profiles of locations 2 to 5

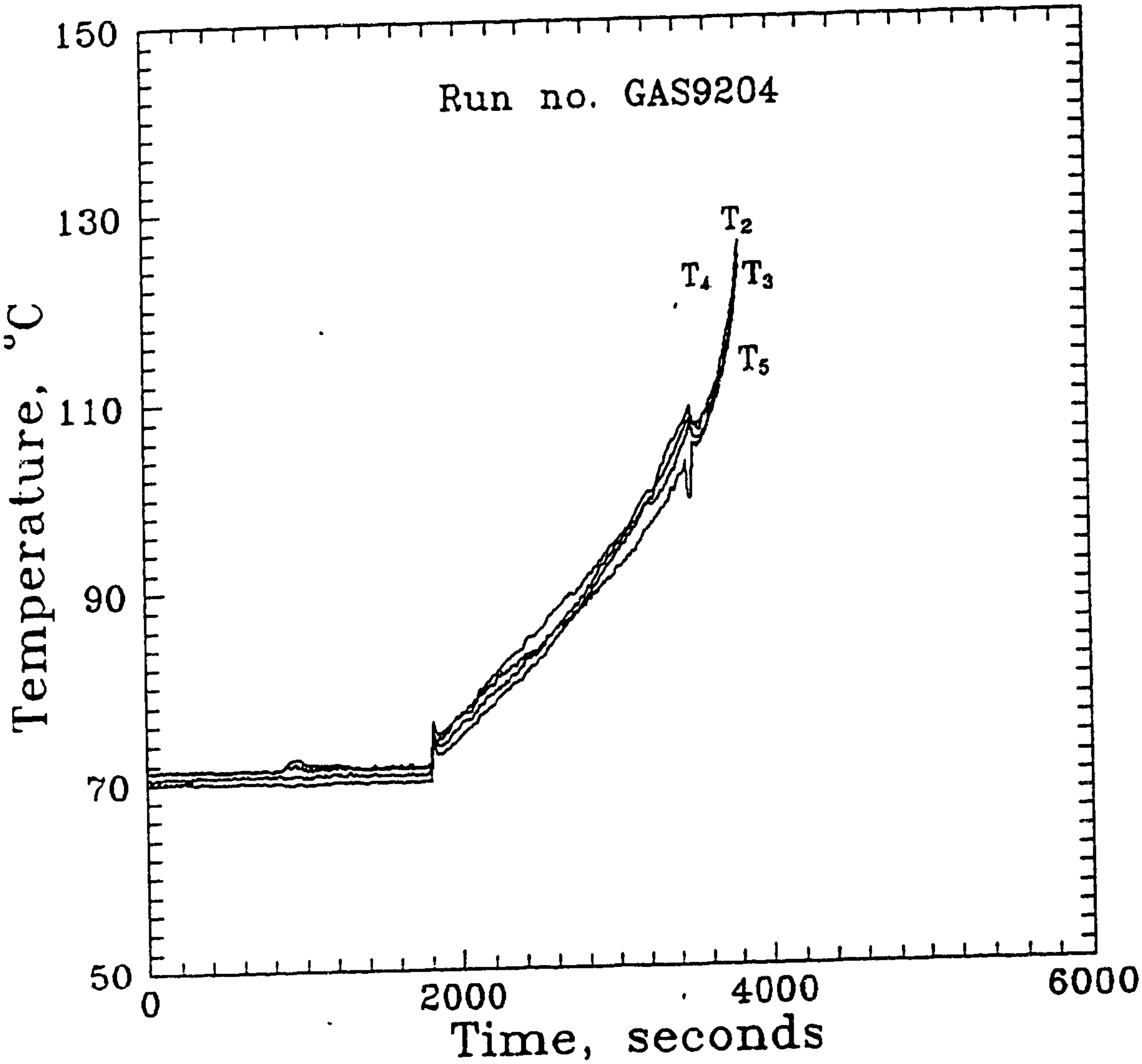


Figure B.9

Temperature profiles of locations 2 to 5

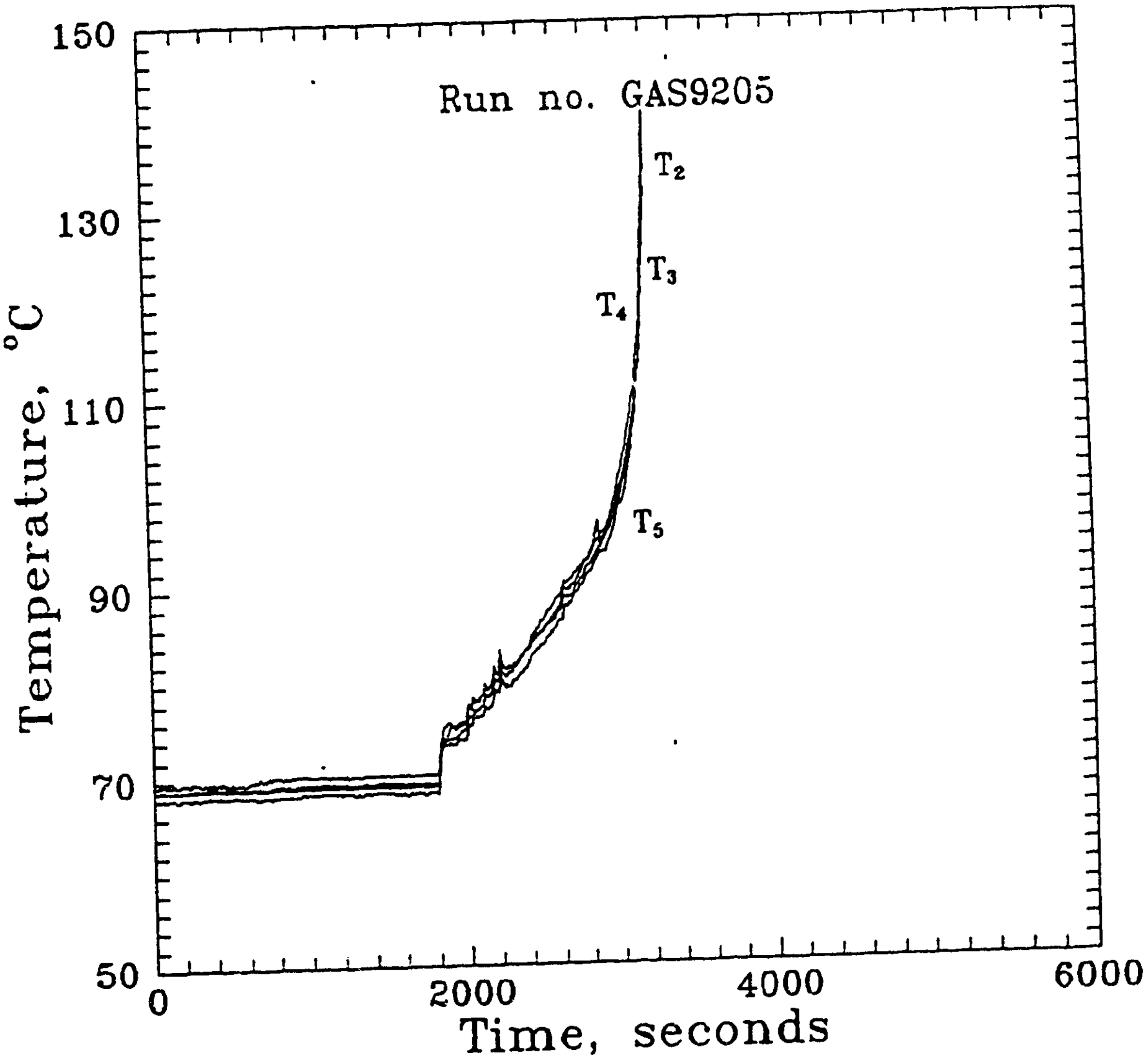


Figure B.10

Temperature profiles of locations 2 to 5

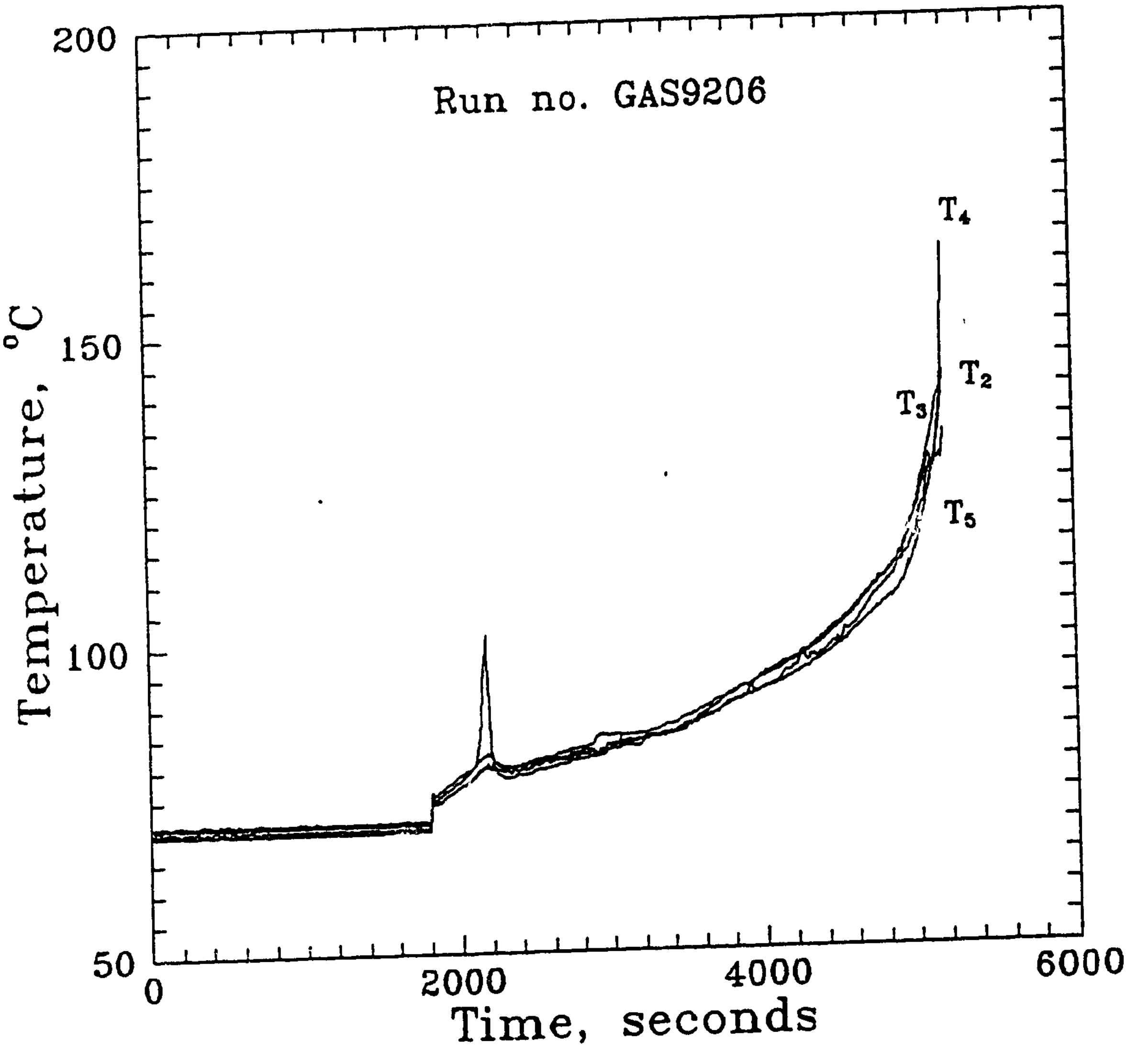


Figure B.11

Temperature profiles of locations 2 to 5

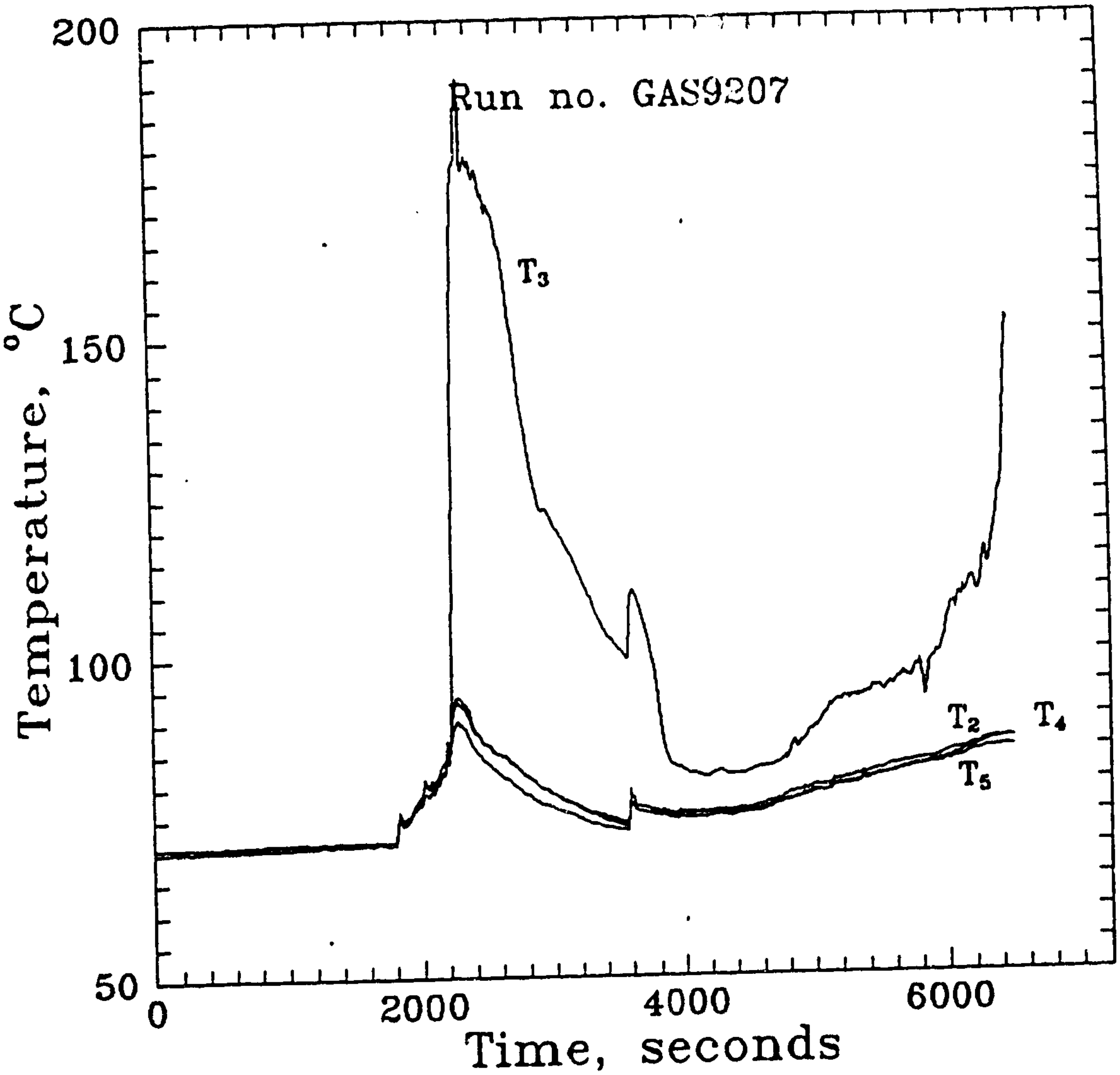


Figure B.12

Temperature profiles of locations 2 to 5

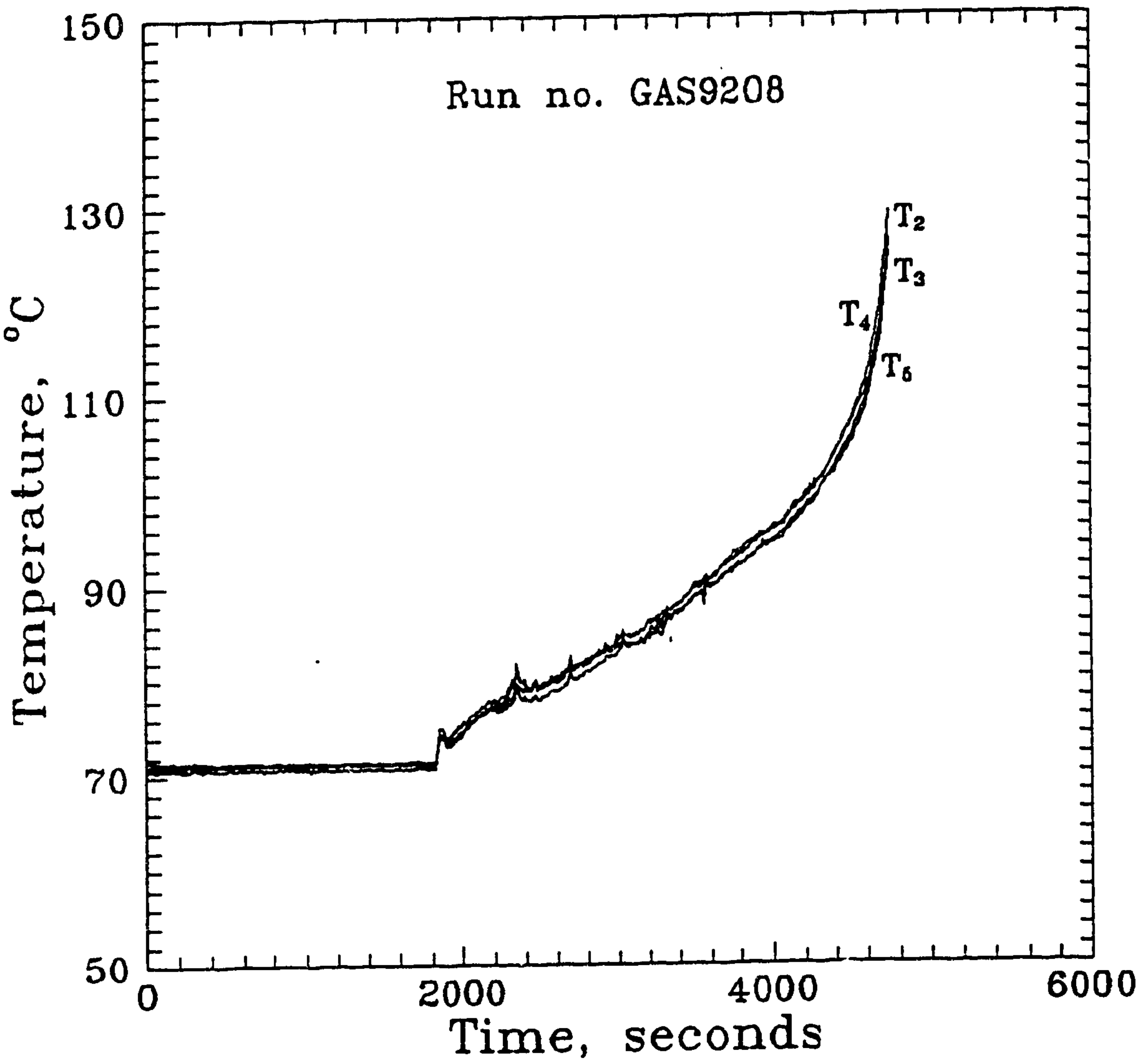


Figure B.13

Temperature profiles of locations 2 to 5

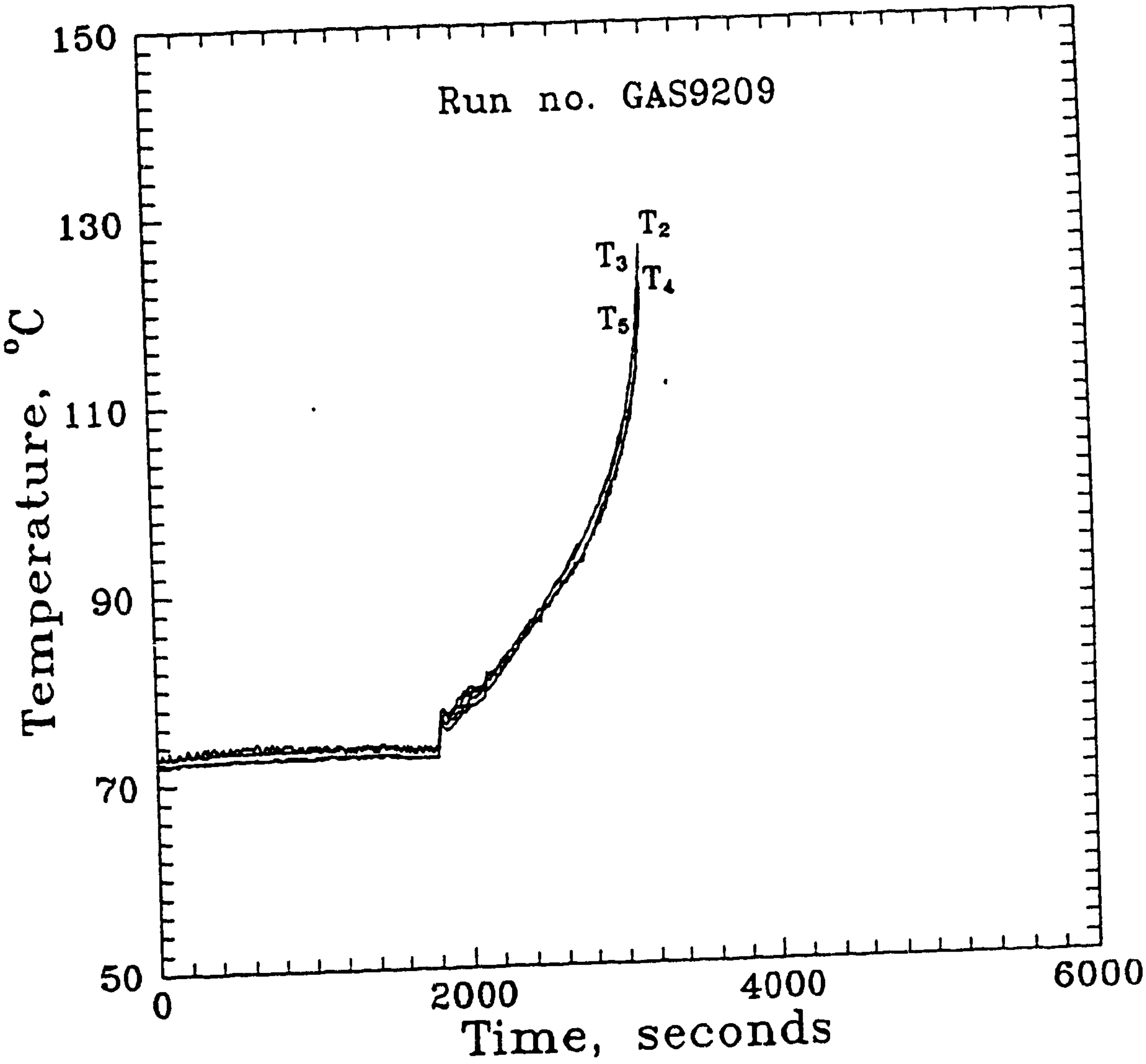


Figure B.14

Temperature profiles of locations 2 to 5

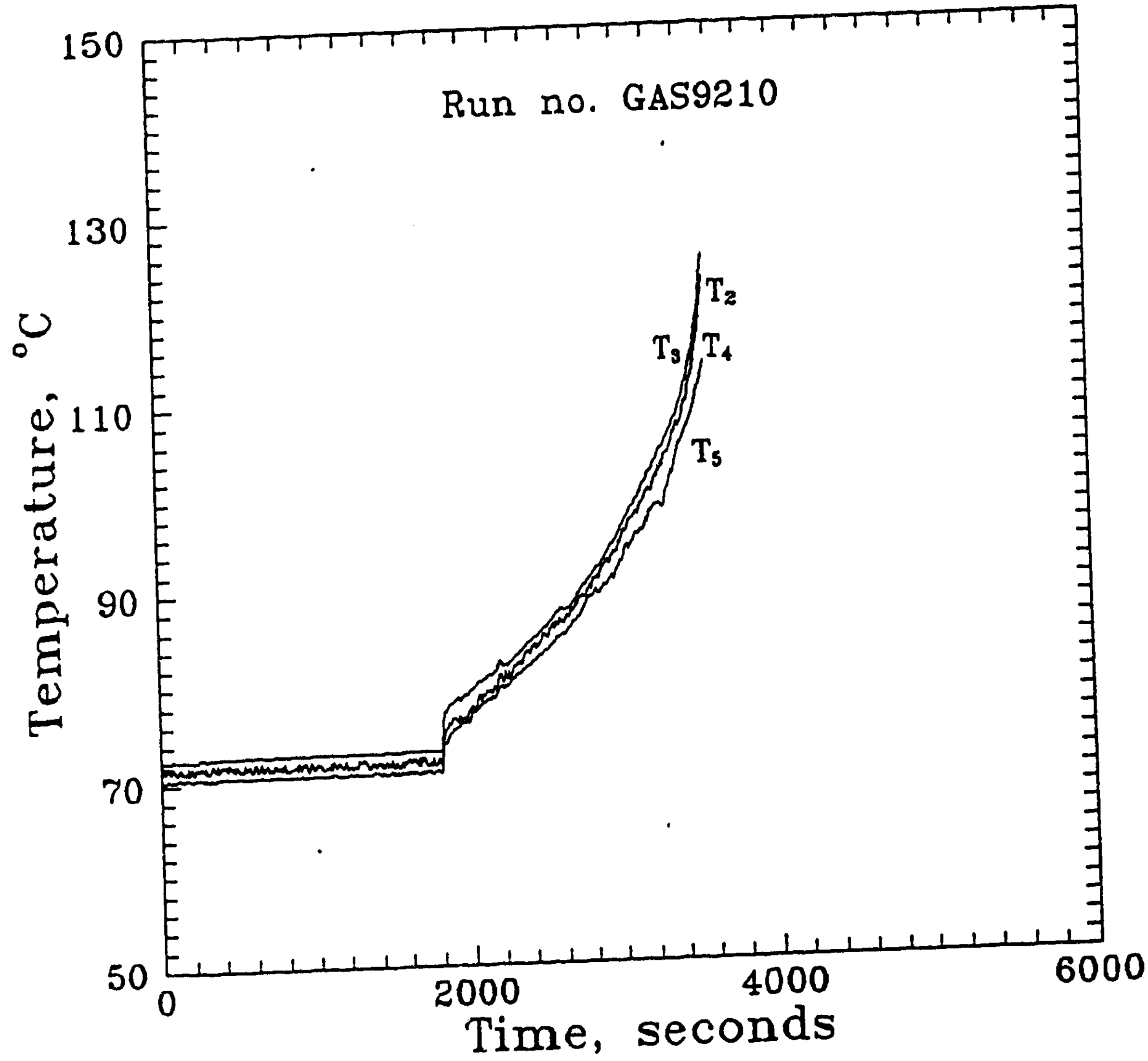


Figure B.15

Temperature profiles of locations 2 to 5

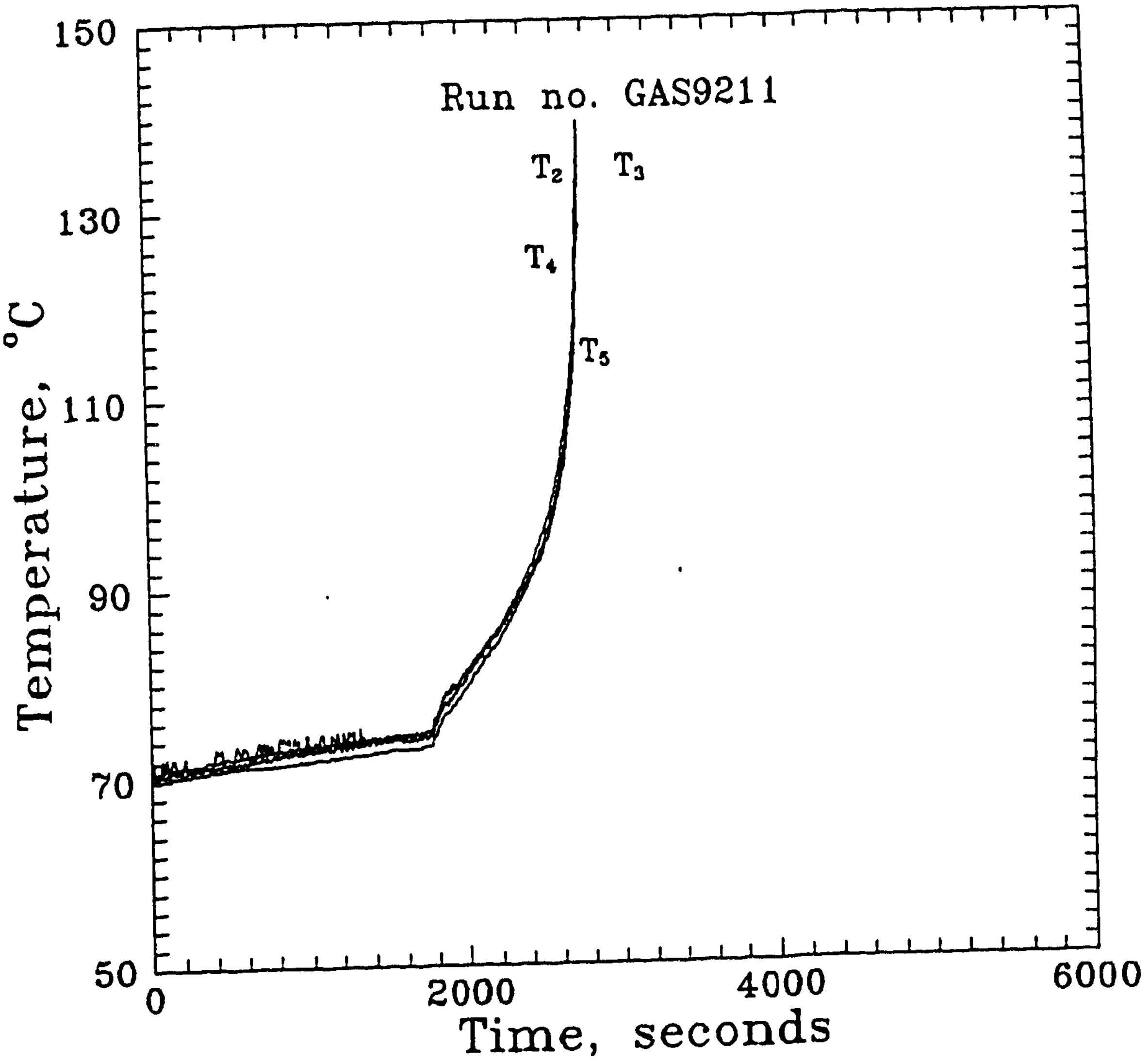


Figure B.16

Temperature profiles of locations 2 to 5

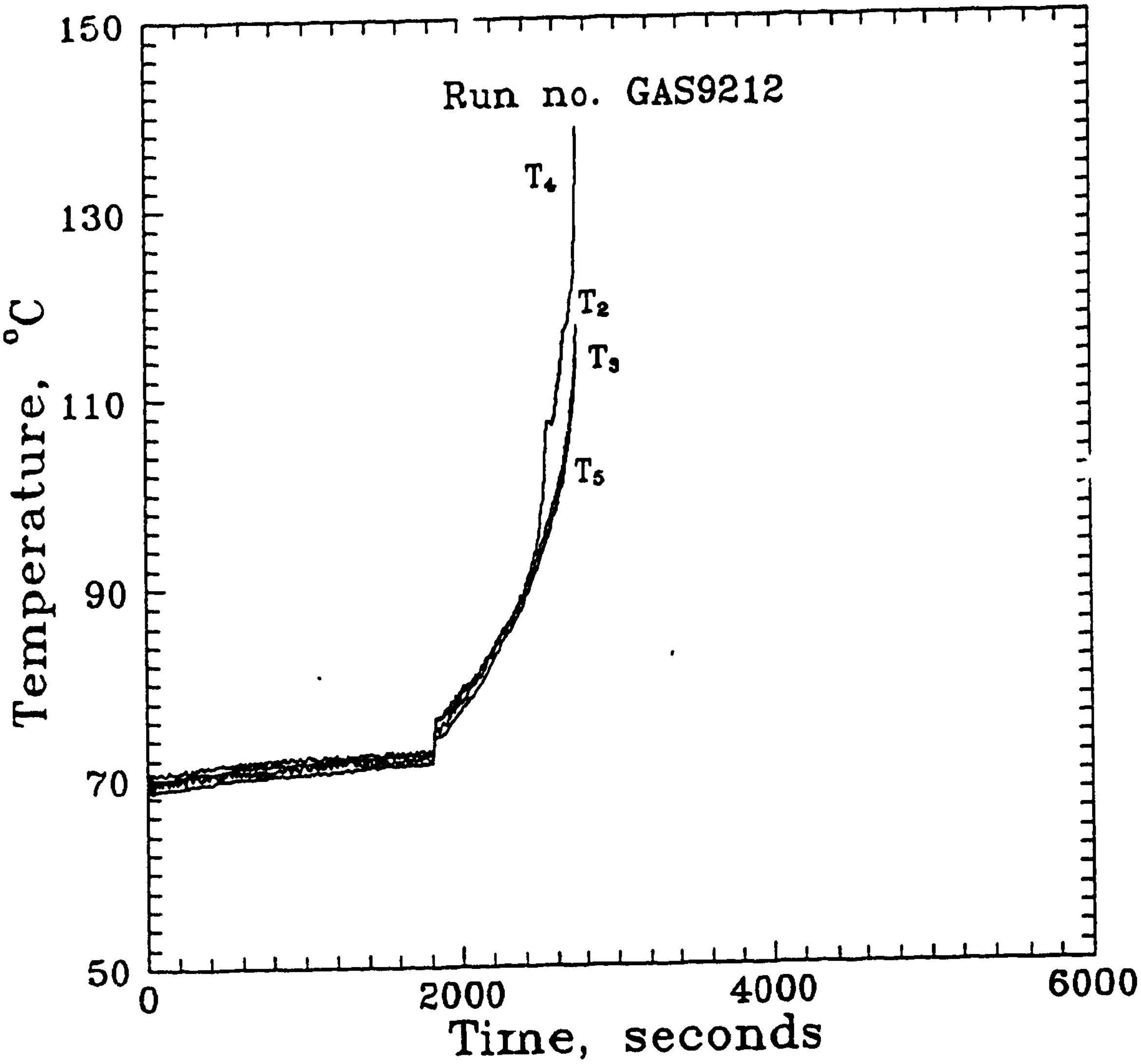


Figure B.17

Temperature profiles of locations 2 to 5

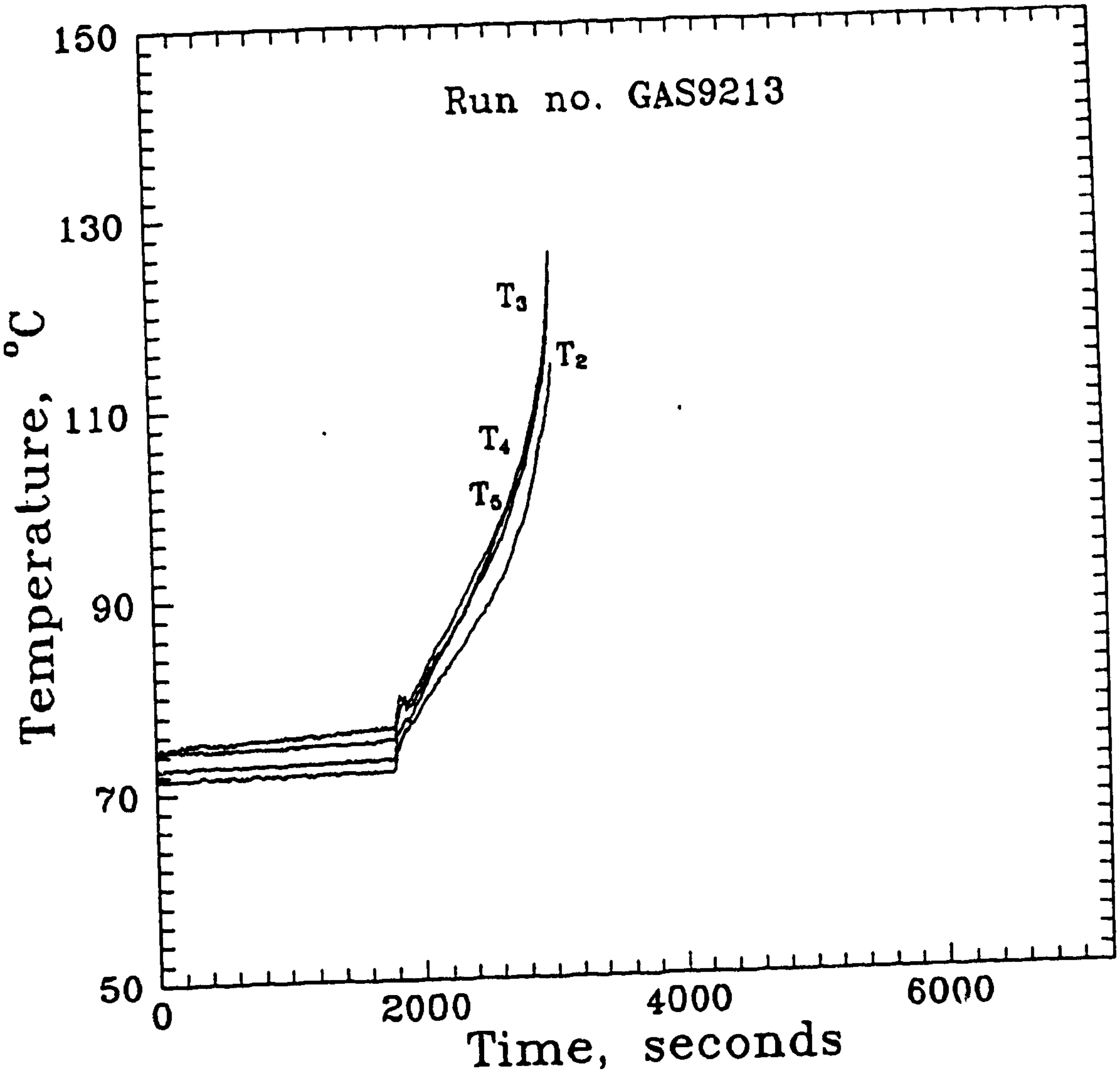


Figure B.18

Temperature profiles of locations 2 to 5

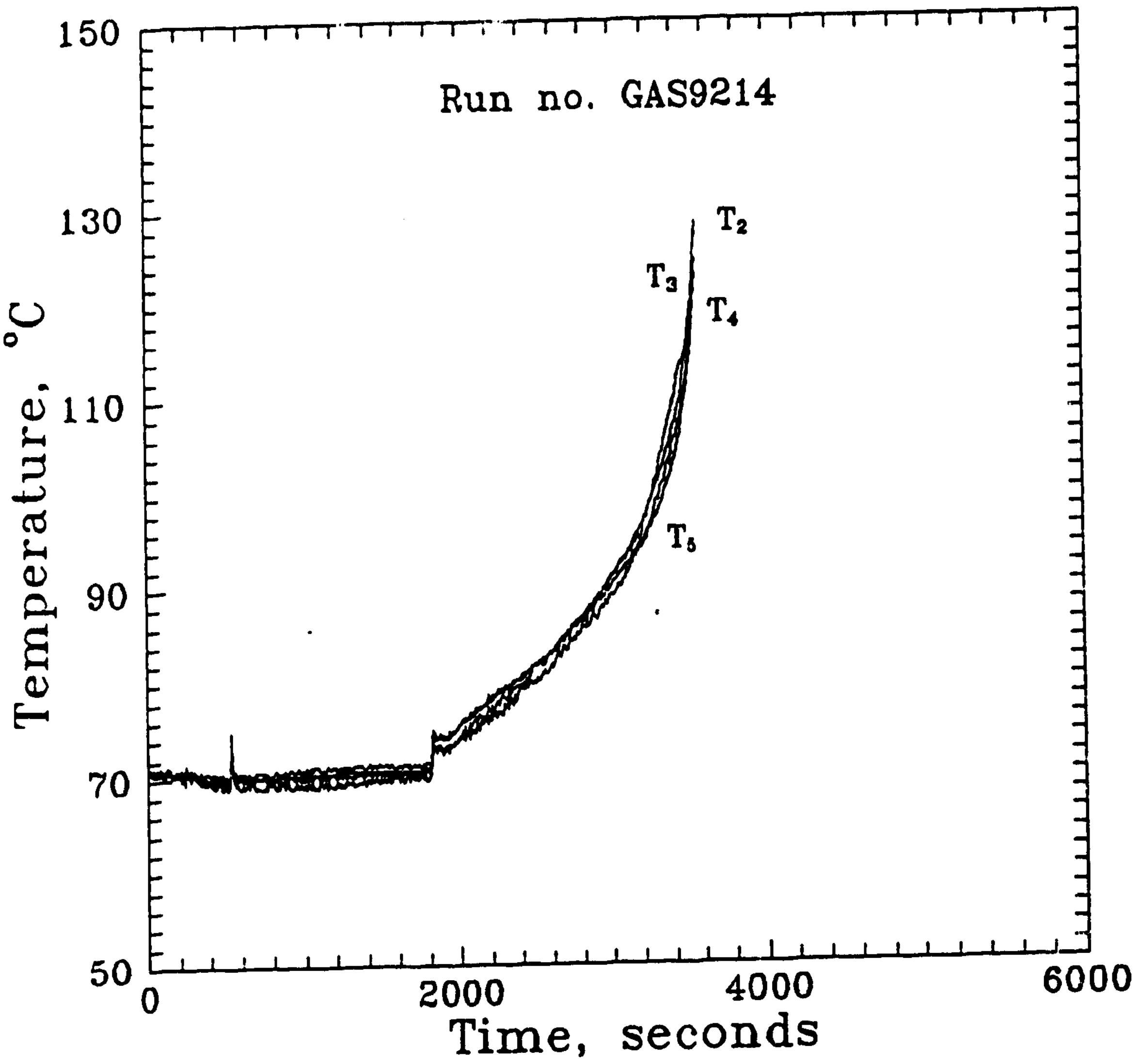


Figure B.19

Temperature profiles of locations 2 to 5

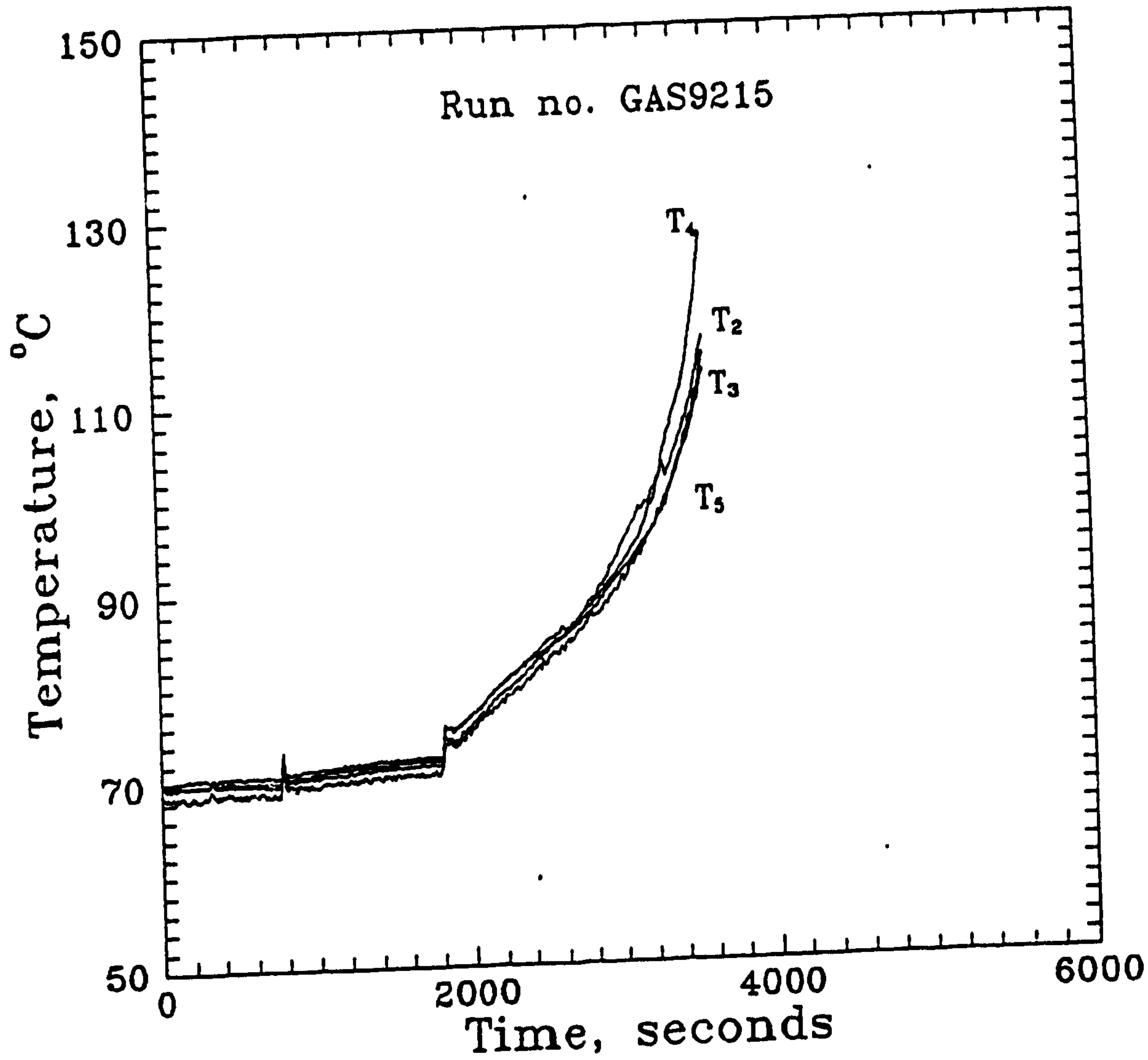


Figure B.20

Temperature profiles of locations 2 to 5

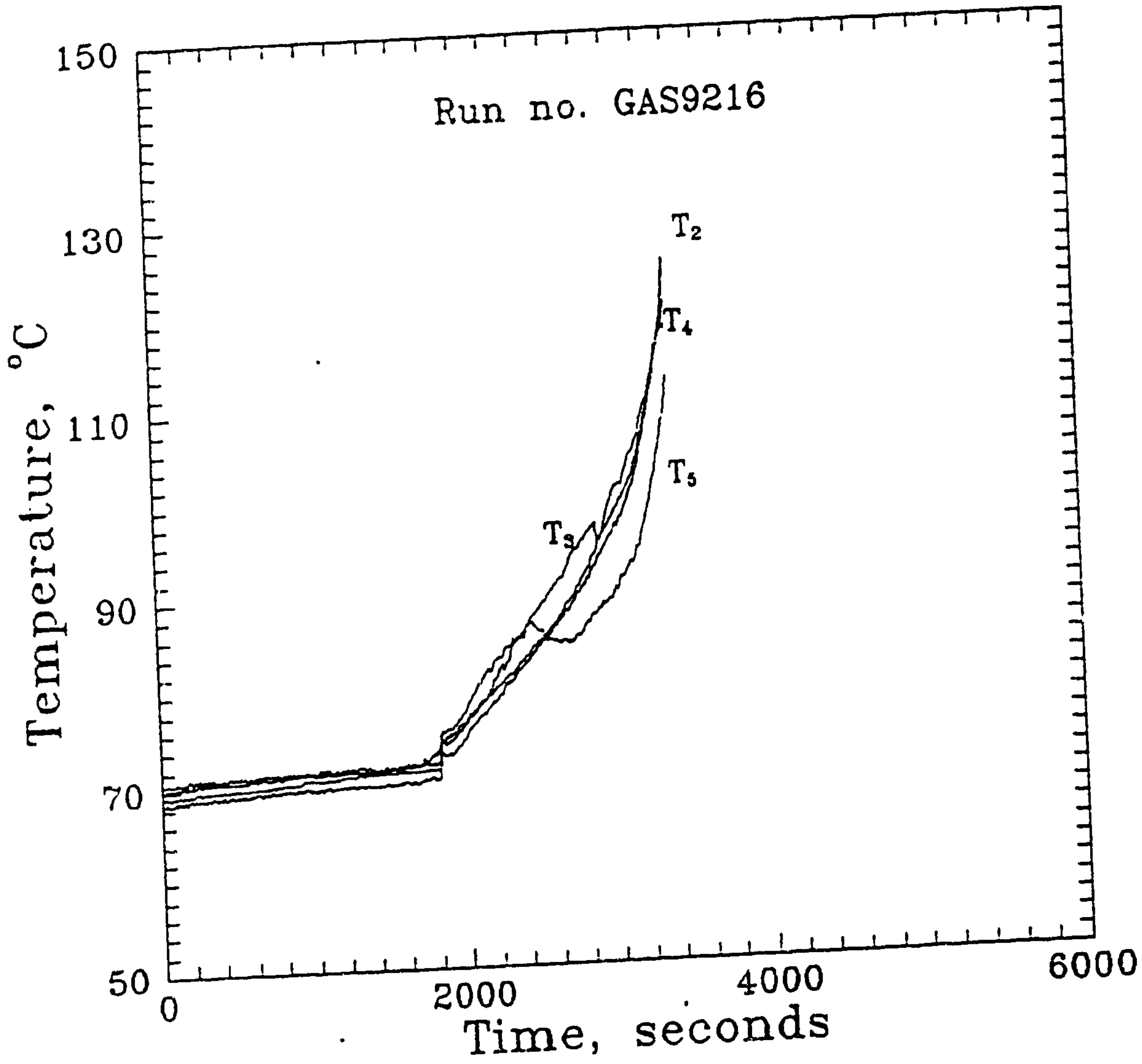


Figure B.21

Temperature profiles of locations 2 to 5

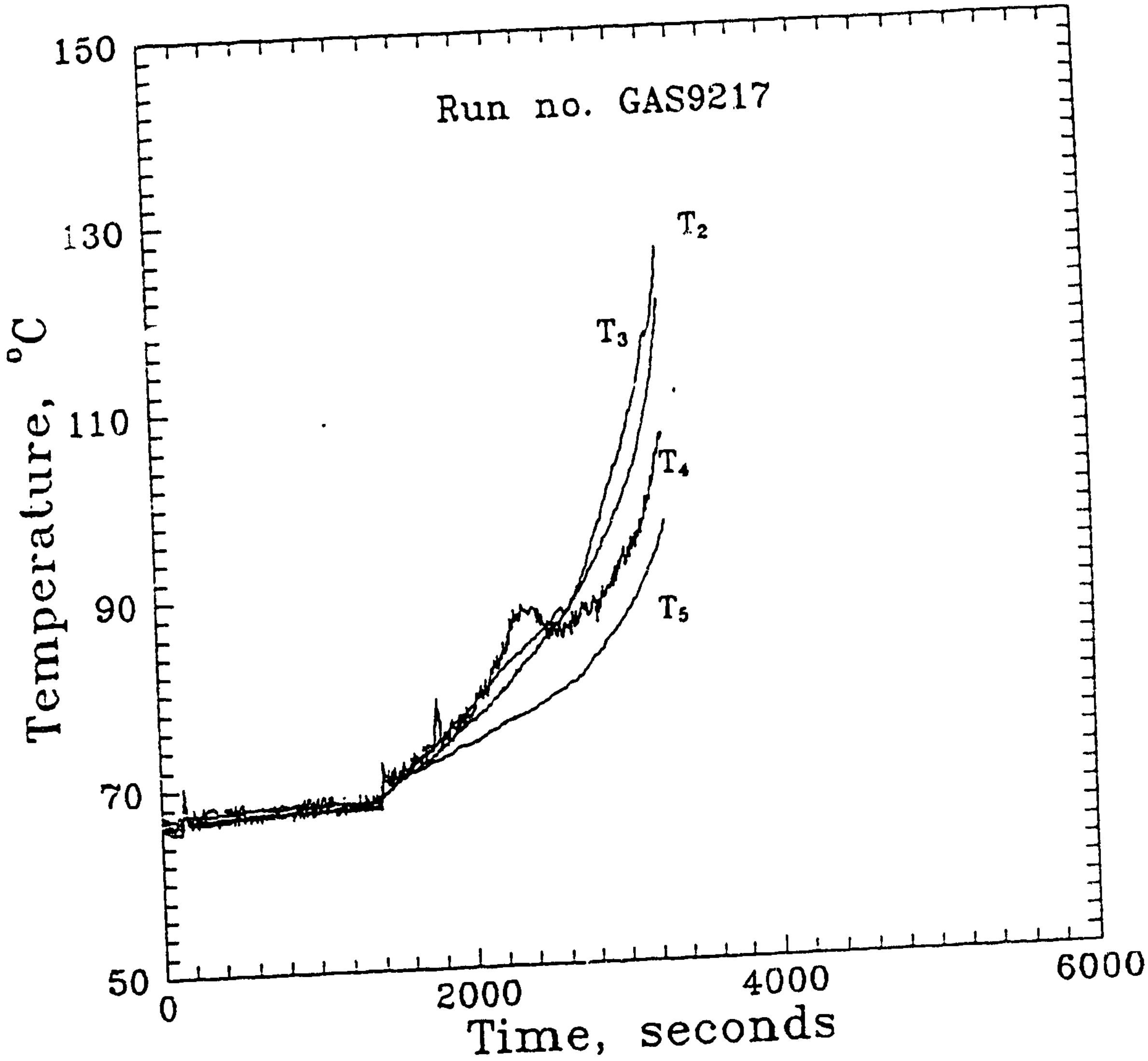


Figure B.22

Temperature profiles of locations 2 to 5

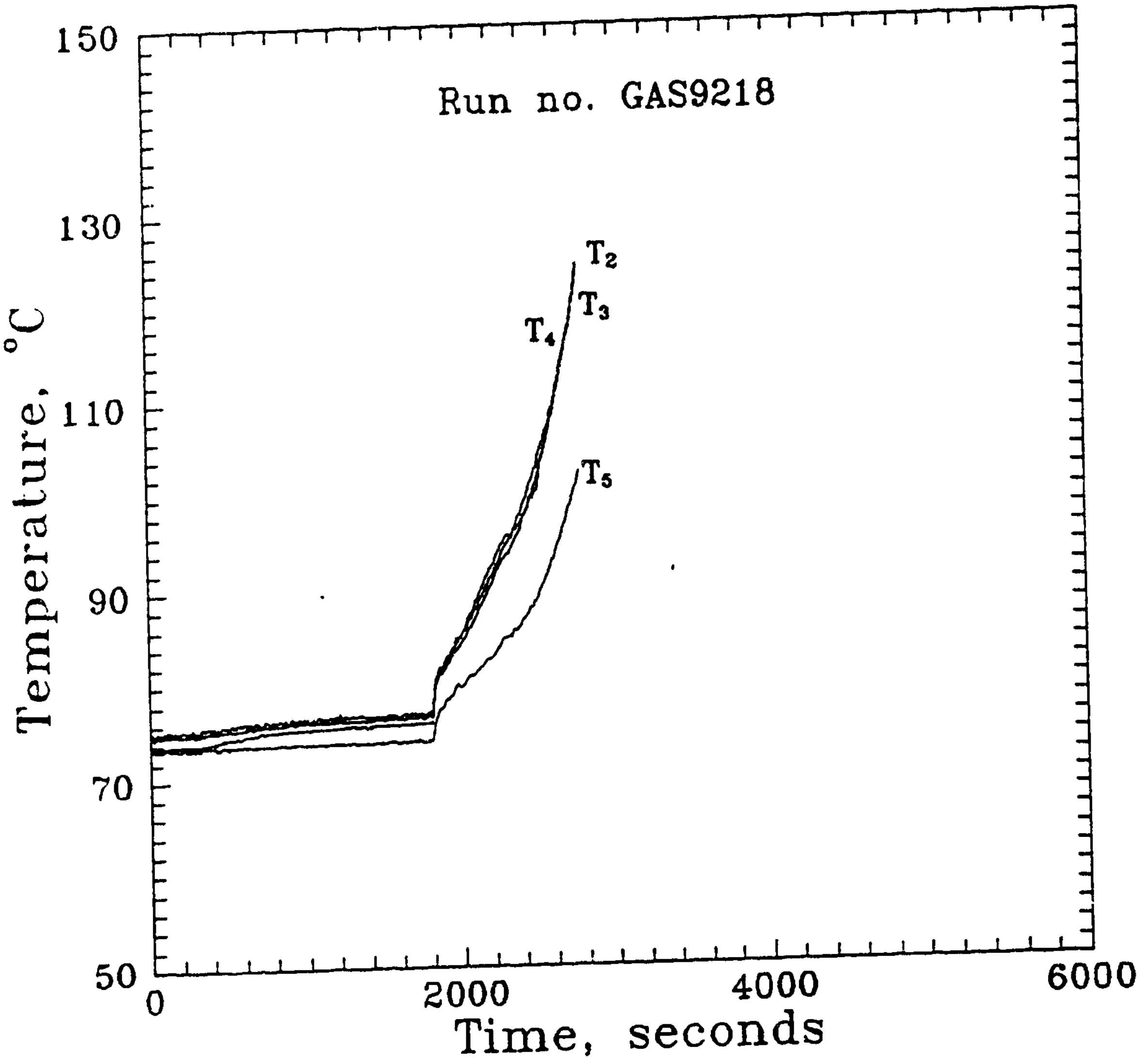


Figure B.23

Temperature profiles of locations 2 to 5

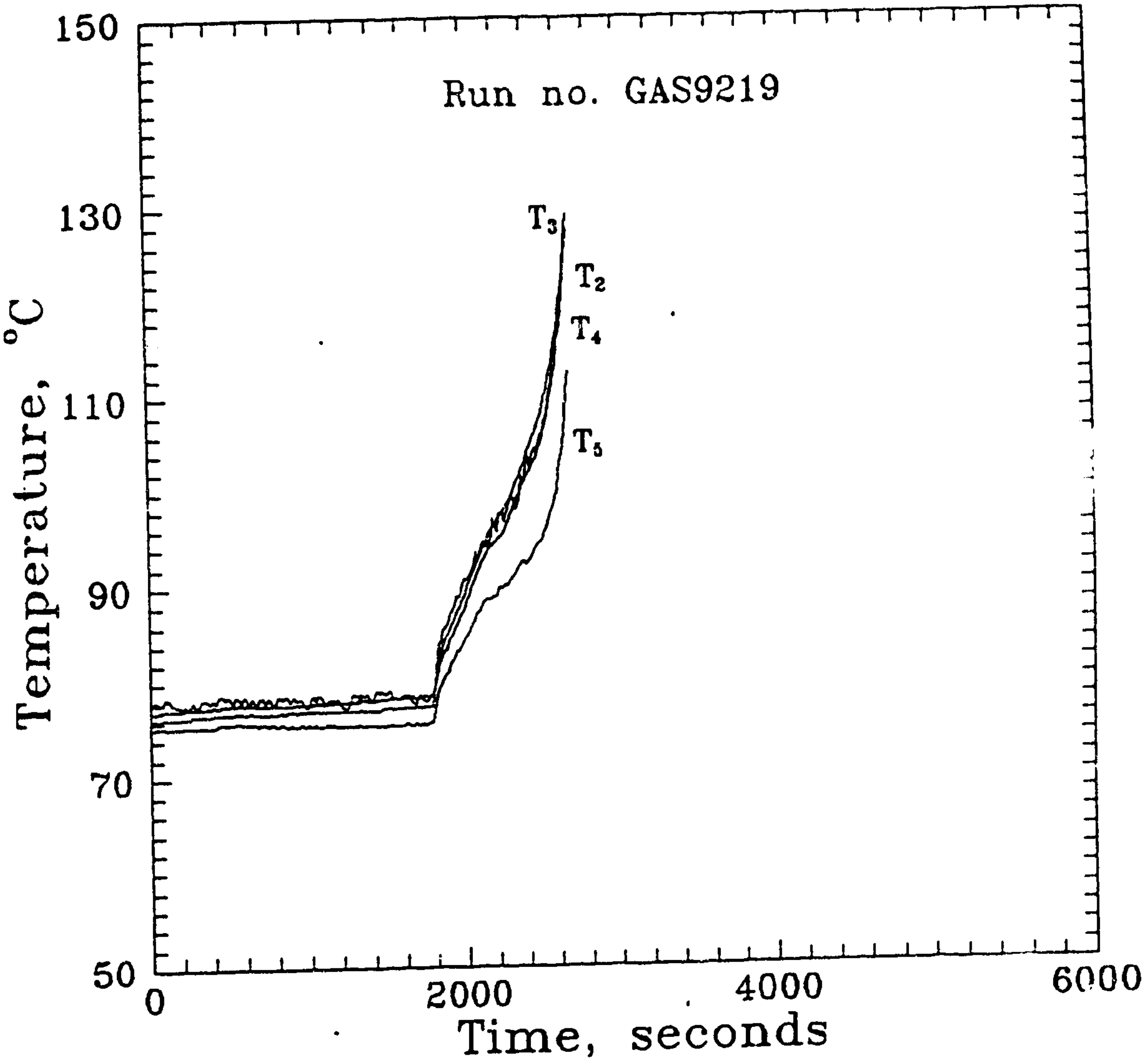


Figure B.24

Temperature profiles of locations 2 to 5

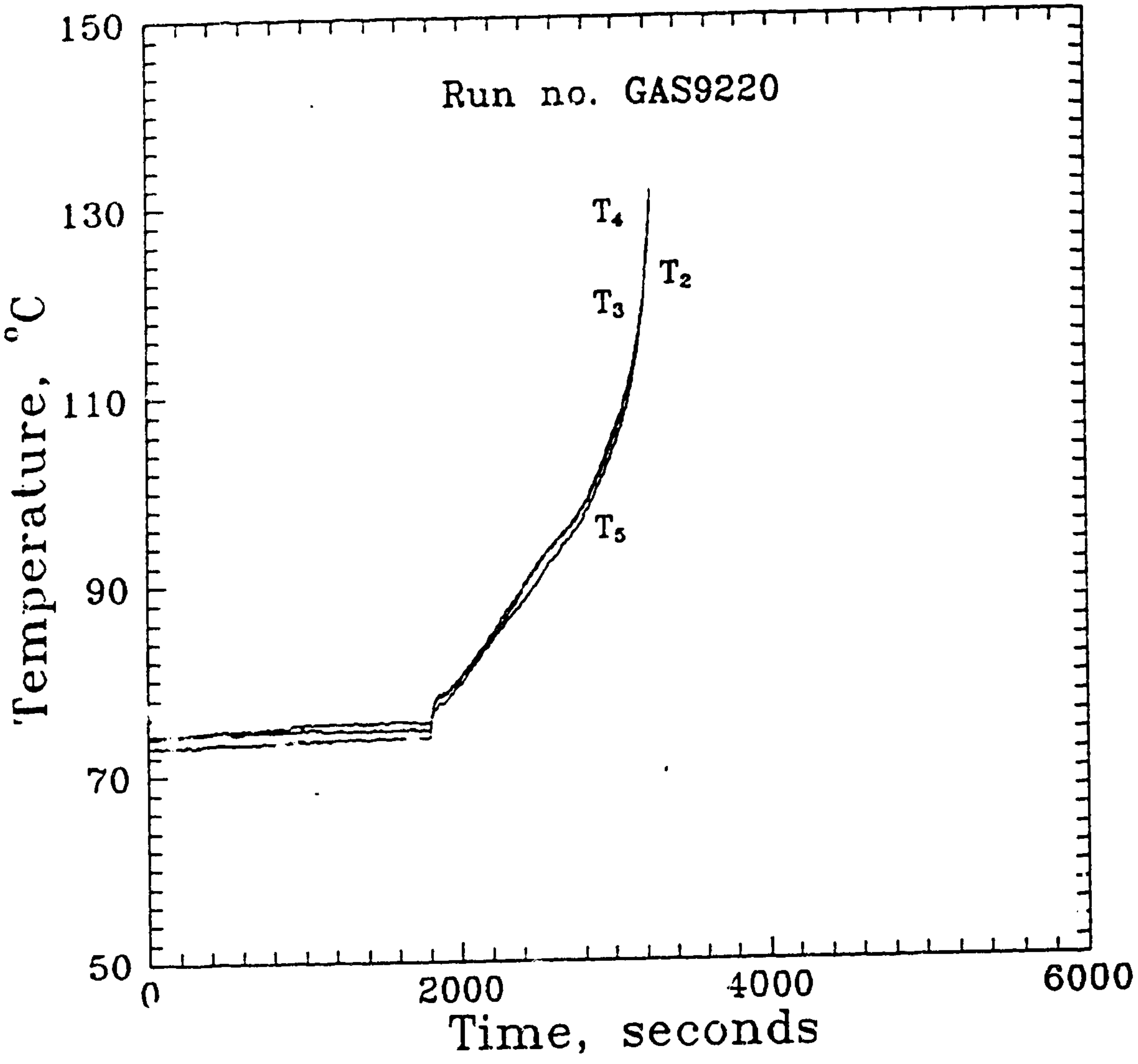


Figure B.25

Temperature profiles of locations 2 to 5

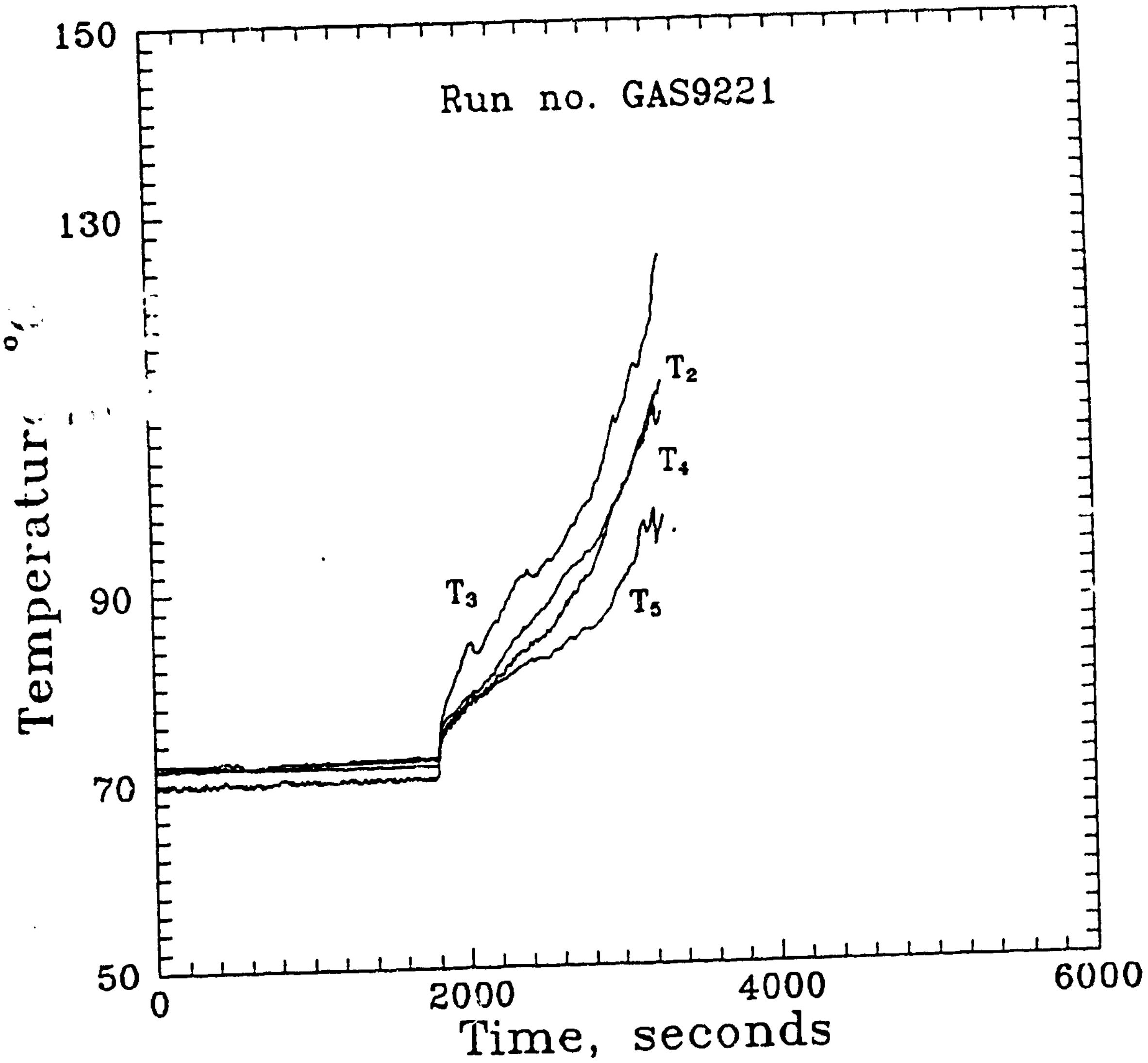


Figure B.26

Temperature profiles of locations 2 to 5

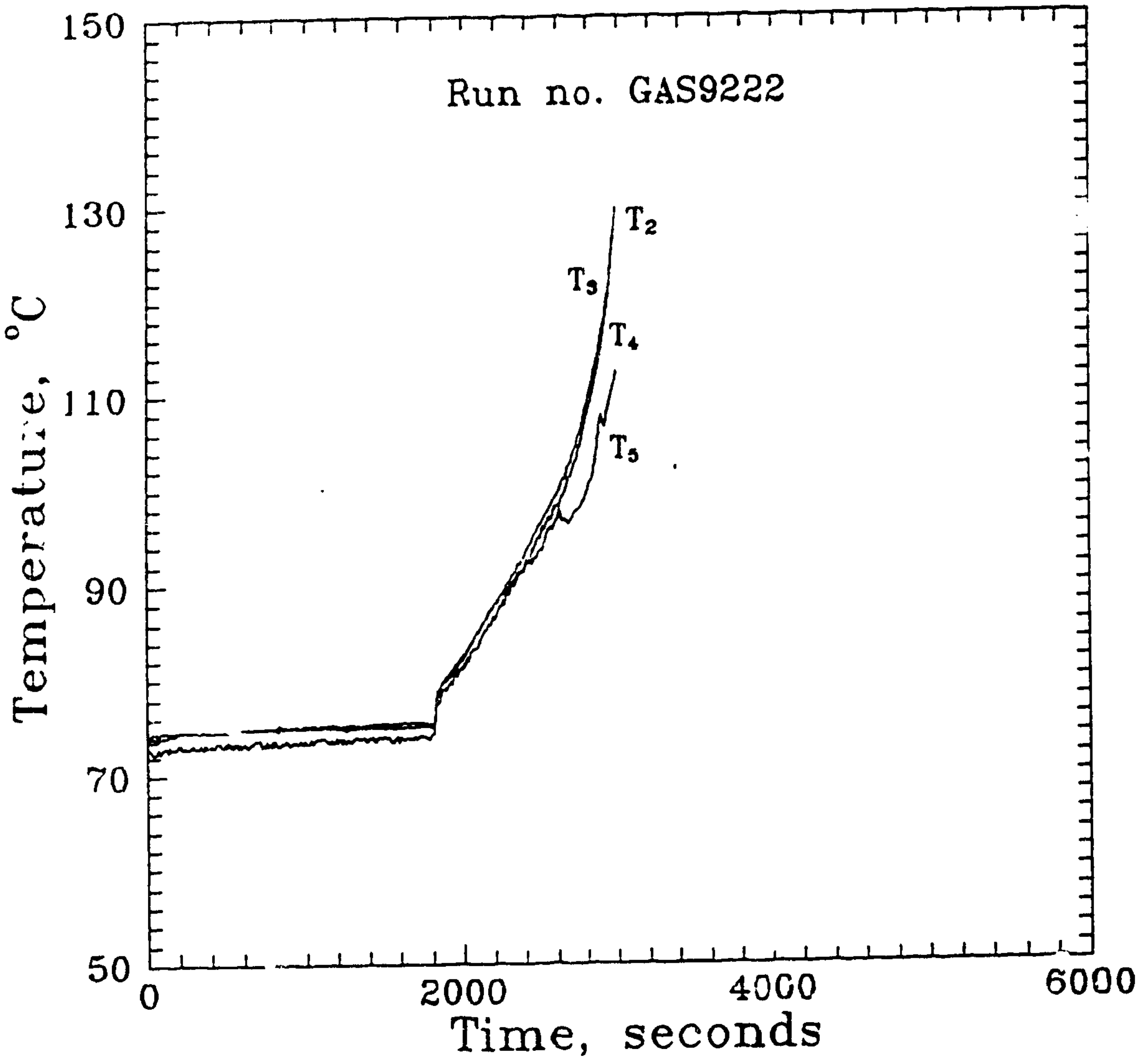


Figure B.27

Temperature profiles of locations 2 to 5

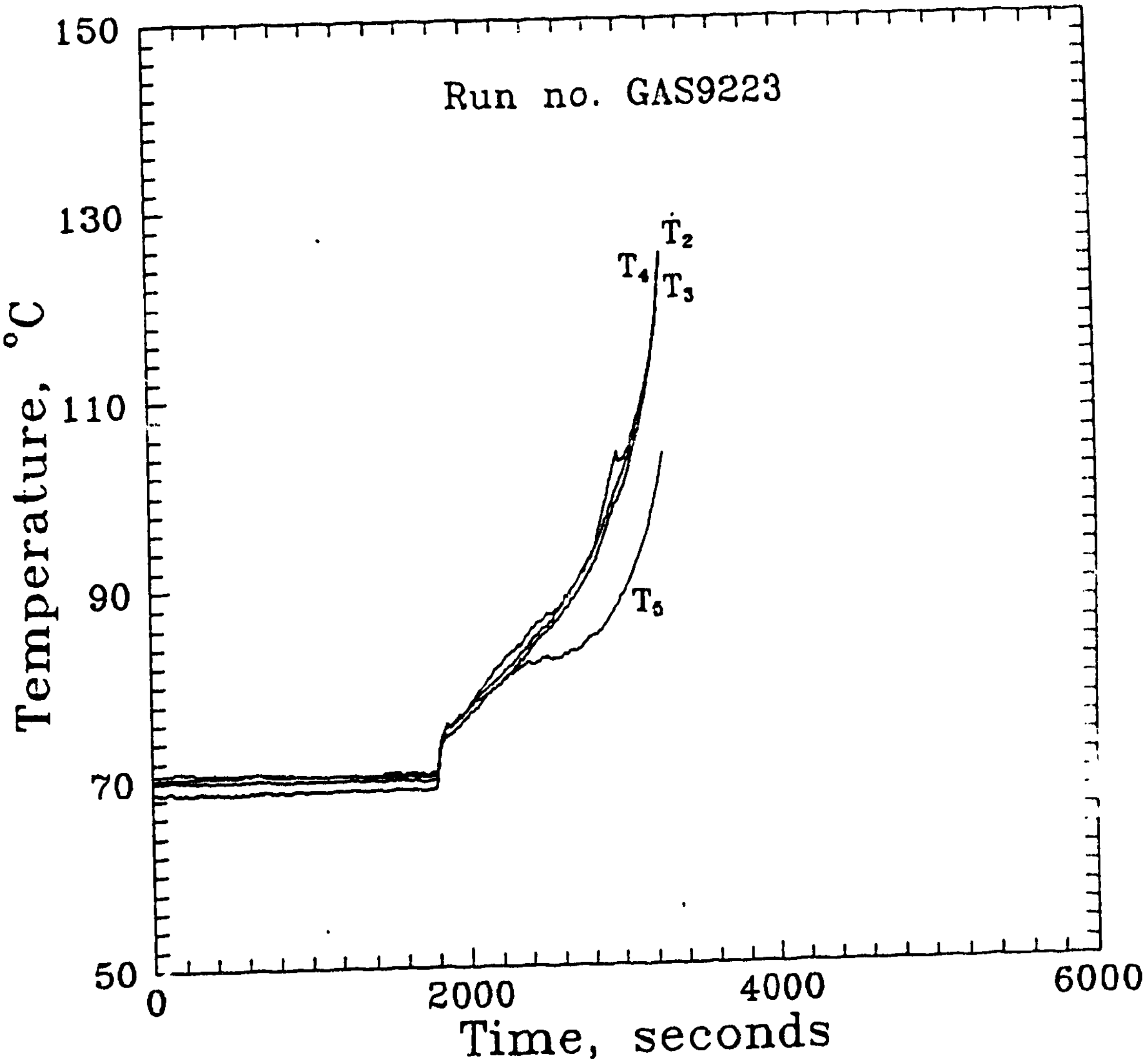


Figure B.28

Temperature profiles of locations 2 to 5

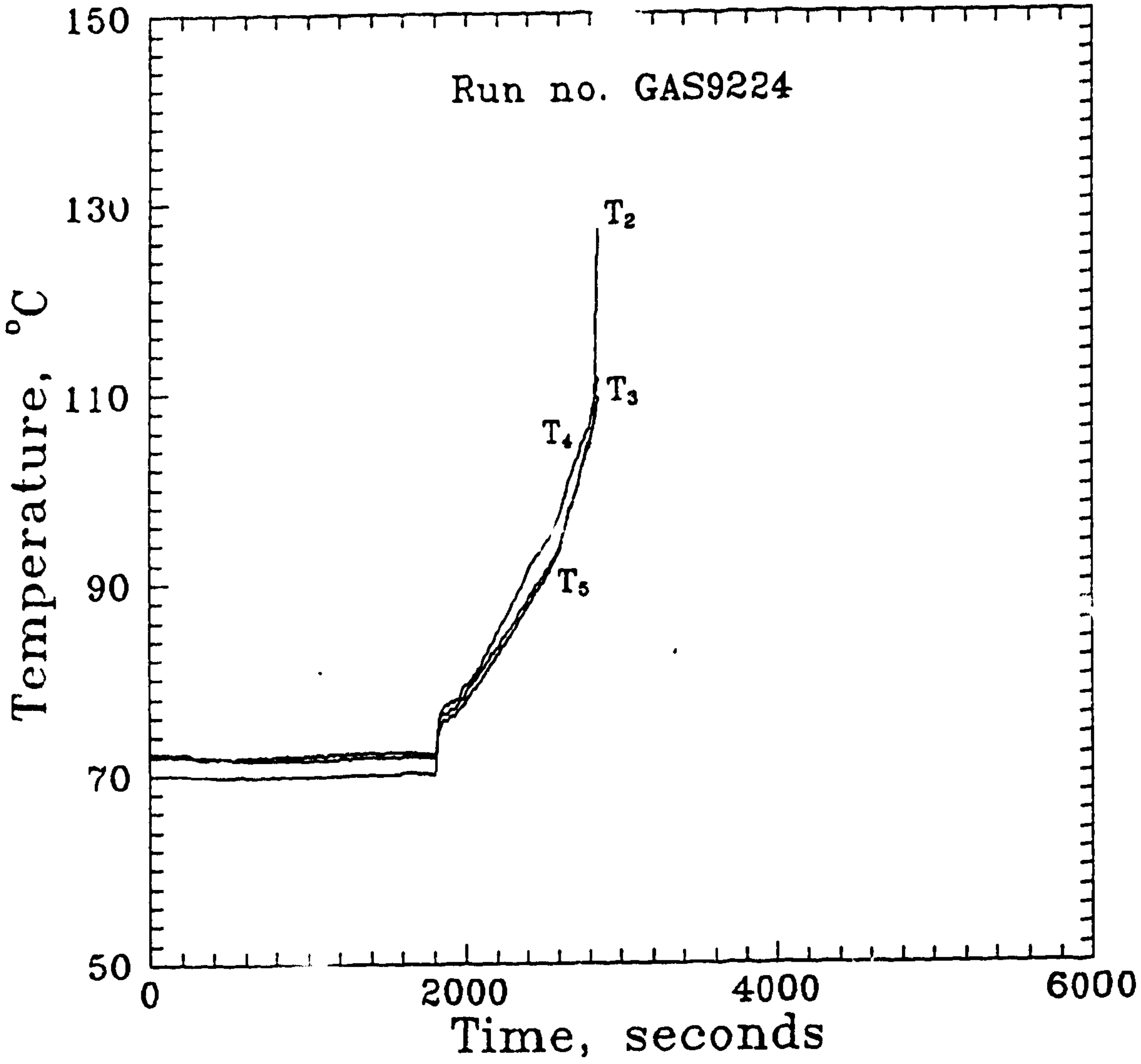


Figure B.29

Temperature profiles of locations 2 to 5

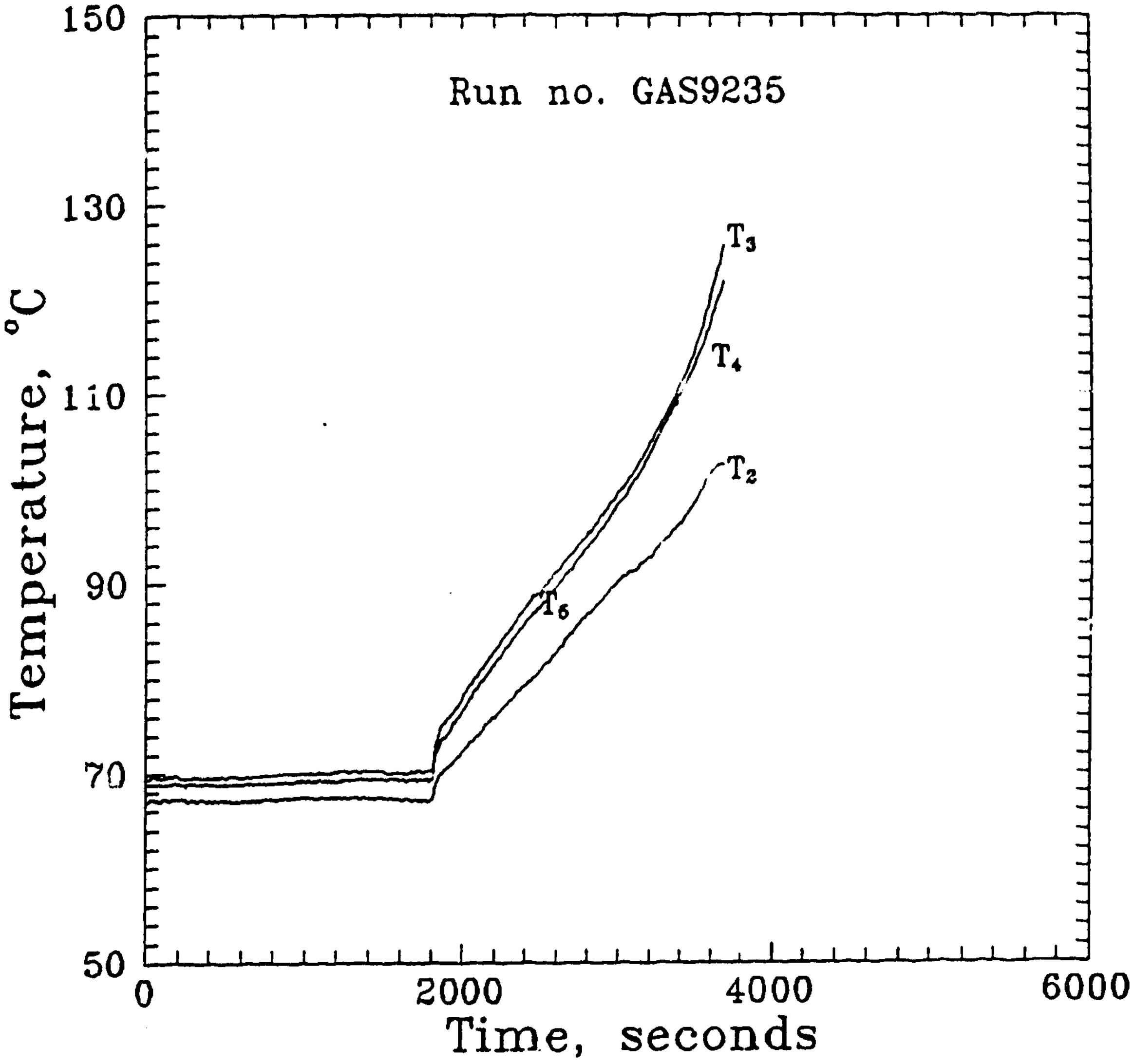


Figure B.30

Temperature profiles of locations 2 to 5

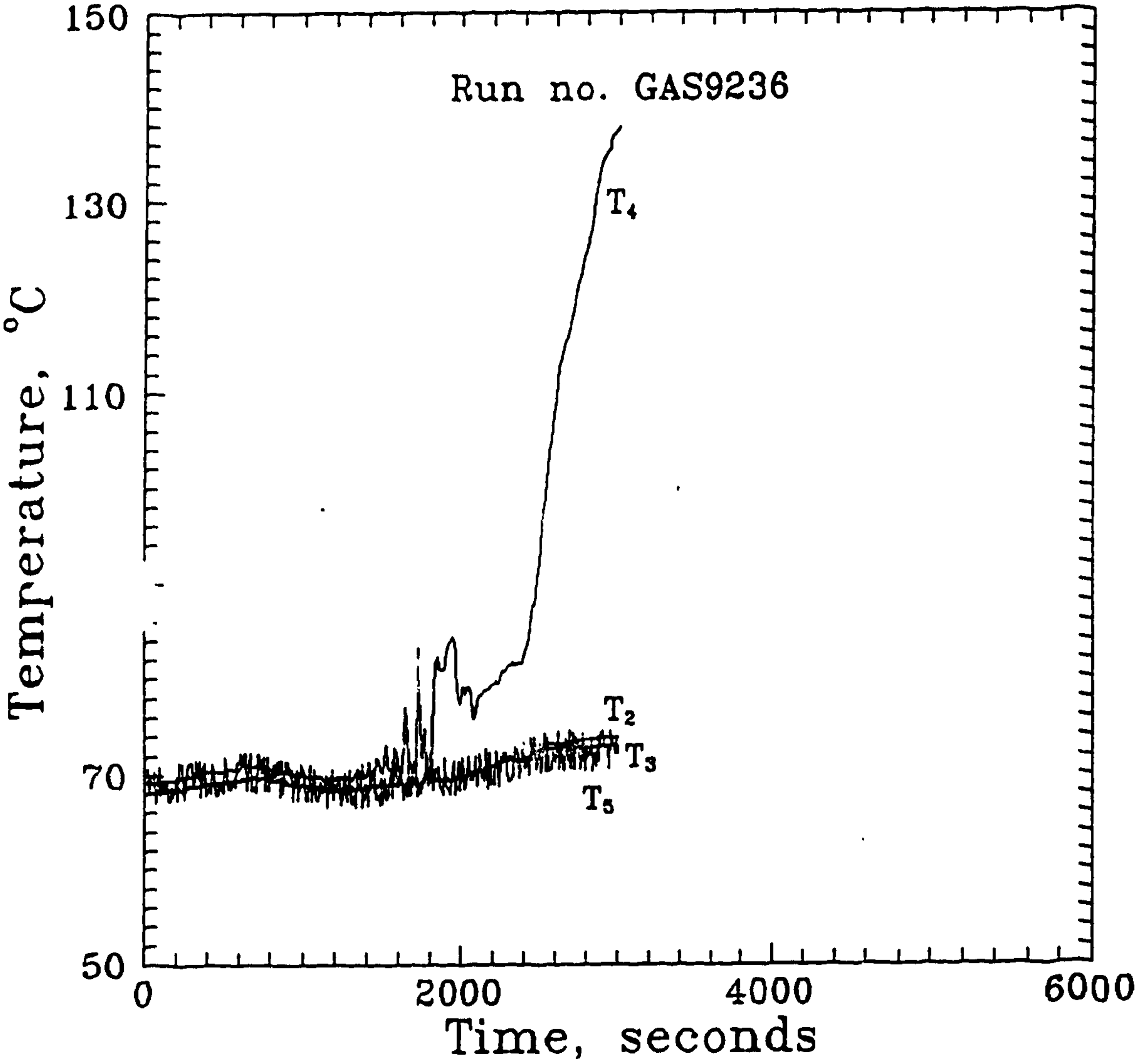


Figure B.31

Temperature profiles of locations 2 to 5

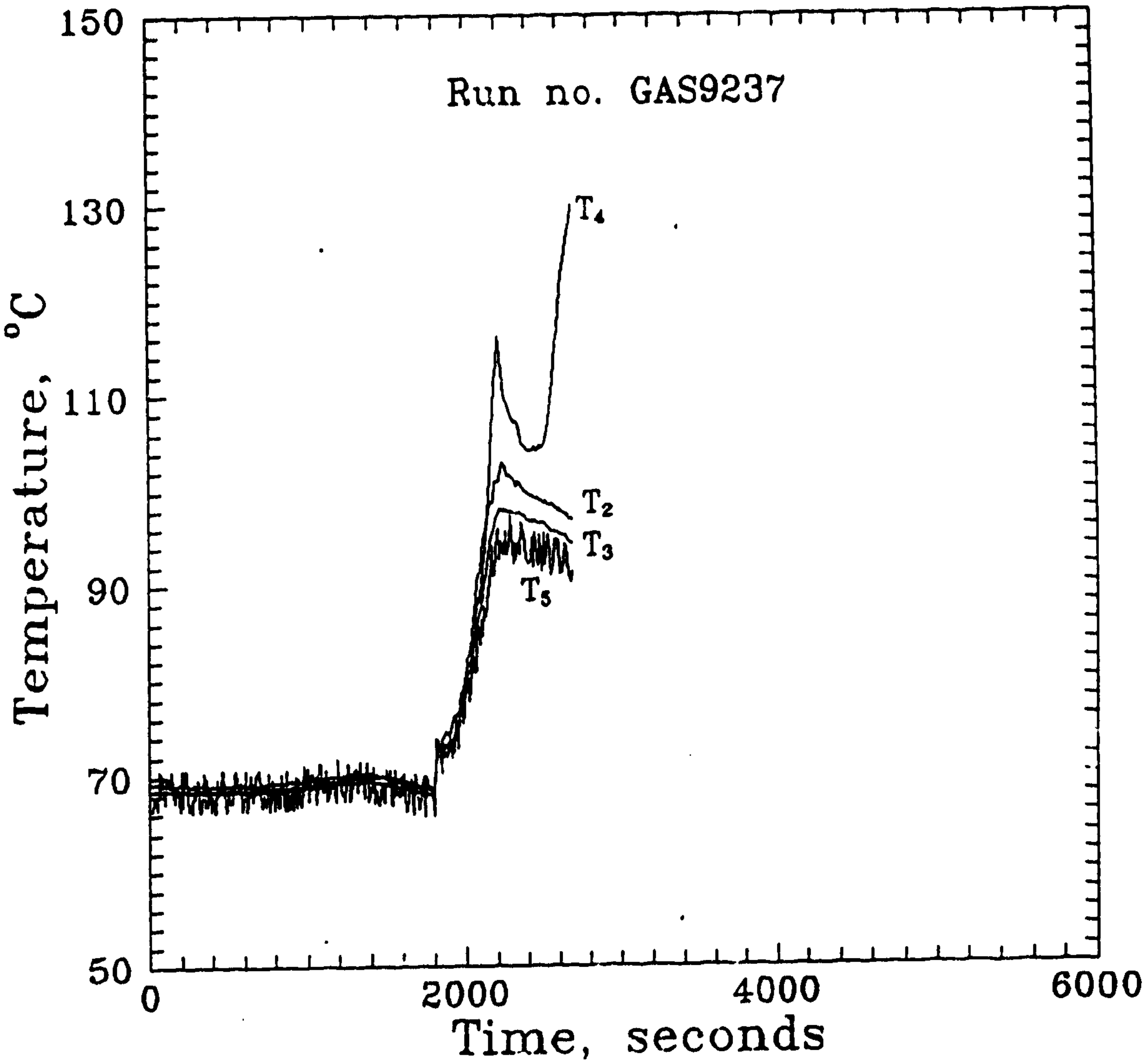


Figure B.32

Temperature profiles of locations 2 to 5

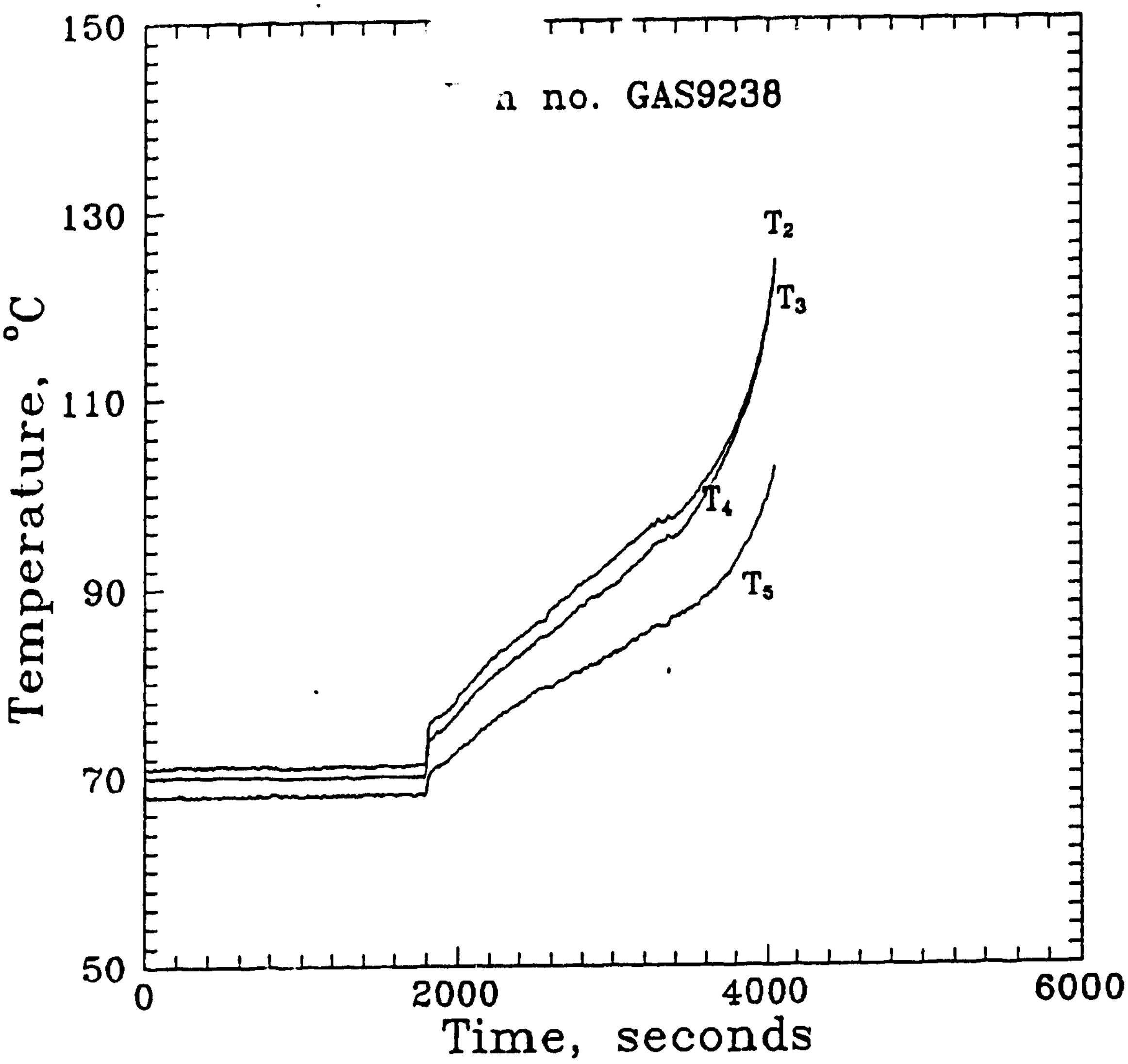


Figure B.33

Temperature profiles of locations 2 to 5

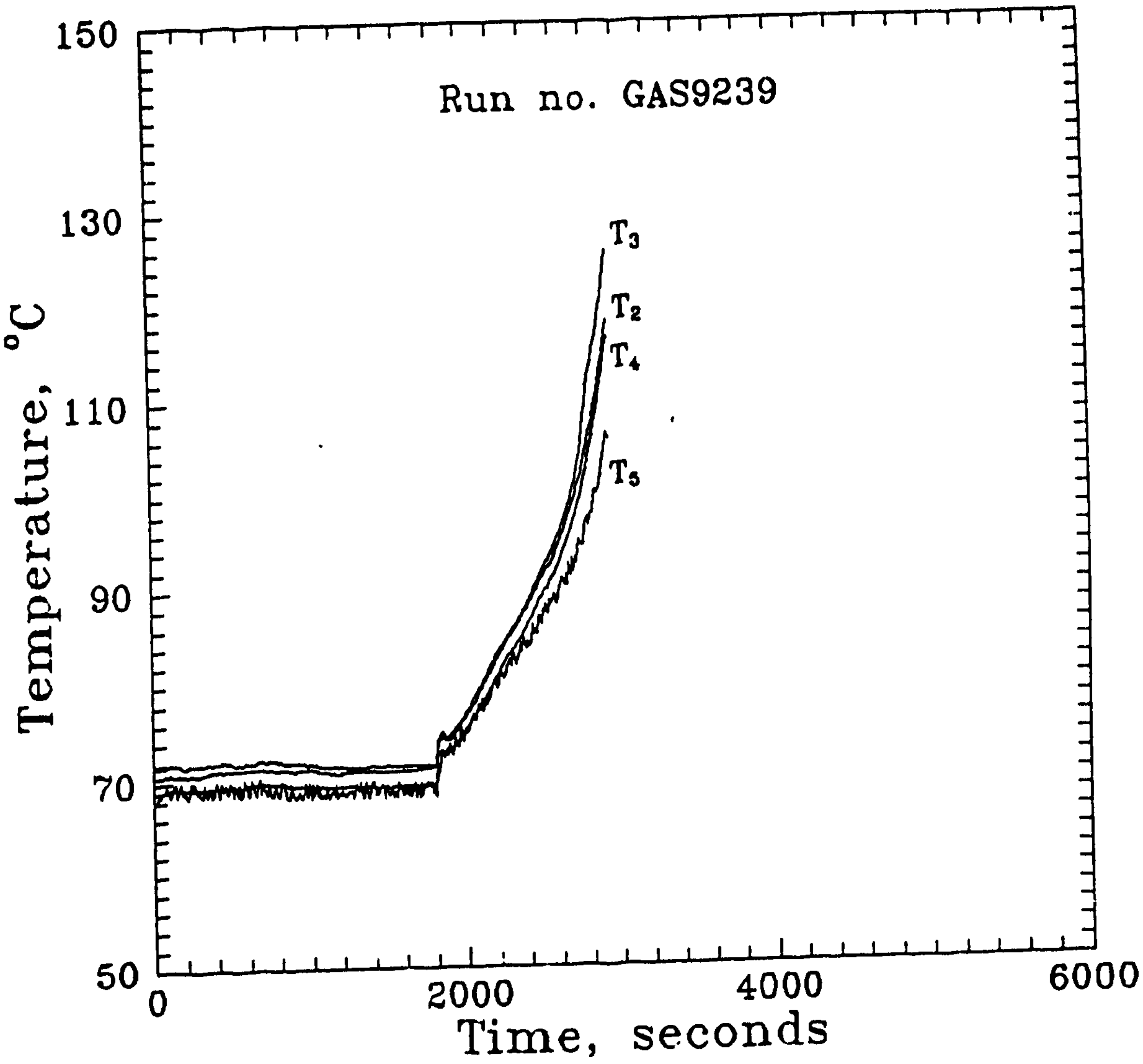


Figure B.34

Temperature profiles of locations 2 to 5

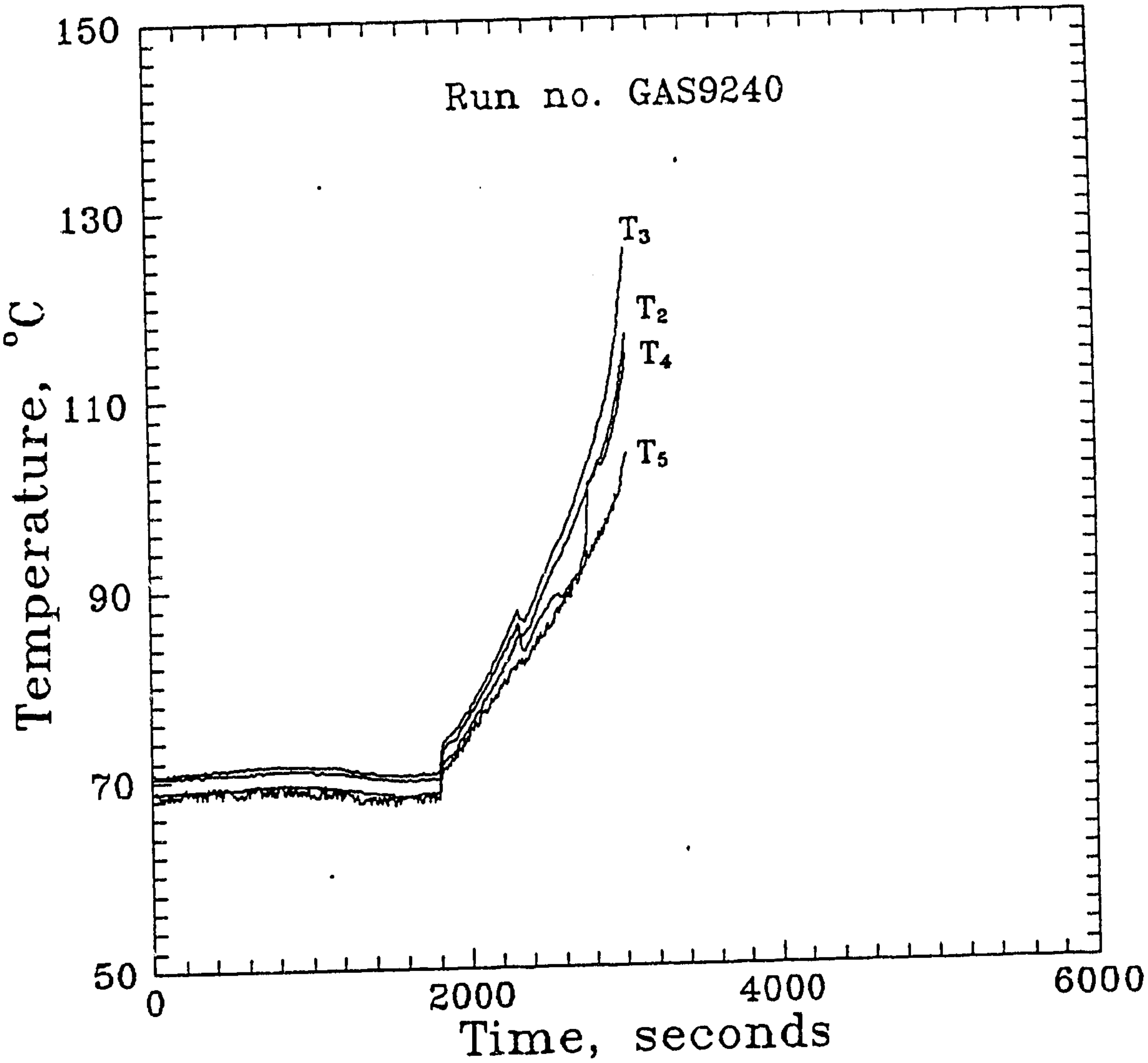


Figure B.35

Temperature profiles of locations 2 to 5

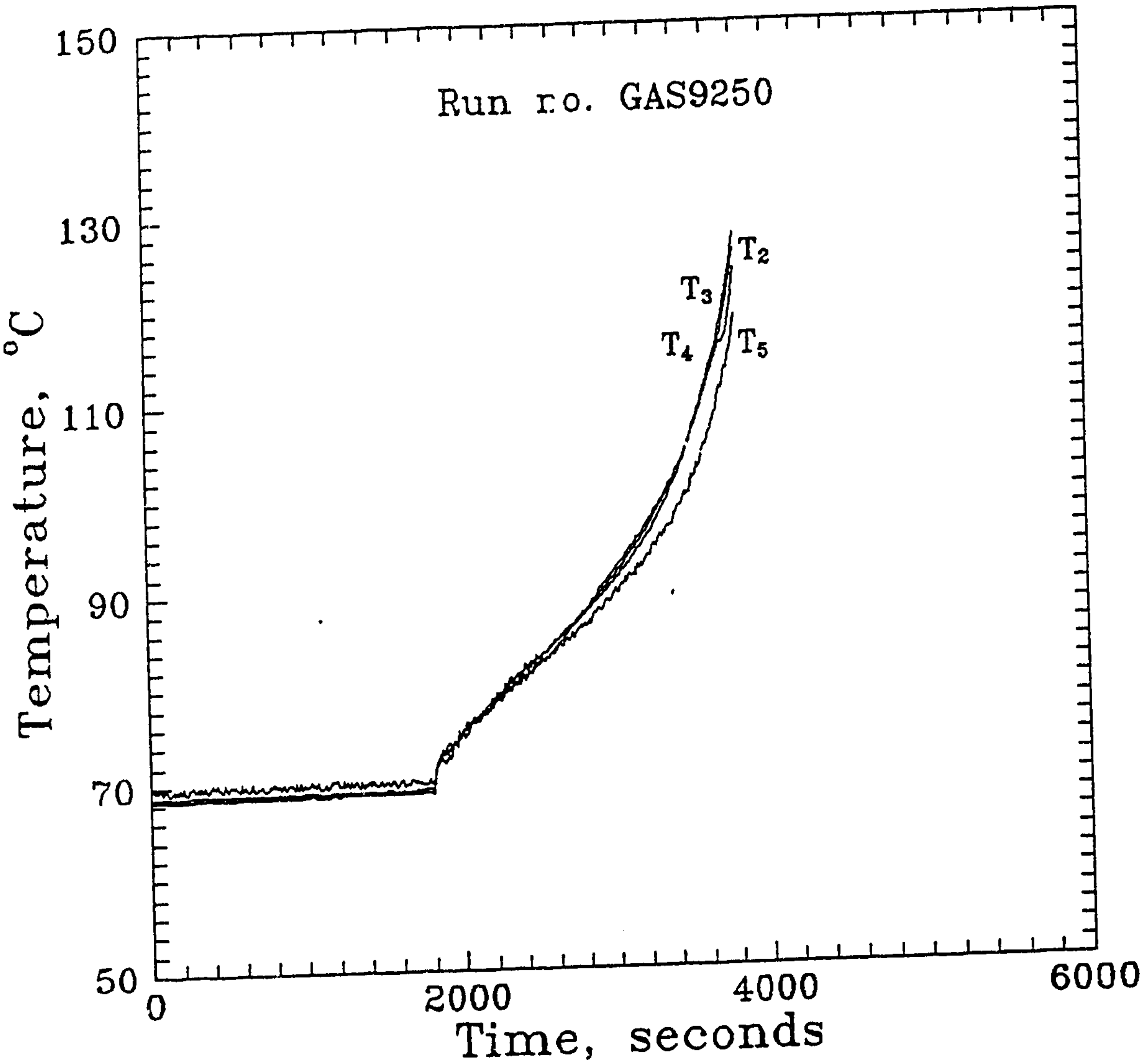


Figure B.36

Temperature profiles of locations 2 to 5

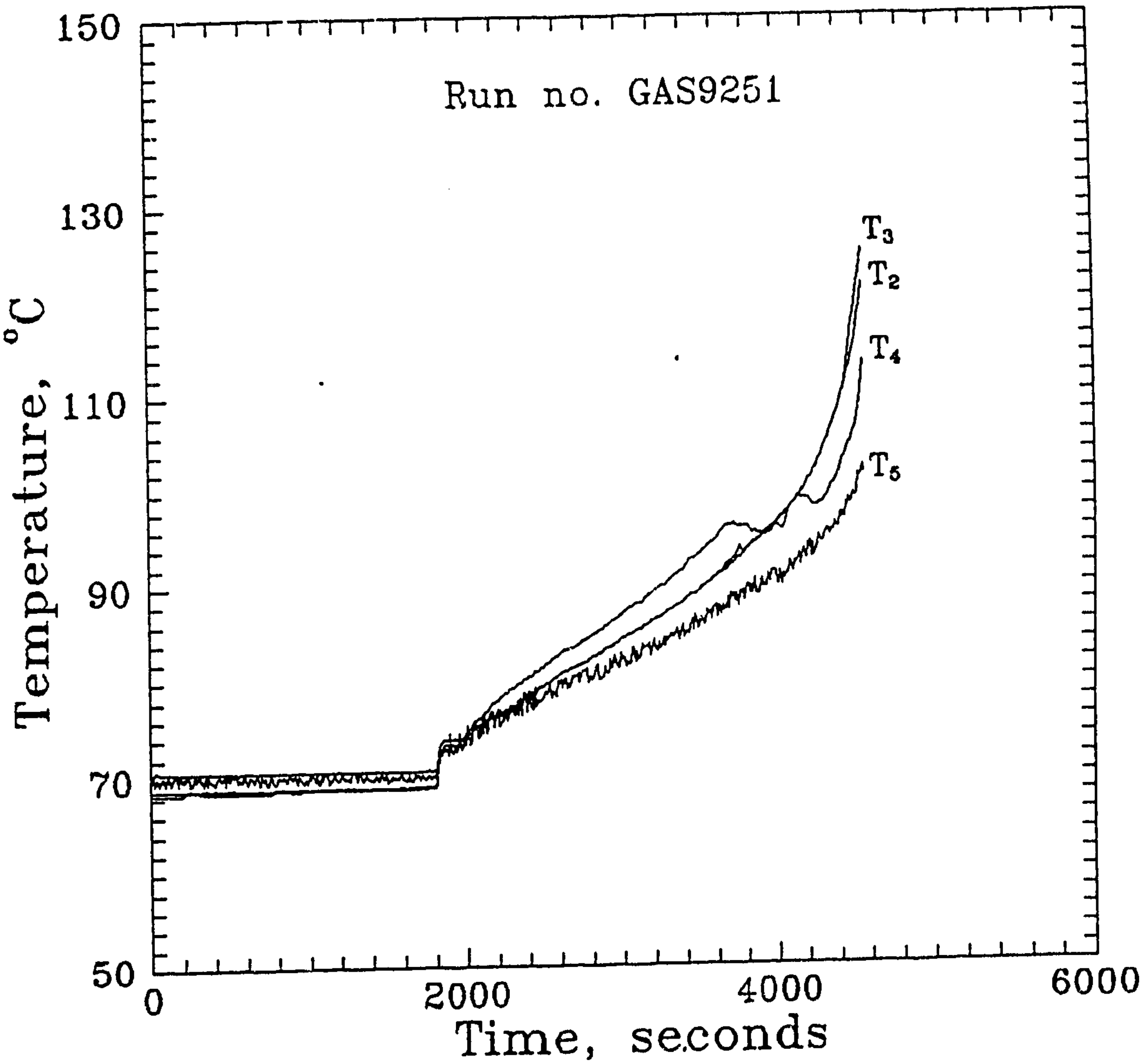


Figure B.37

Temperature profiles of locations 2 to 5

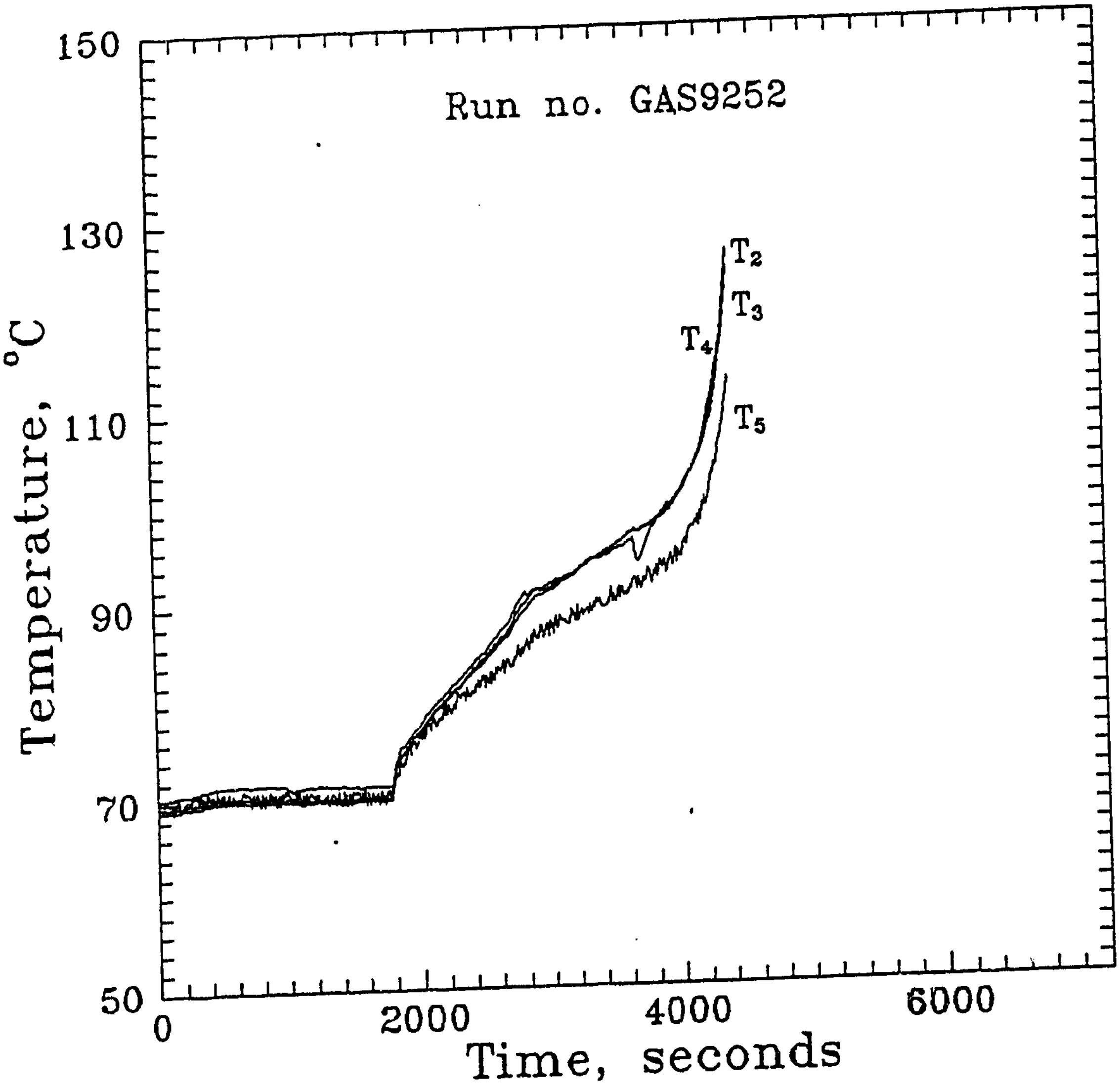


Figure B.38

Temperature profiles of locations 2 to 5

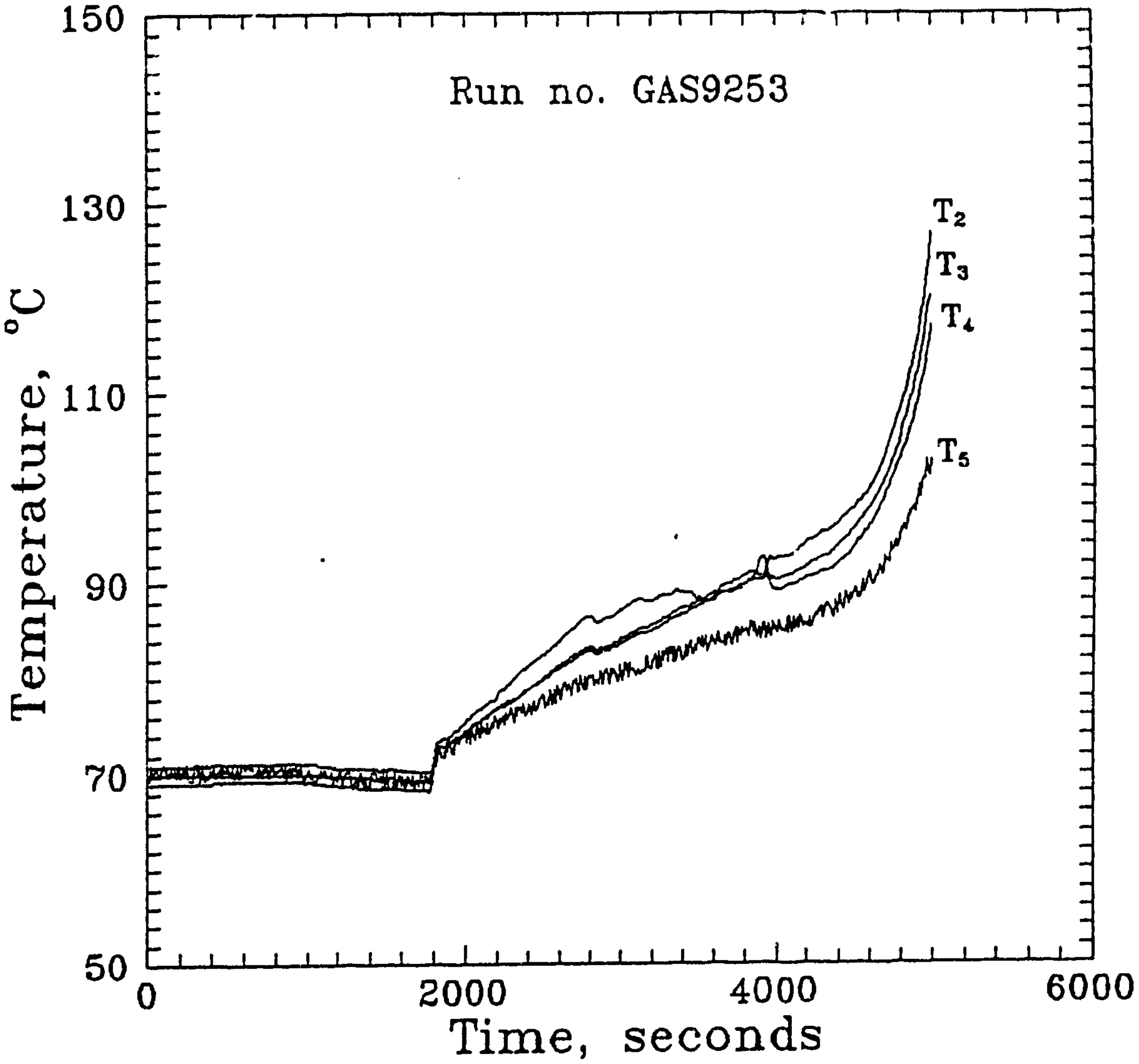


Figure B.39

Temperature profiles of locations 2 to 5

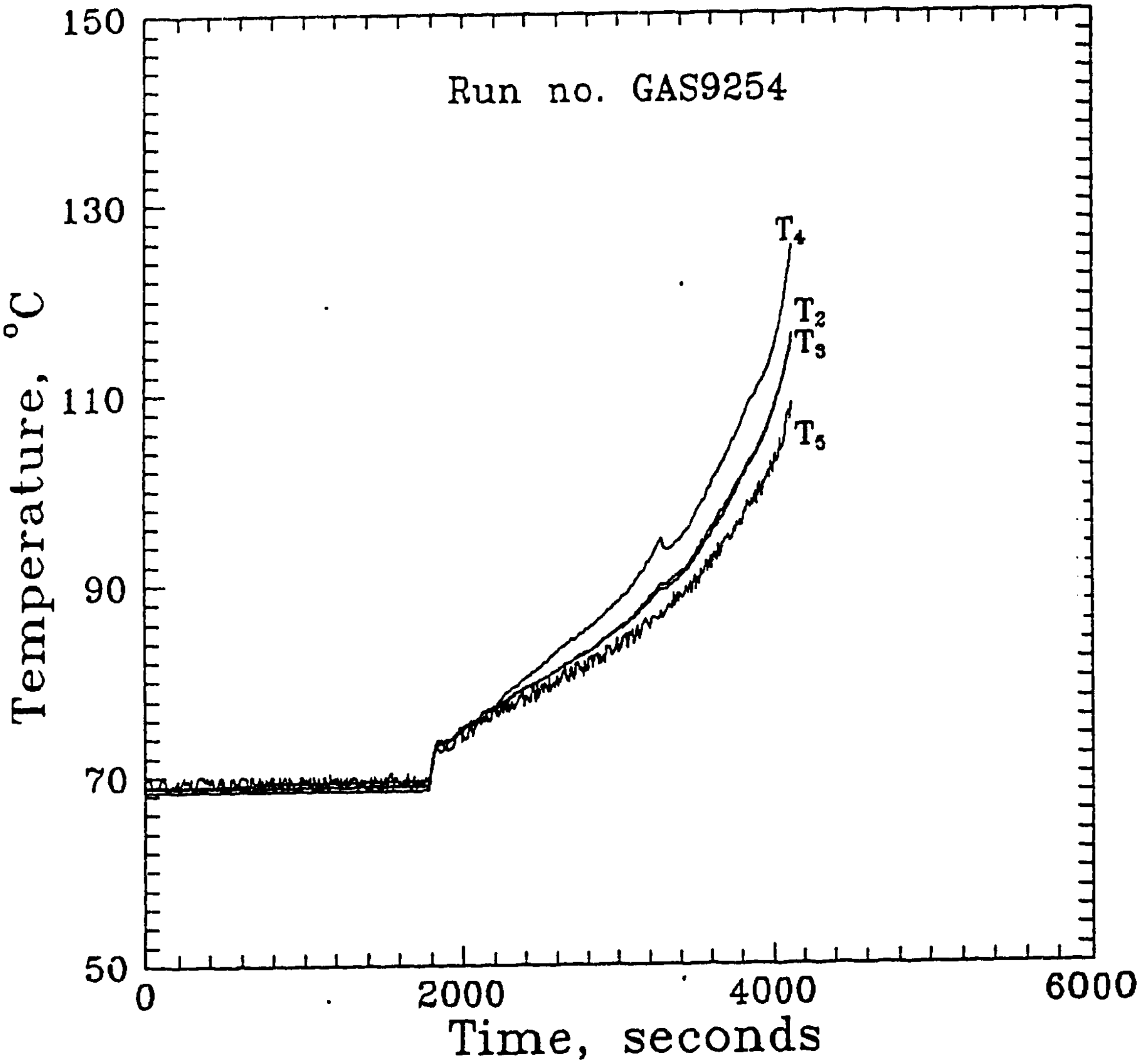


Figure B.40

Temperature profiles of locations 2 to 5

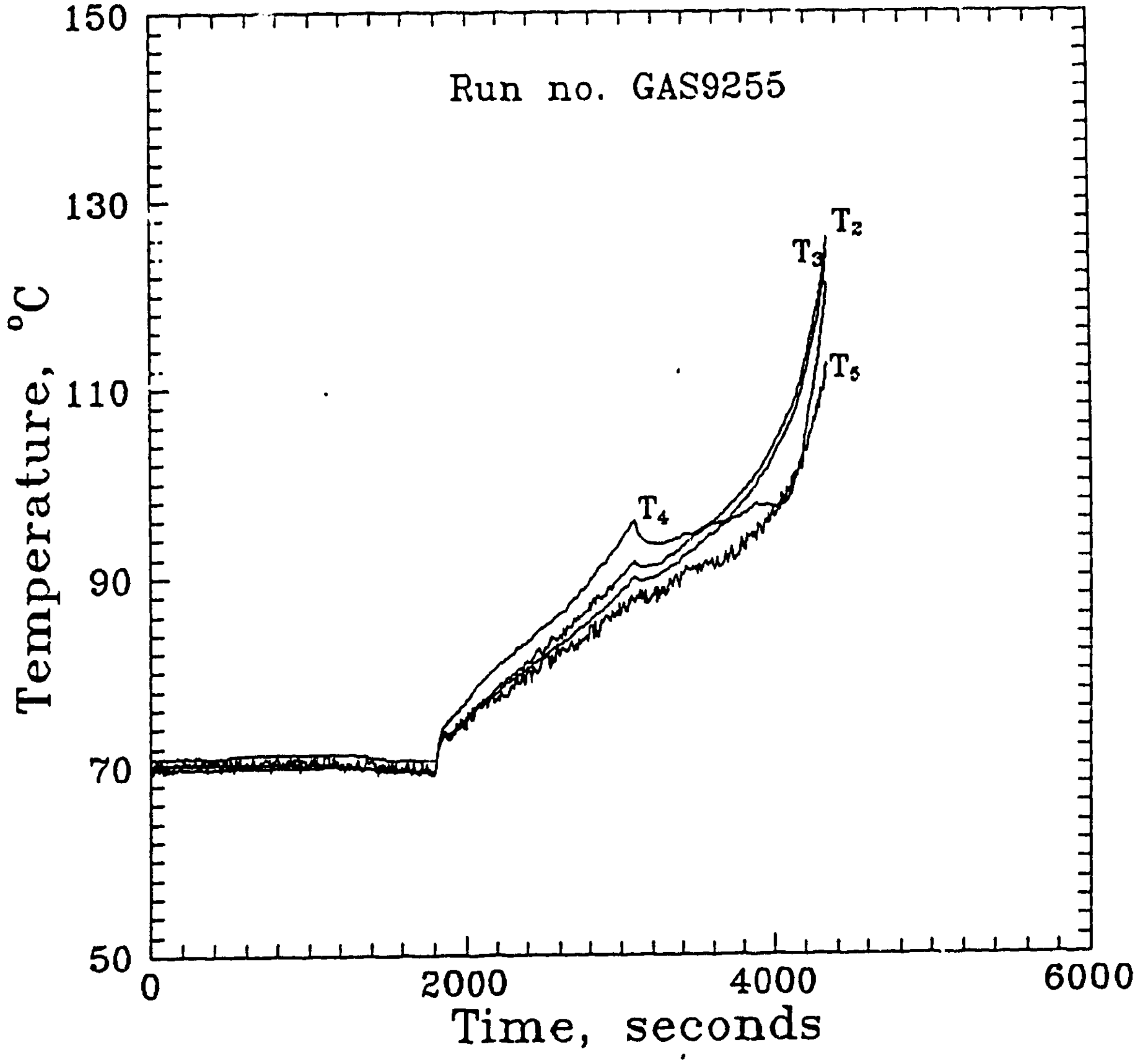


Figure B.41

Temperature profiles of locations 2 to 5

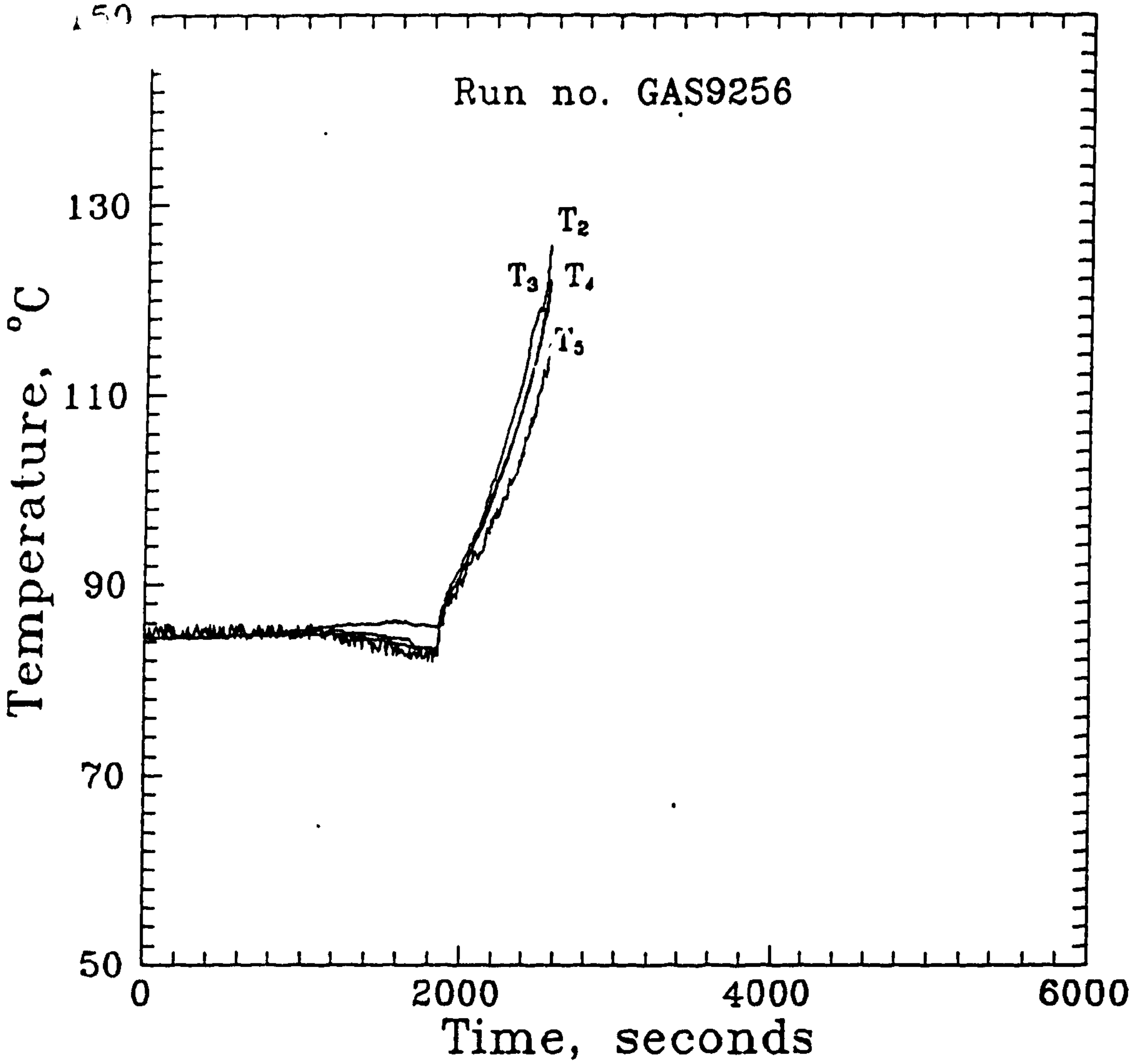


Figure B.42

Temperature profiles of locations 2 to 5

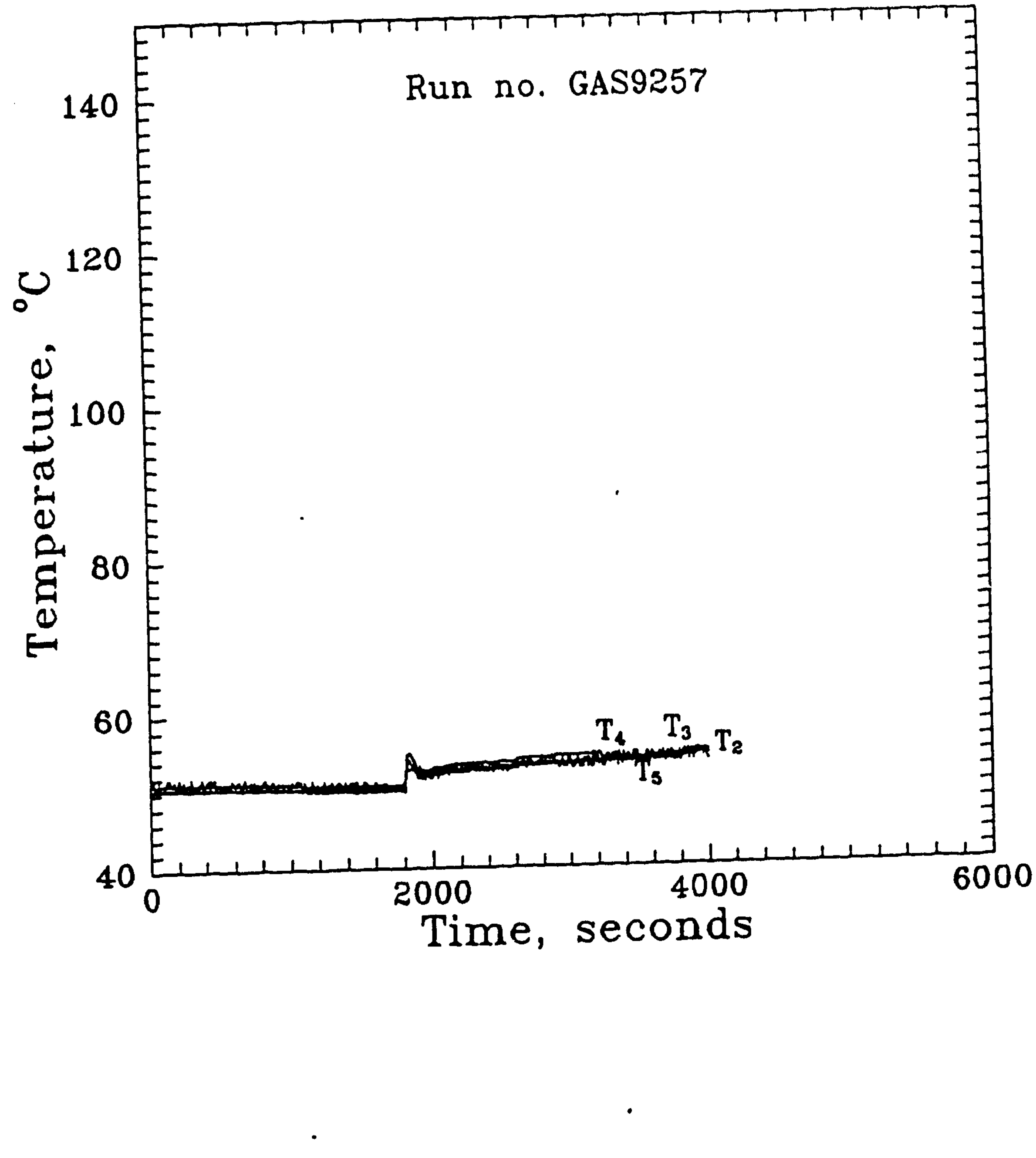


Figure B.43

Temperature profiles of locations 2 to 5

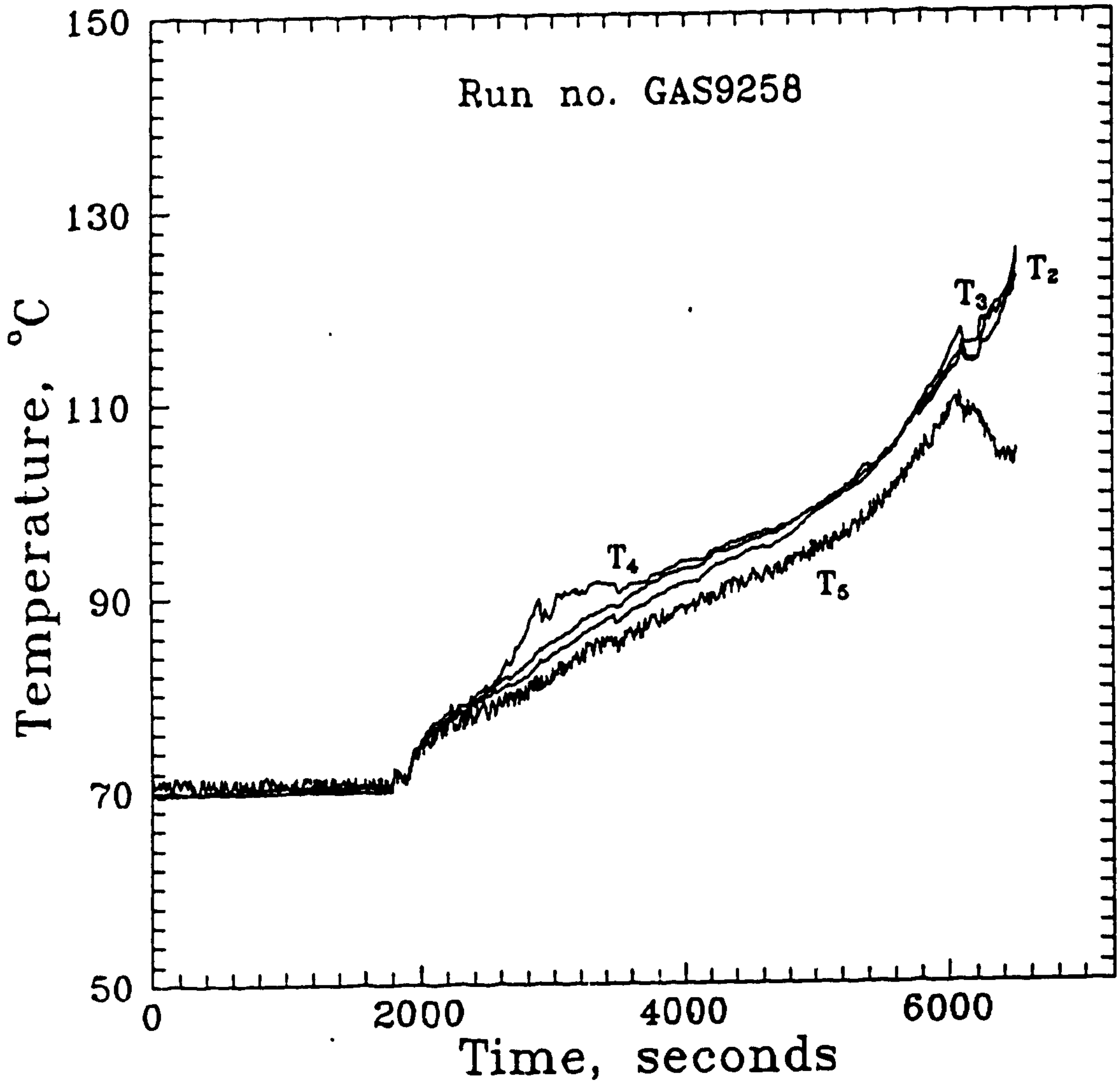


Figure B.44

Temperature profiles of locations 2 to 5

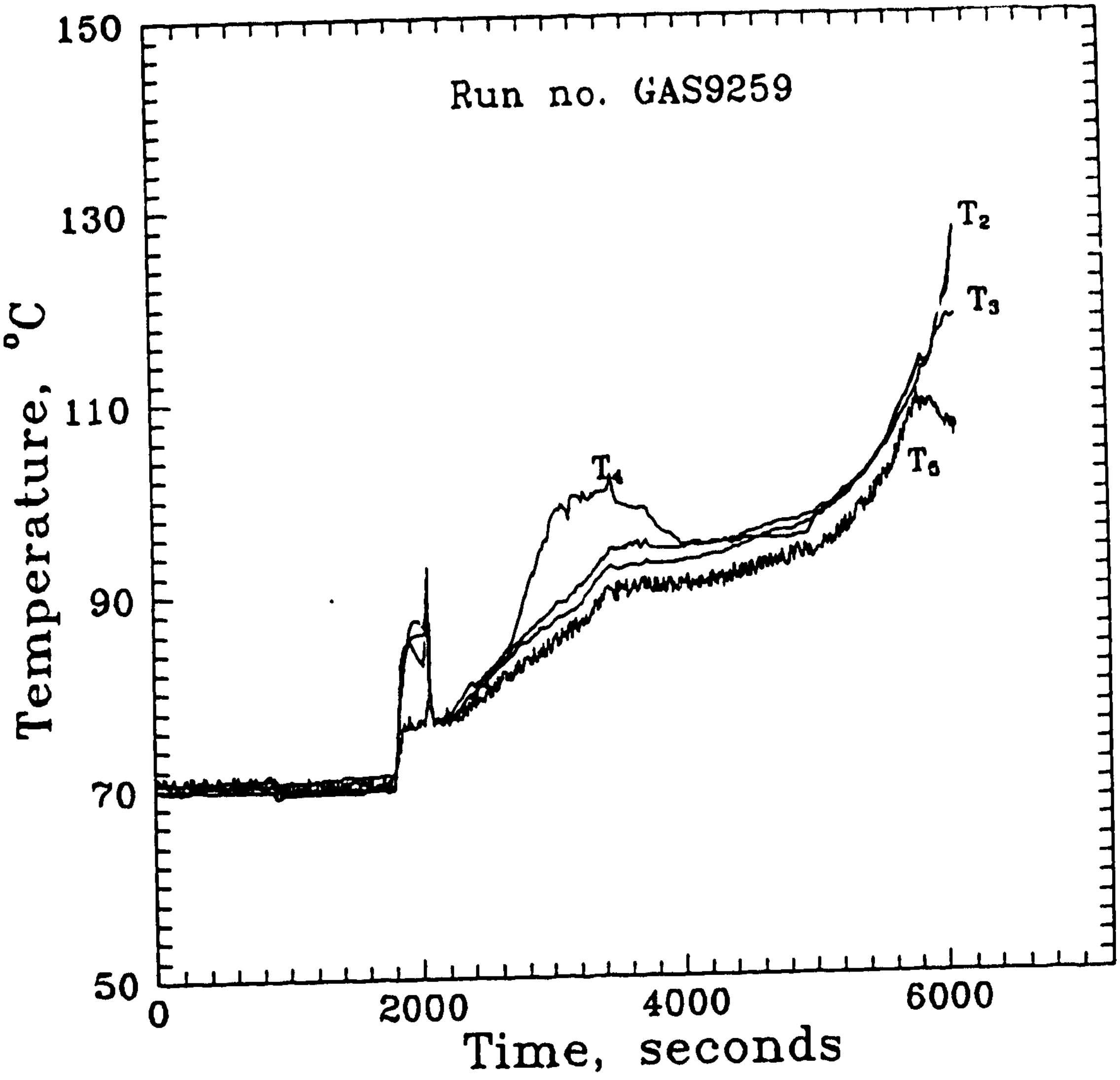


Figure B.45

Temperature profiles of locations 2 to 5

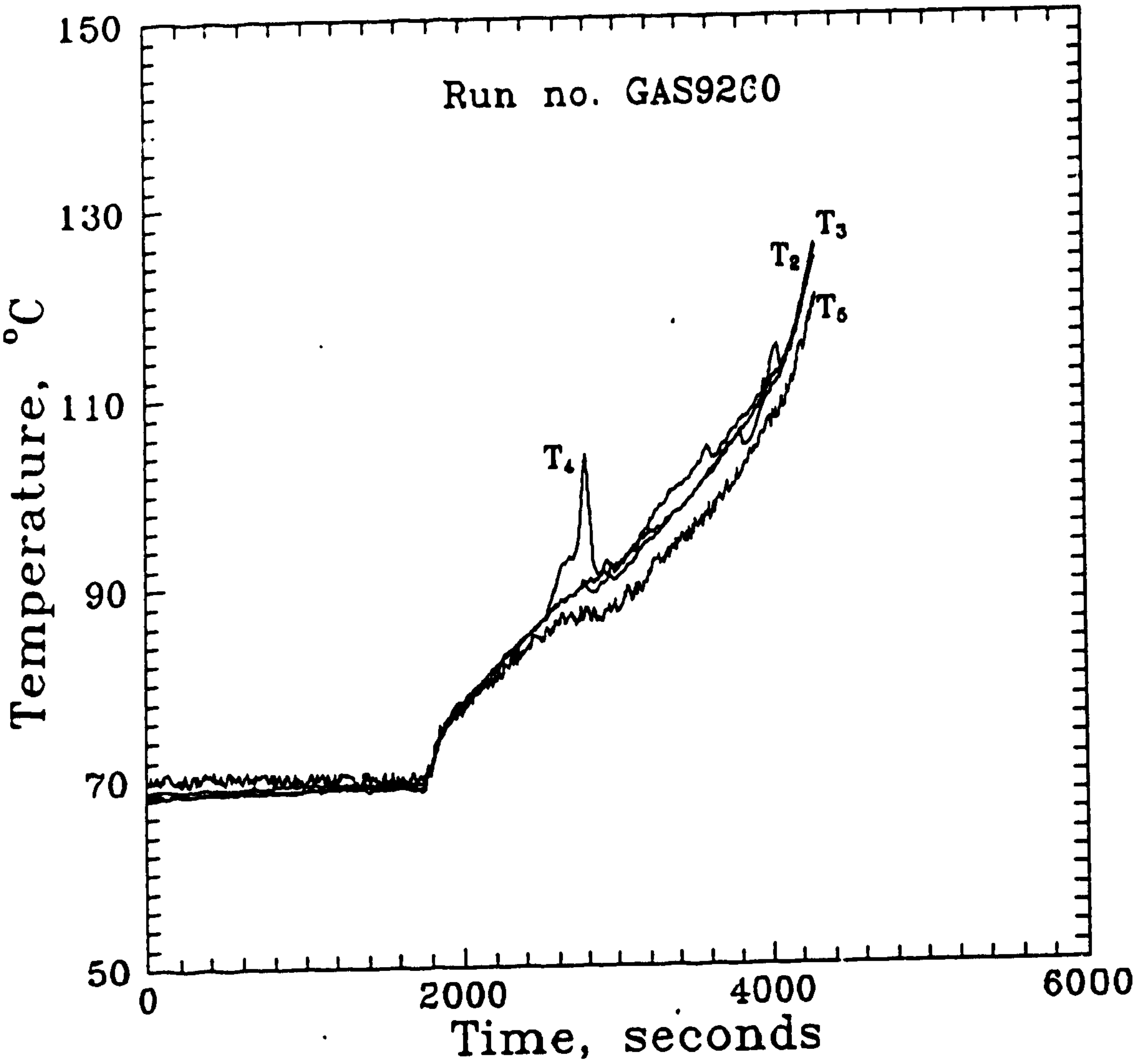


Figure B.46

Temperature profiles of locations 2 to 5

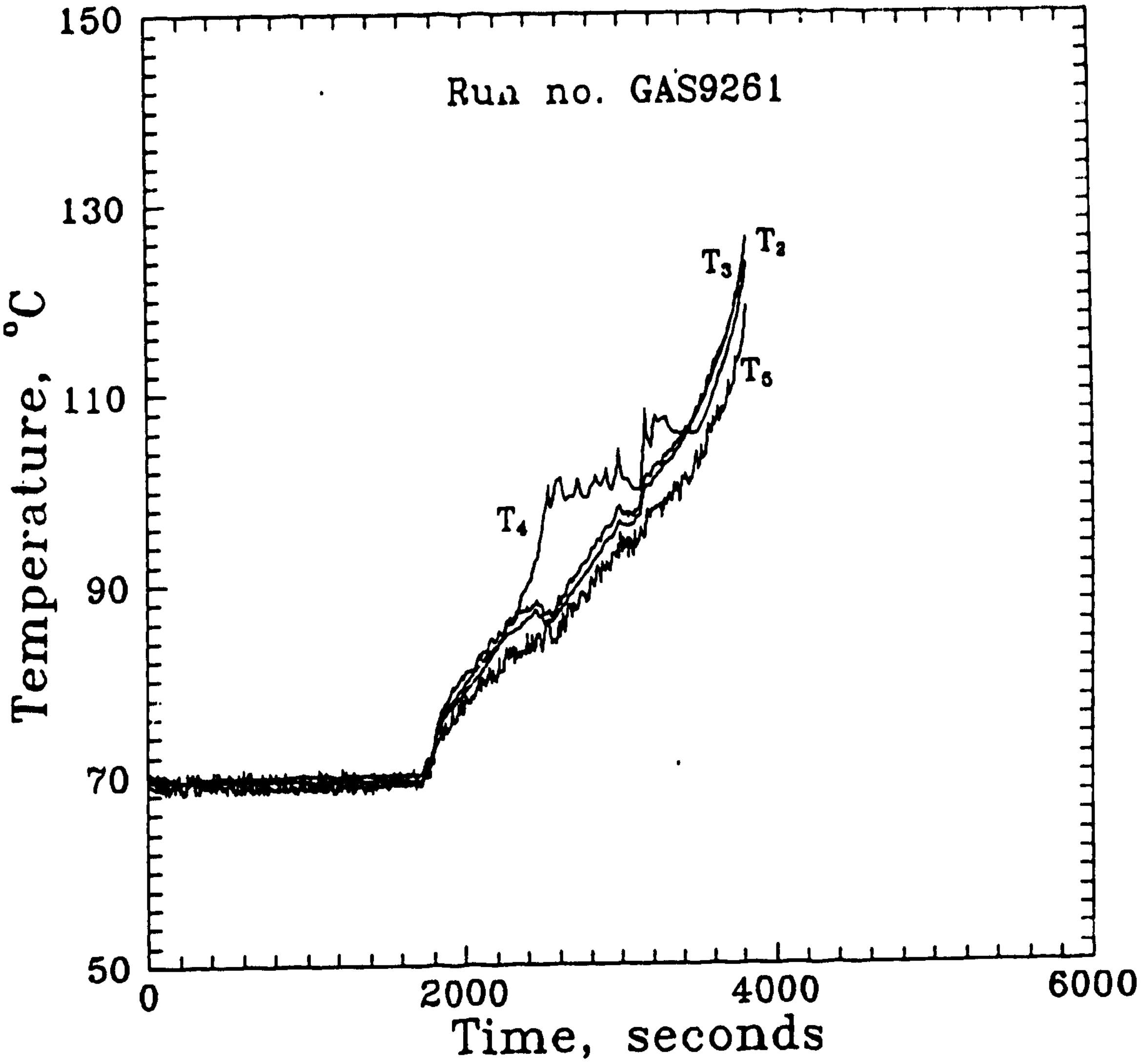


Figure B.47
Temperature profiles of locations 2 to 5

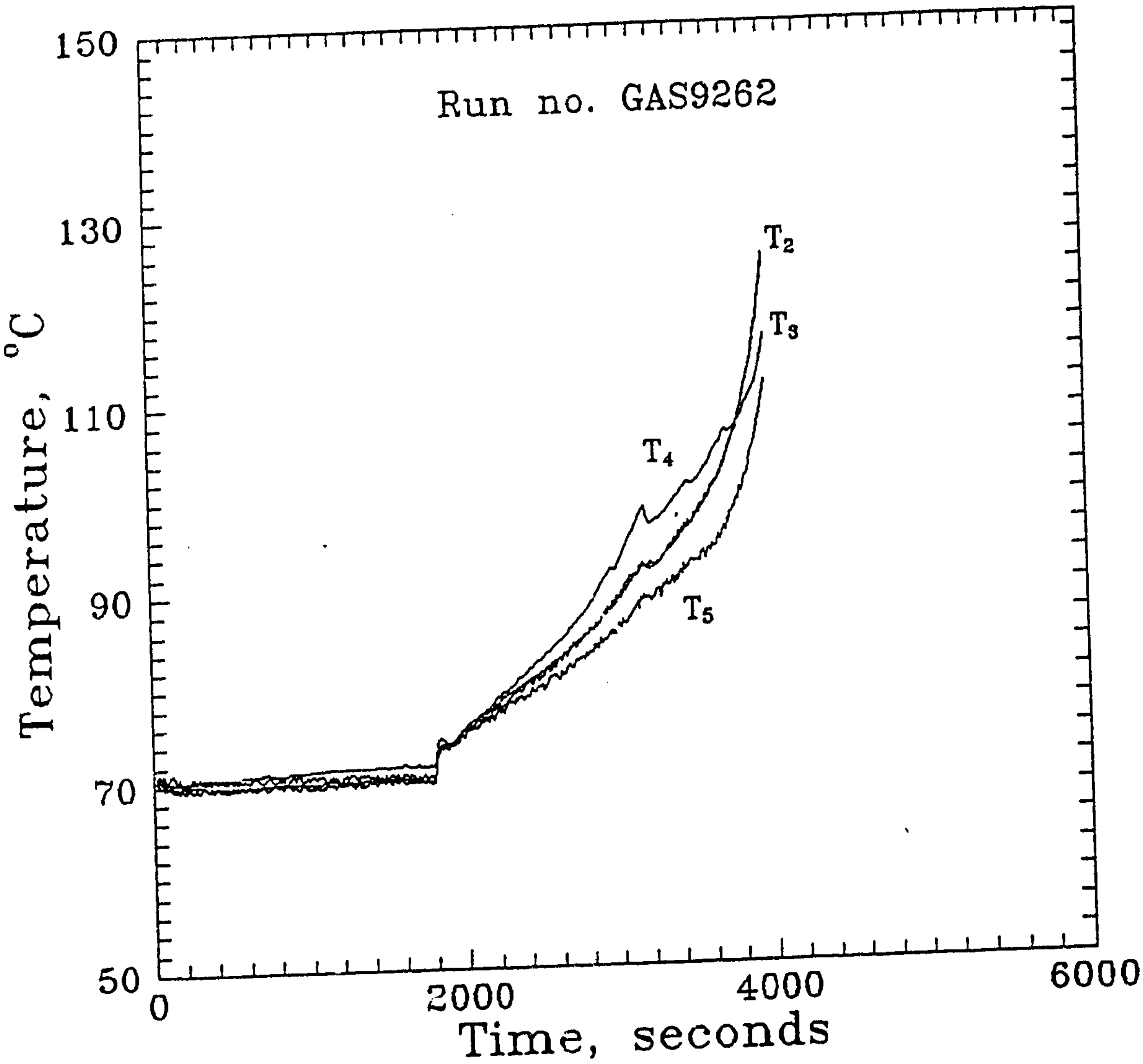


Figure B.48

Temperature profiles of locations 2 to 5

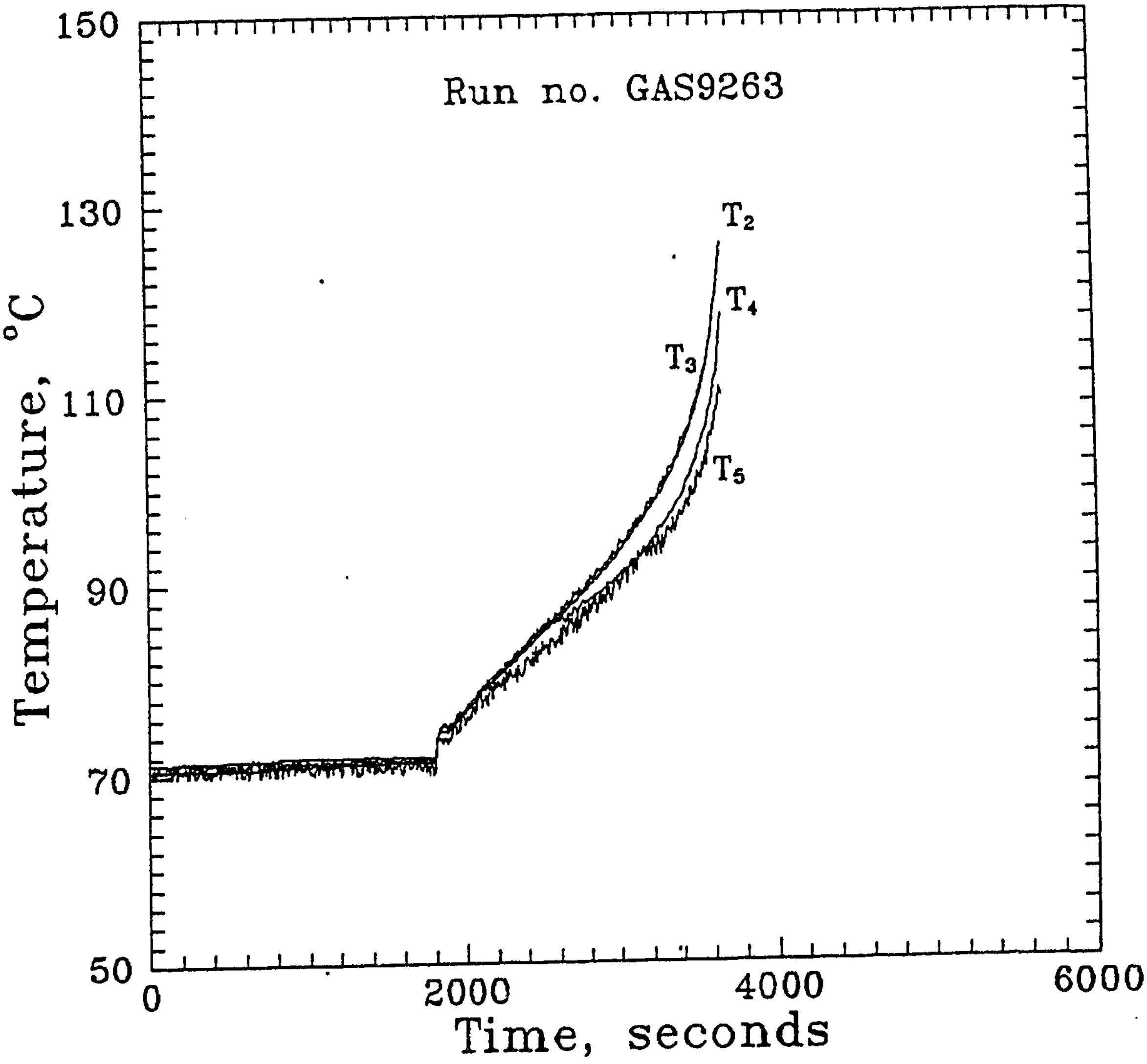


Figure B.49

Temperature profiles of locations 2 to 5

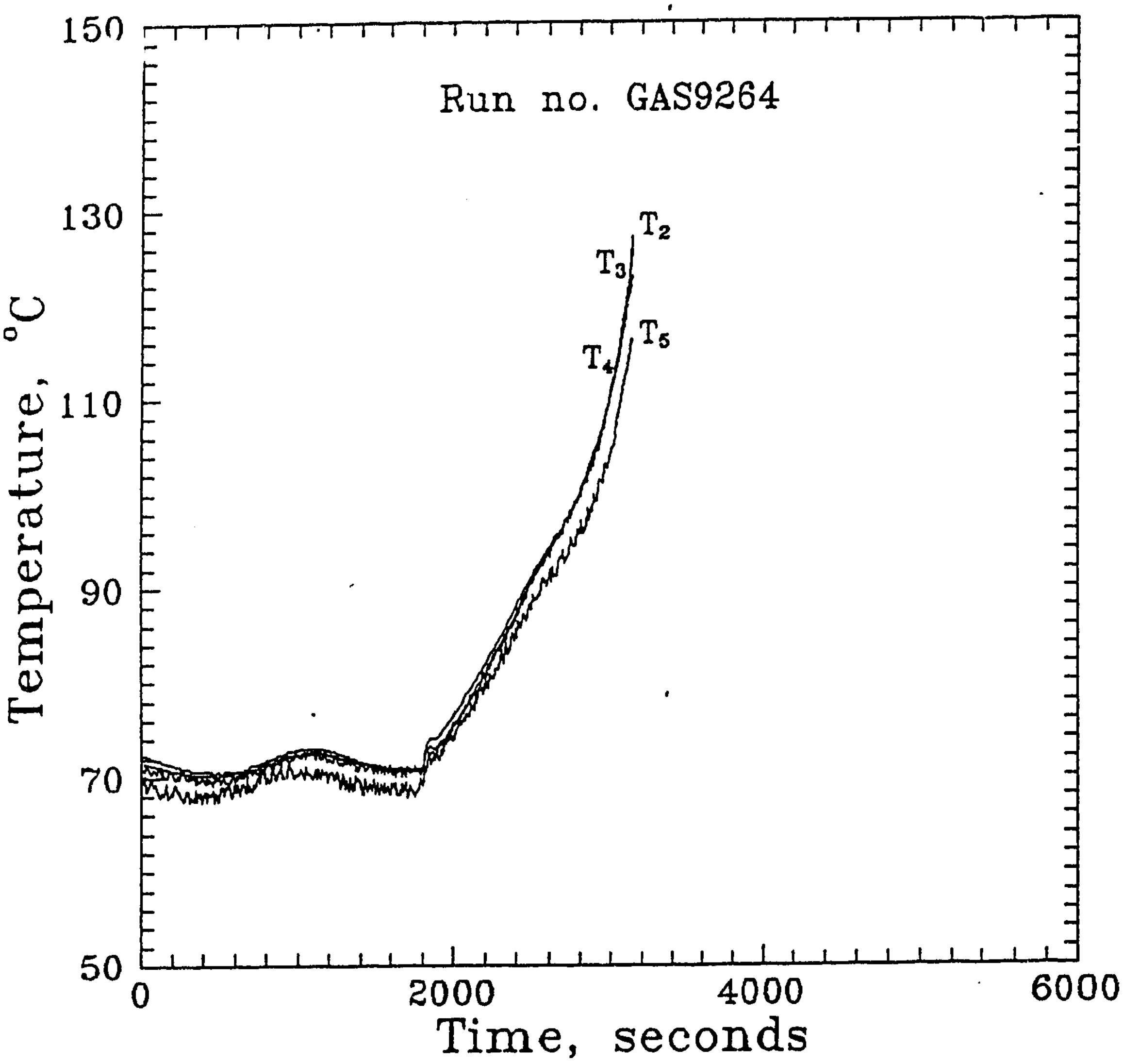


Figure B.50

Temperature profiles of locations 2 to 5

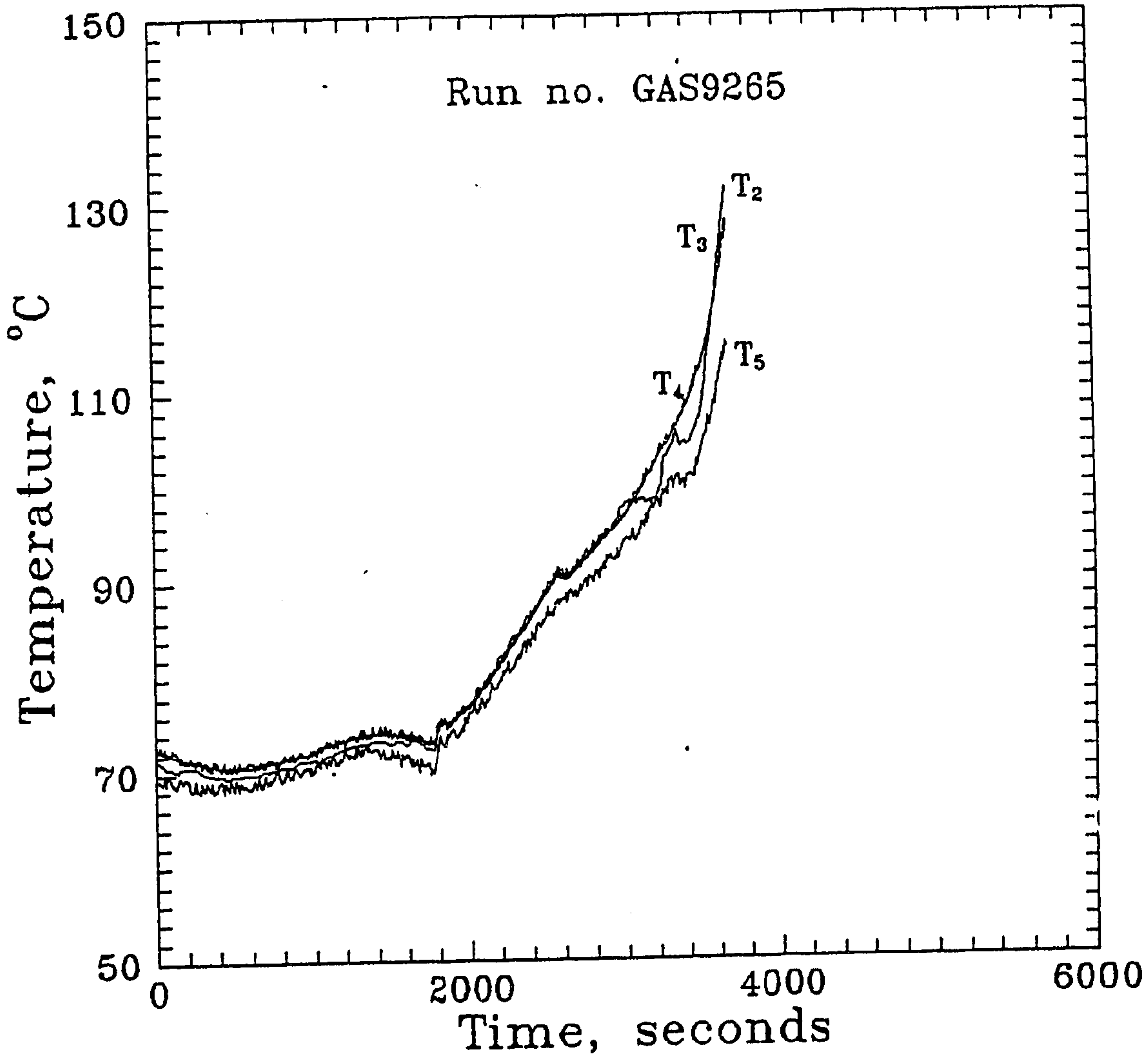


Figure B.51

Temperature profiles of locations 2 to 5

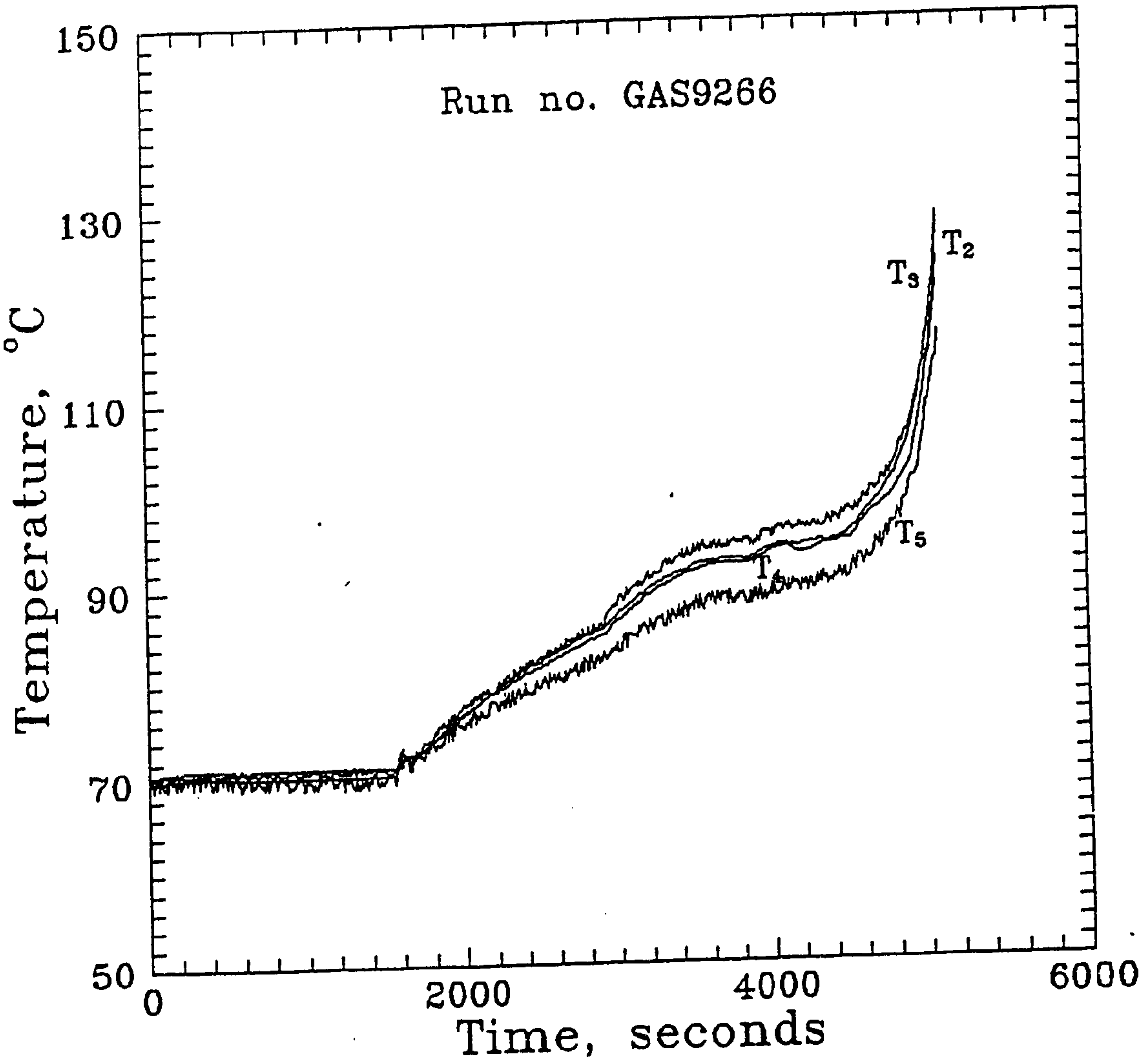


Figure B.52

Temperature profiles of locations 2 to 5

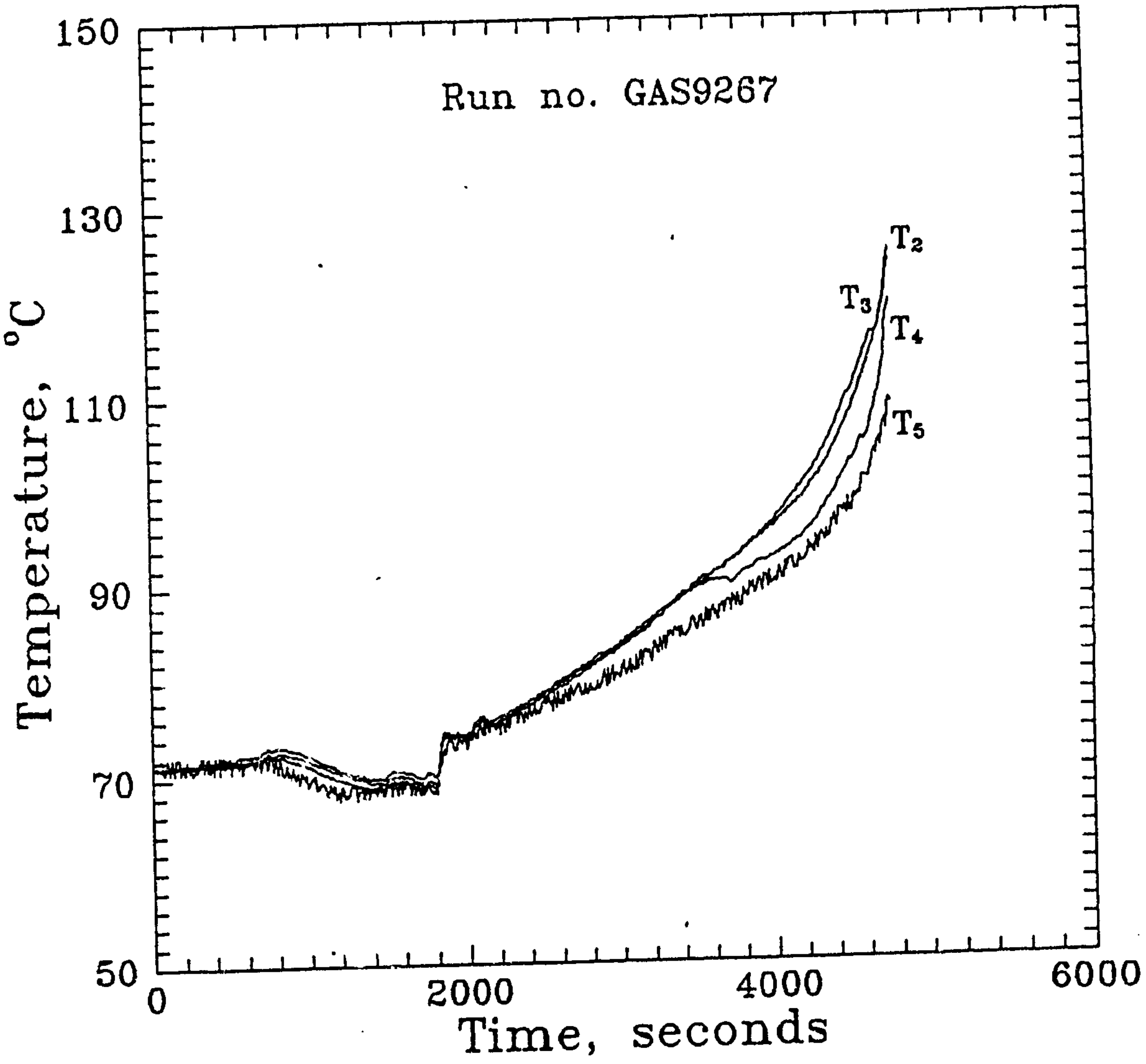


Figure B.53

Temperature profiles of locations 2 to 5

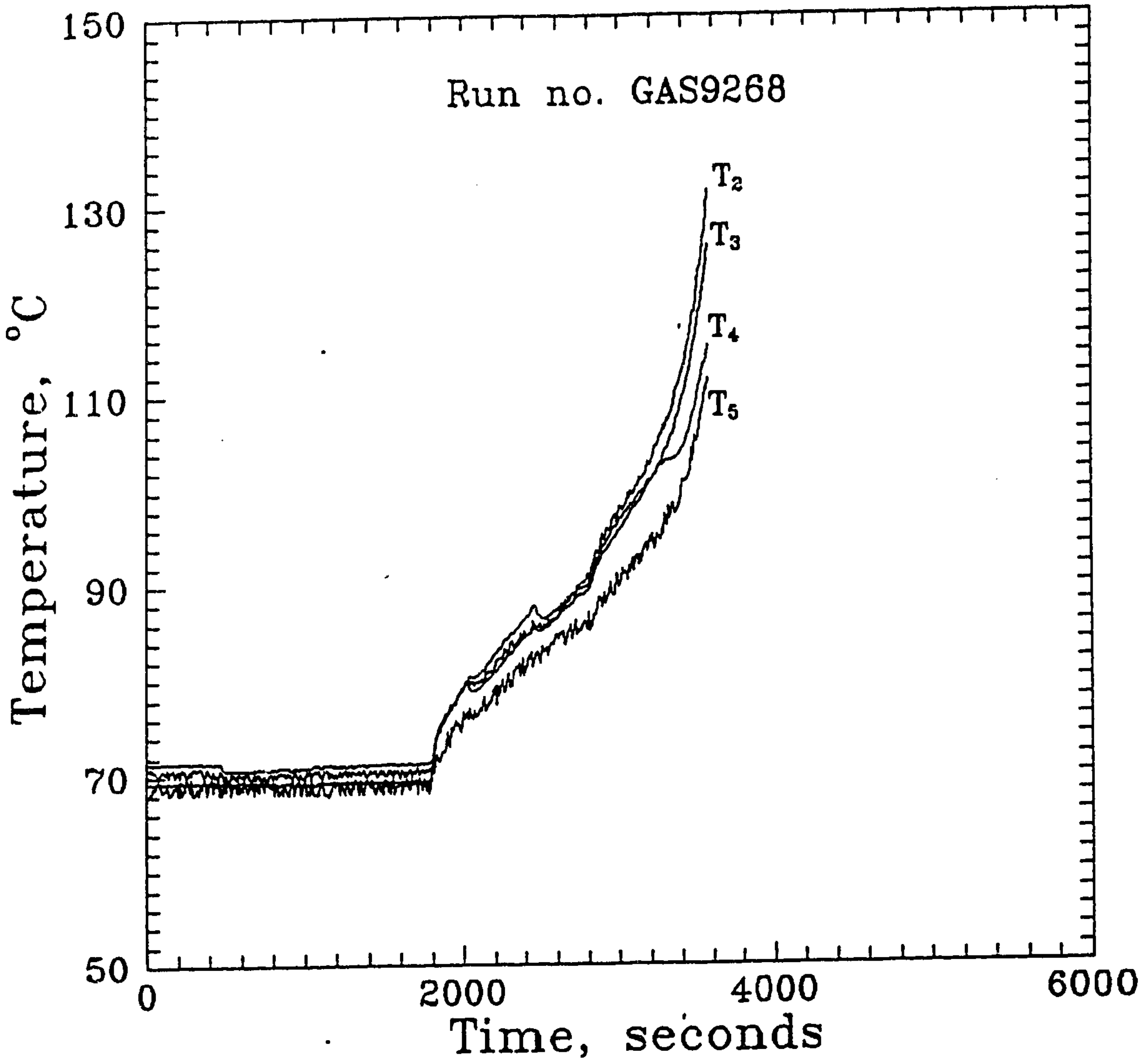


Figure B.54

Temperature profiles of locations 2 to 5

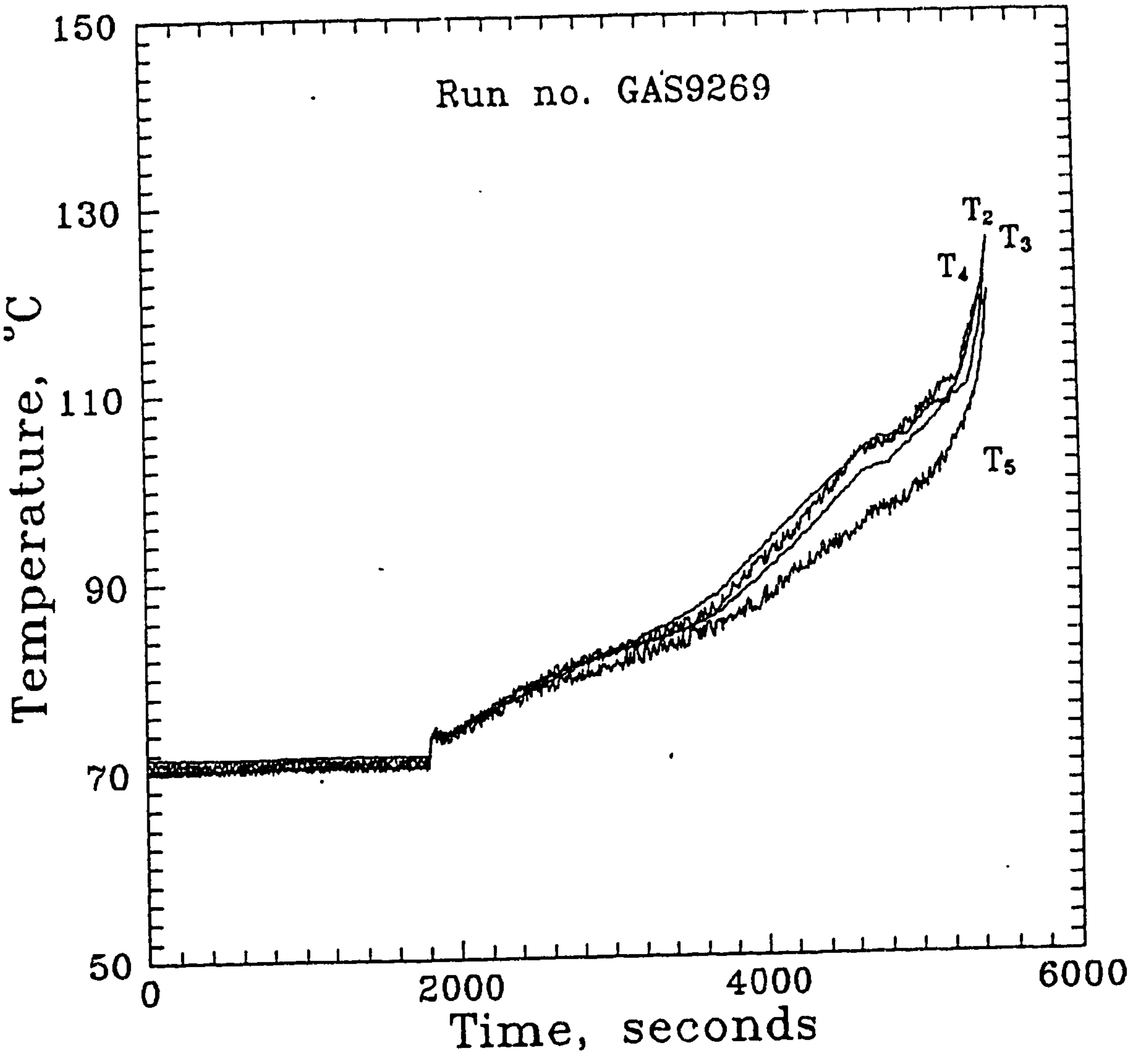


Figure B.55

Temperature profiles of locations 2 to 5

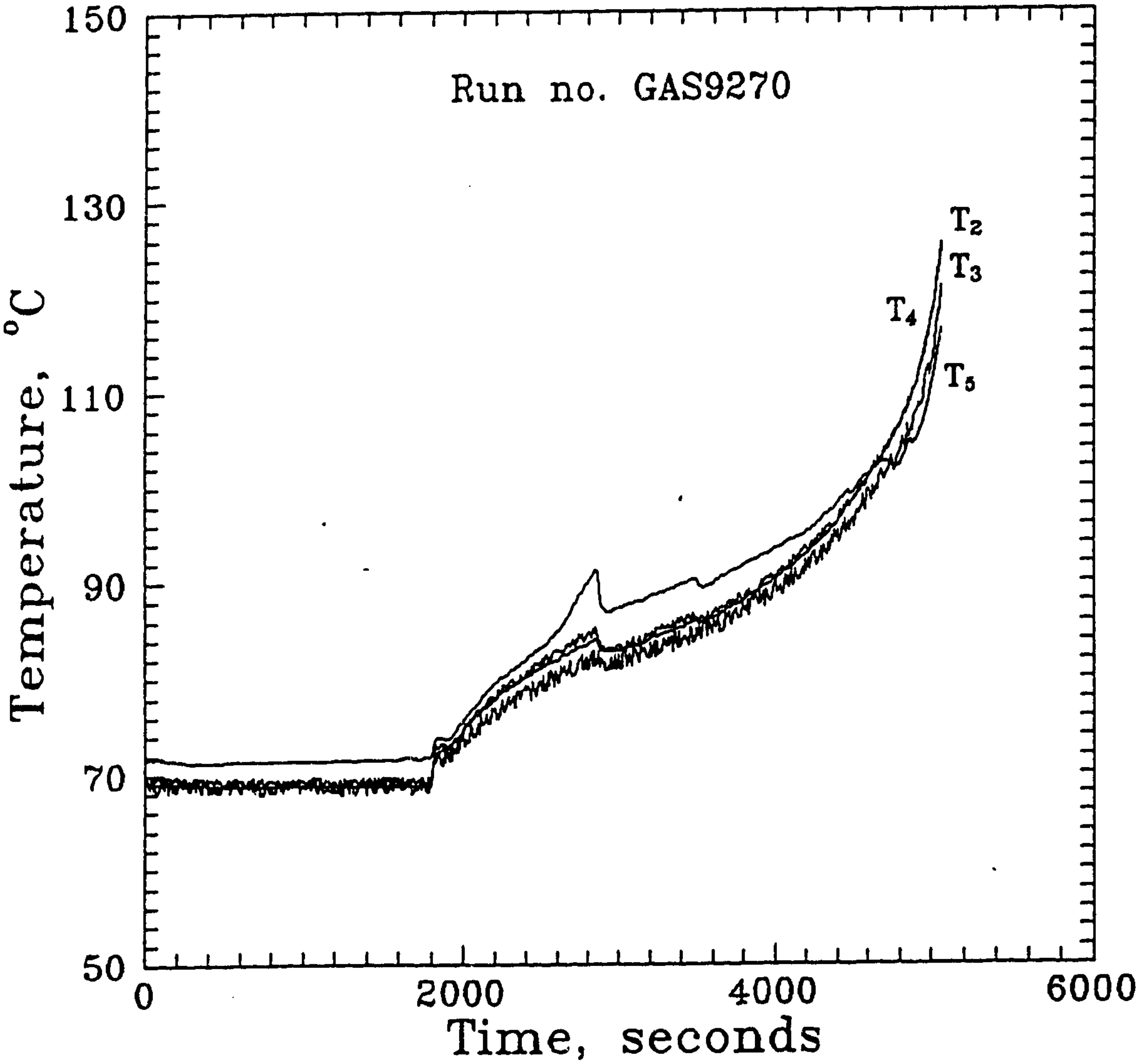


Figure B.56

Temperature profiles of locations 2 to 5

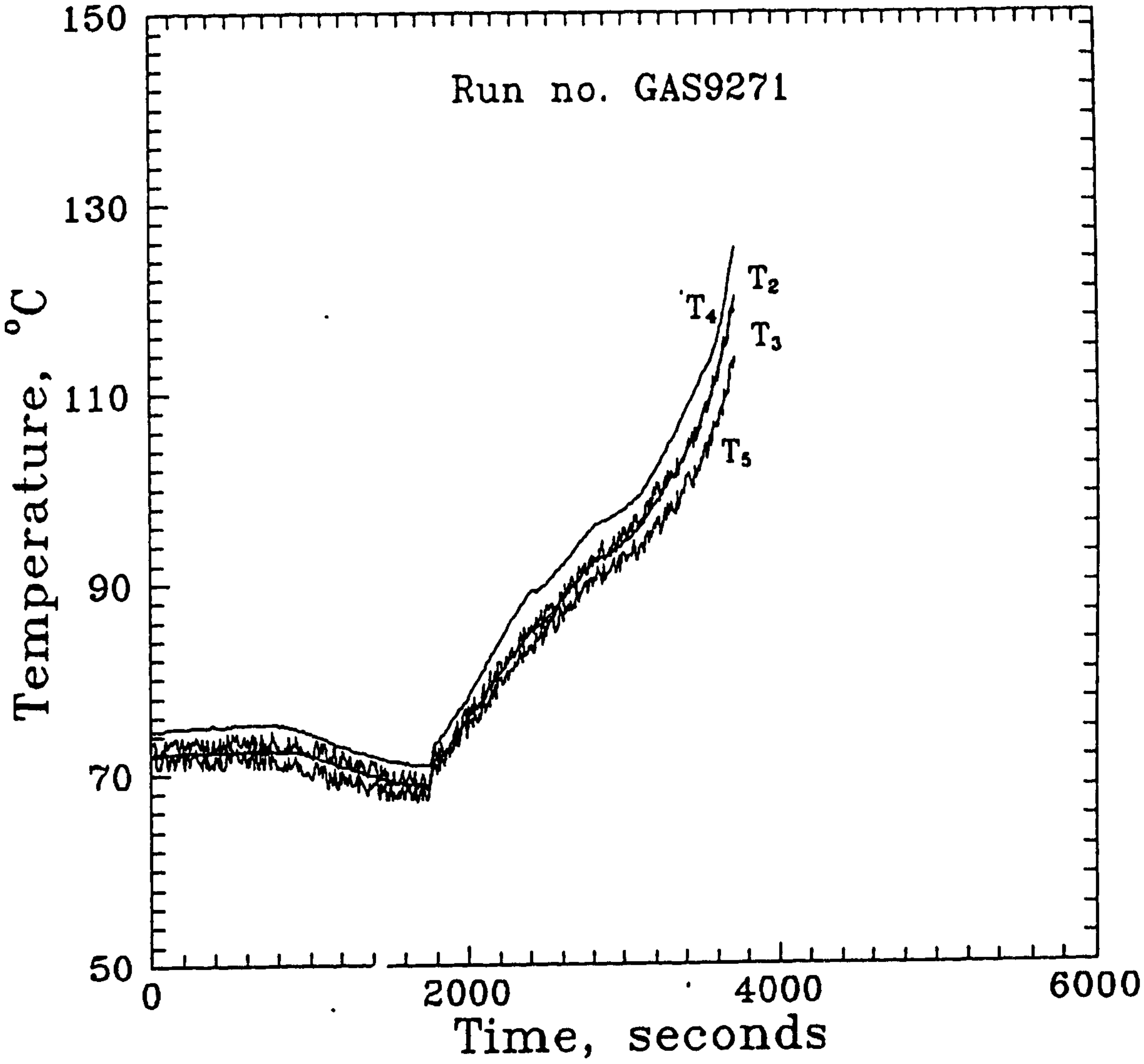


Figure B.57

Temperature profiles of locations 2 to 5

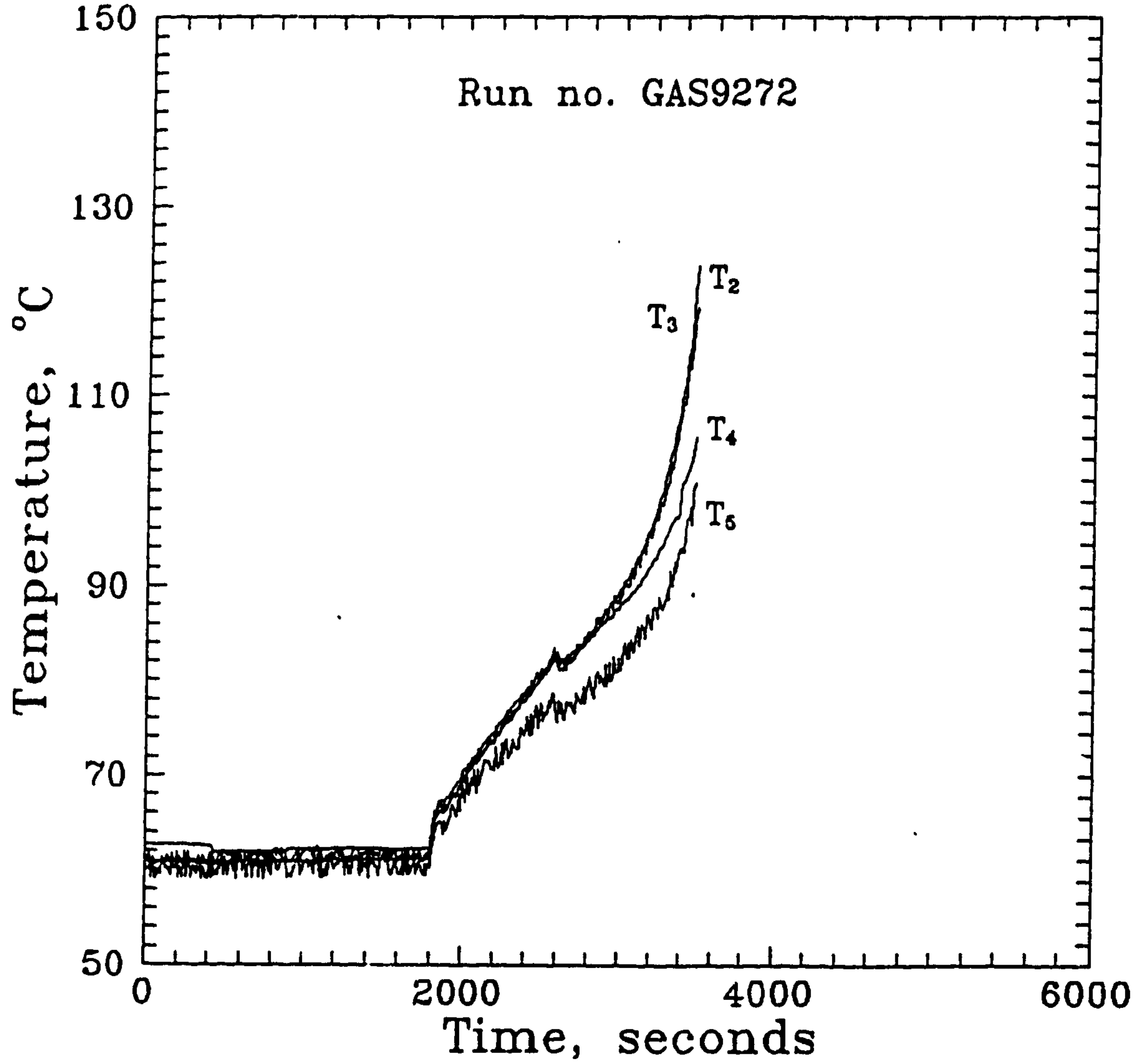
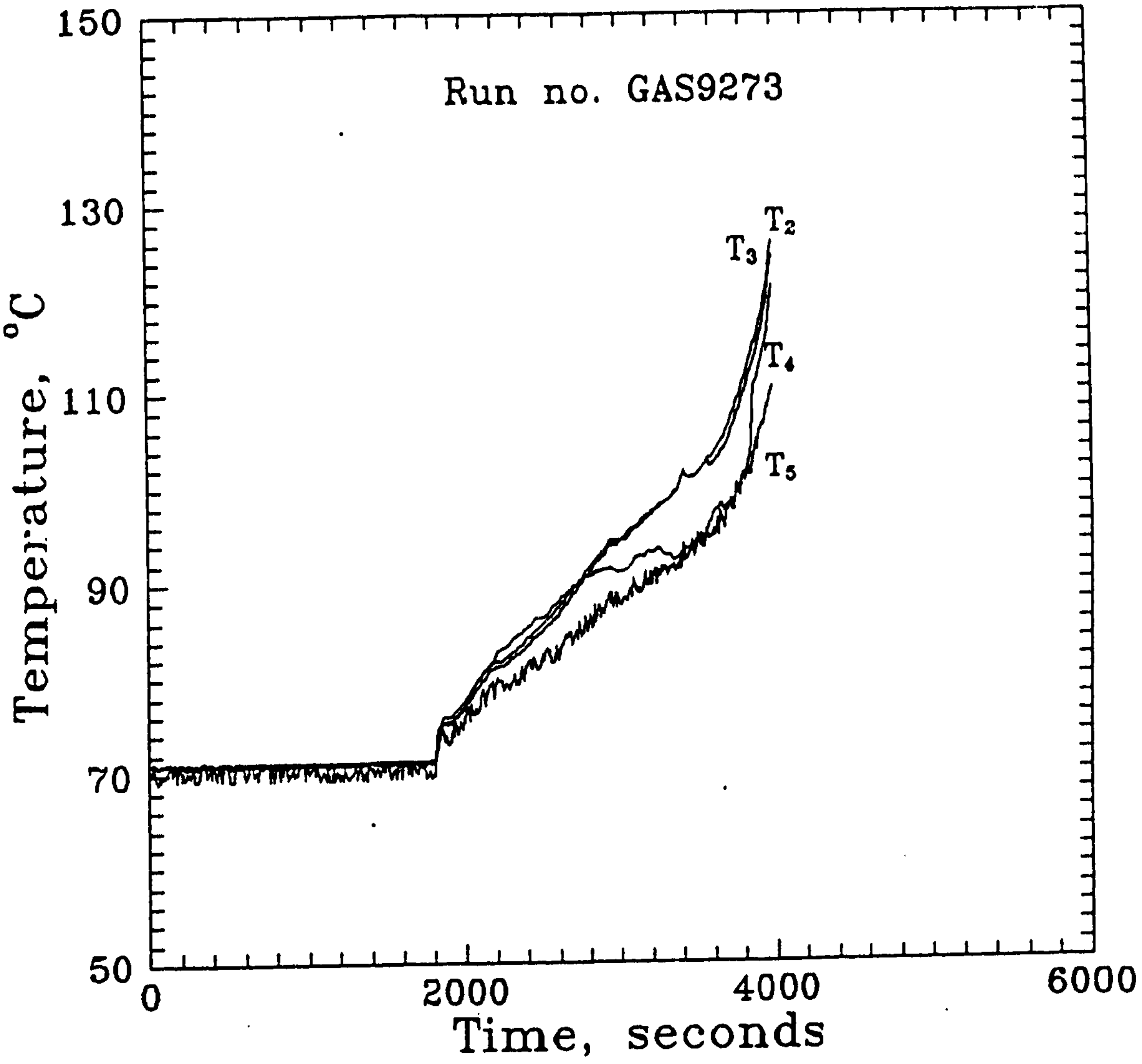


Figure B.58

Temperature profiles of locations 2 to 5



APPENDIX C

Effect of Background Gas on Thermal Runaway

In chapter 4, the effect of replacing nitrogen with helium as the background gas was described briefly. The effect of replacing nitrogen with helium as the background gas on the thermal runaway of the gas-phase reactor was observed for various seed and prepolymer amounts. Some of the results observed for different seed bed and prepolymerization amounts, using nitrogen and helium as background gas, are given in this appendix.

Figure C.1

VARIATION OF BACKGROUND GAS AT CONSTANT SEED AND PREPOLYMER AMOUNT

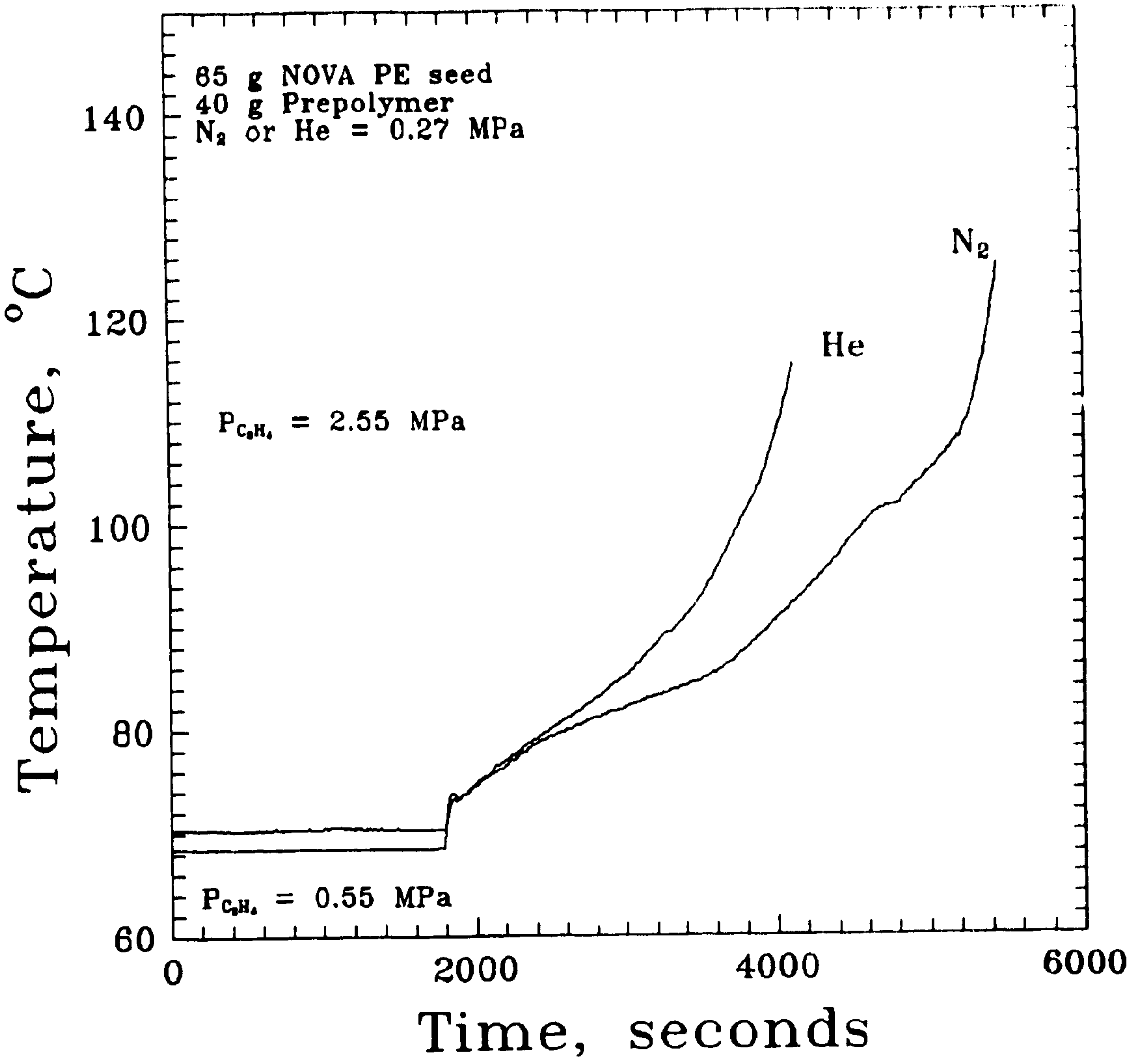


Figure C.2

VARIATION OF BACKGROUND GAS AT CONSTANT SEED AND PREPOLYMER AMOUNT

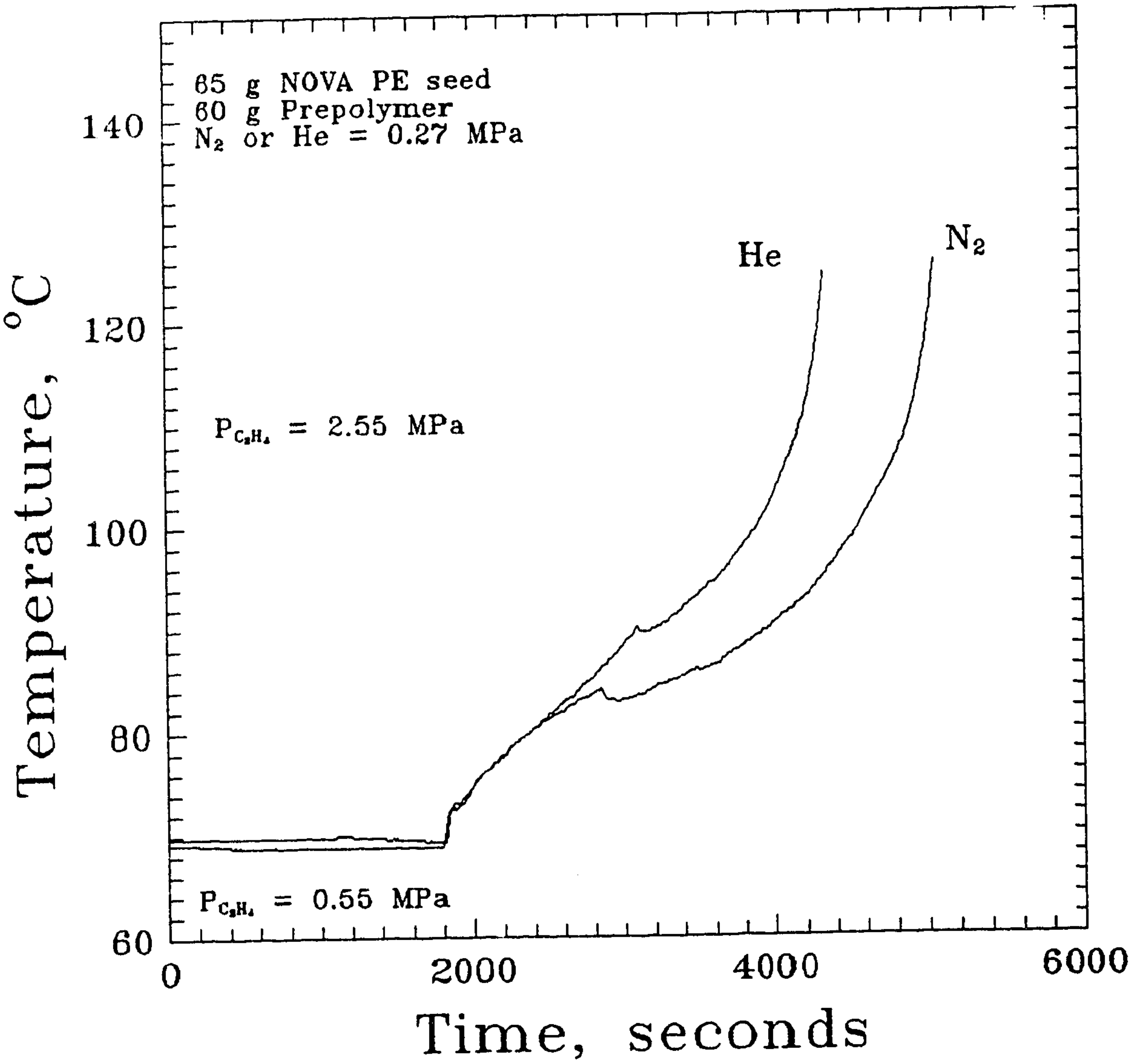


Figure C.3
VARIATION OF BACKGROUND GAS AT CONSTANT SEED AND PREPOLYMER AMOUNT

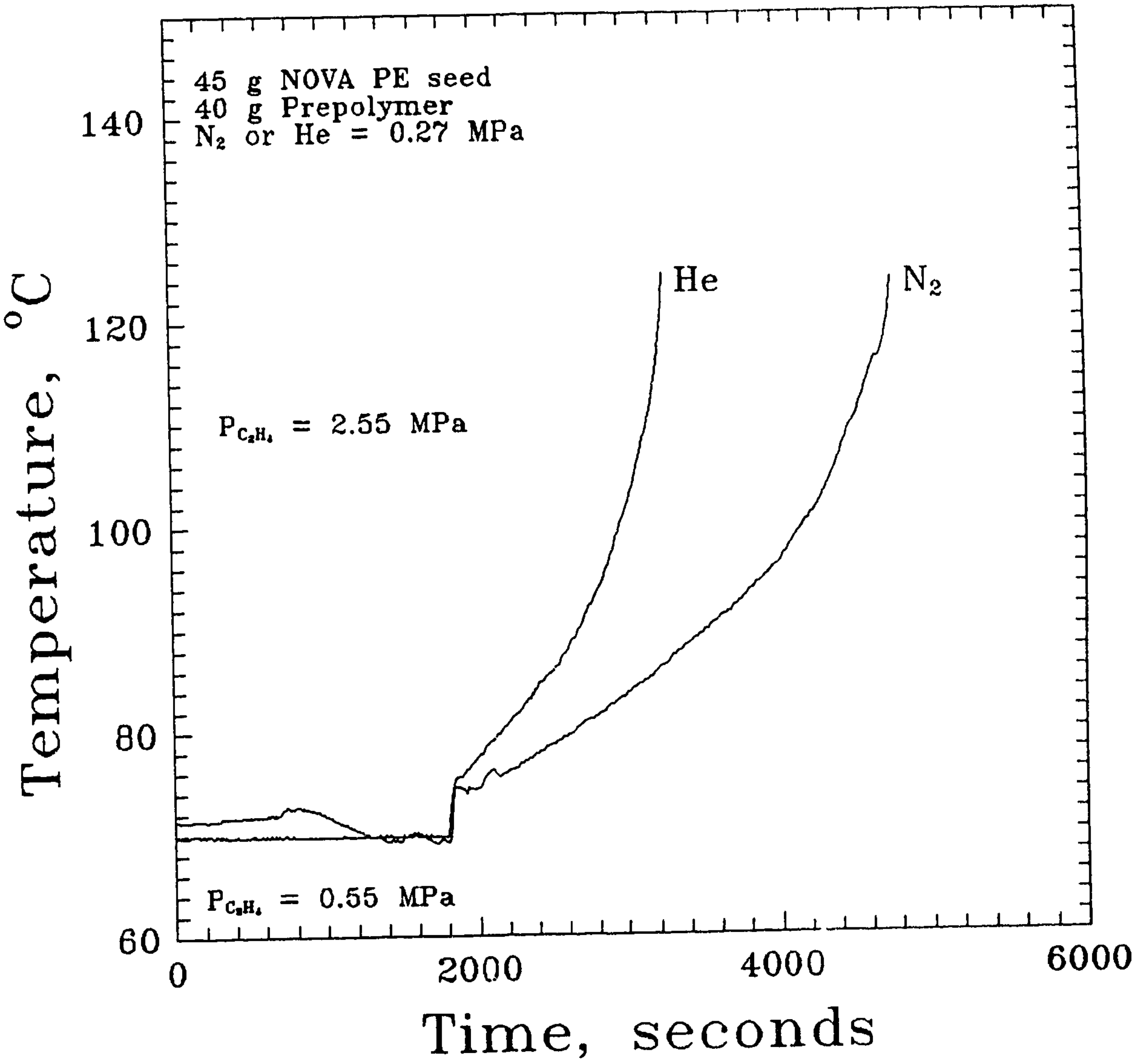


Figure C.4
VARIATION OF BACKGROUND GAS AT CONSTANT SEED AND PREPOLYMER AMOUNT

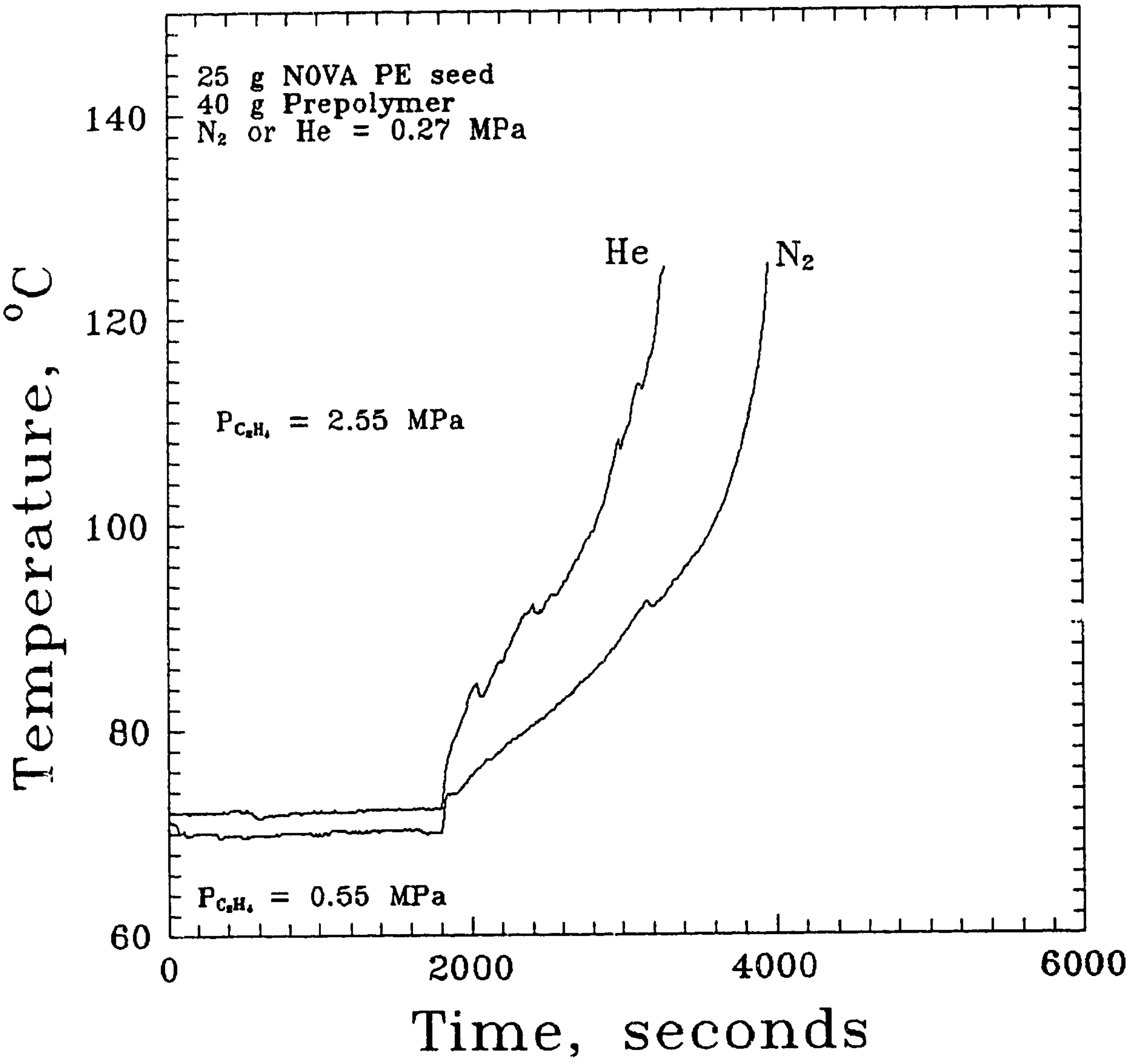


Figure C.5
VARIATION OF BACKGROUND GAS AT CONSTANT SEED AND PREPOLYMER AMOUNT

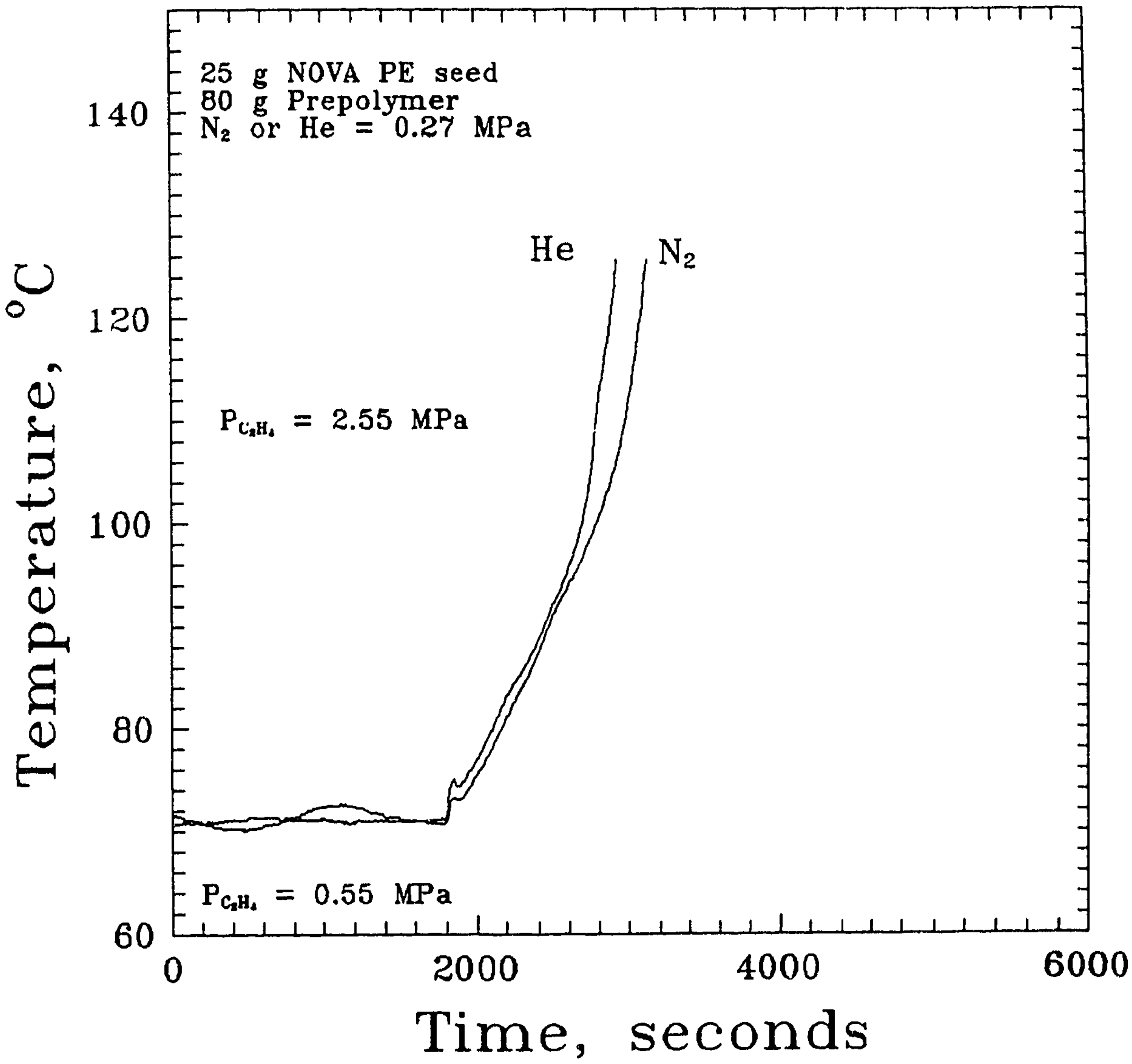
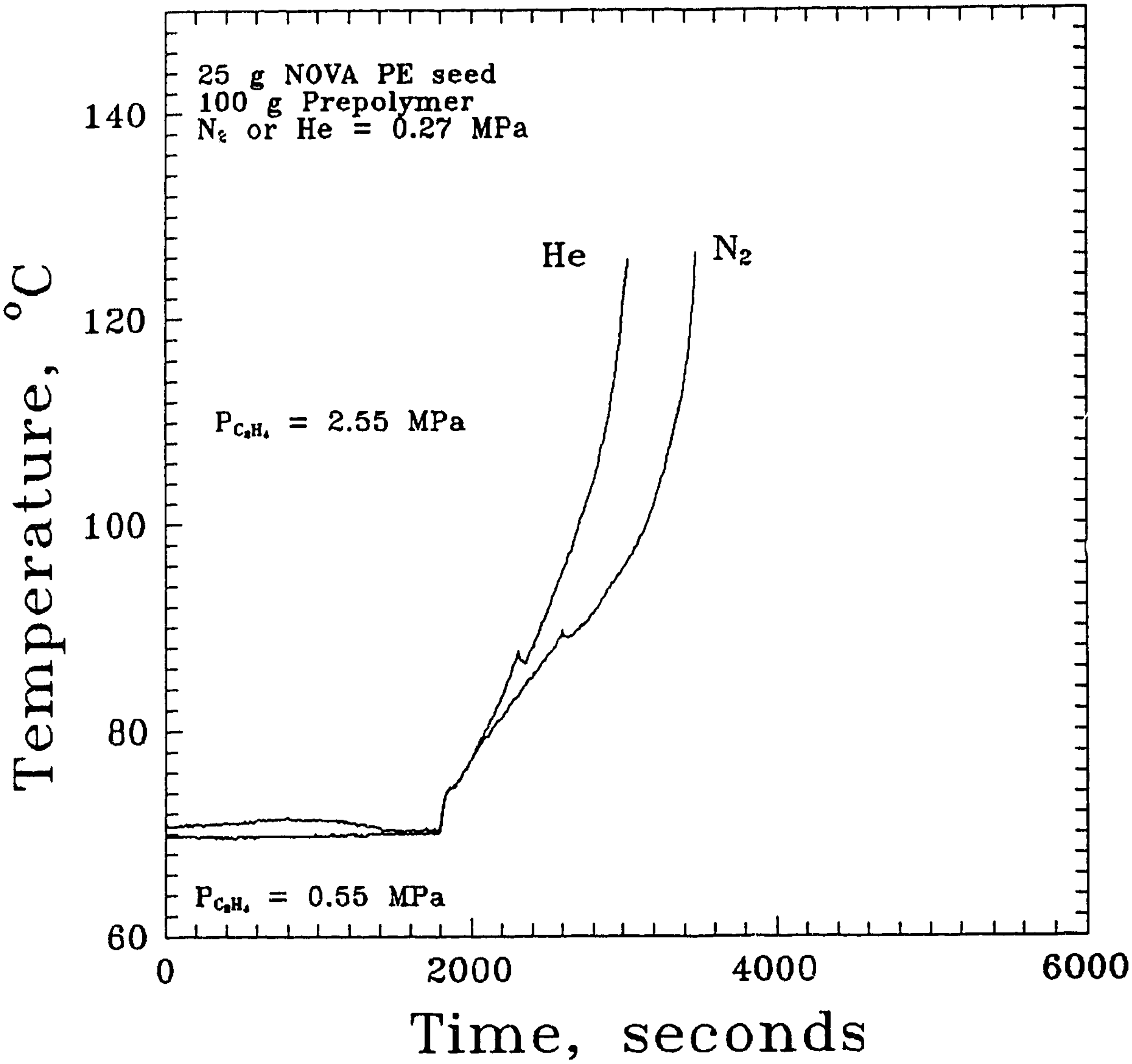


Figure C.6
VARIATION OF BACKGROUND GAS AT CONSTANT
SEED AND PREPOLYMER AMOUNT



APPENDIX D

Catalyst Activity Profile after Thermal Runaway Occurred

The polymerization rate of the Stauffer AA Type 2.1 catalyst used for gas-phase polymerization of ethylene was observed after thermal runaway occurred in the reactor. The catalyst activity was observed at the same conditions as the initial operating conditions so as to ascertain the extent of deactivation due to thermal excursion of the reactor contents. This appendix summarizes the catalyst activity profile for some of the gas phase runs, after thermal runaway occurred during the reaction.

Figure D.1

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED

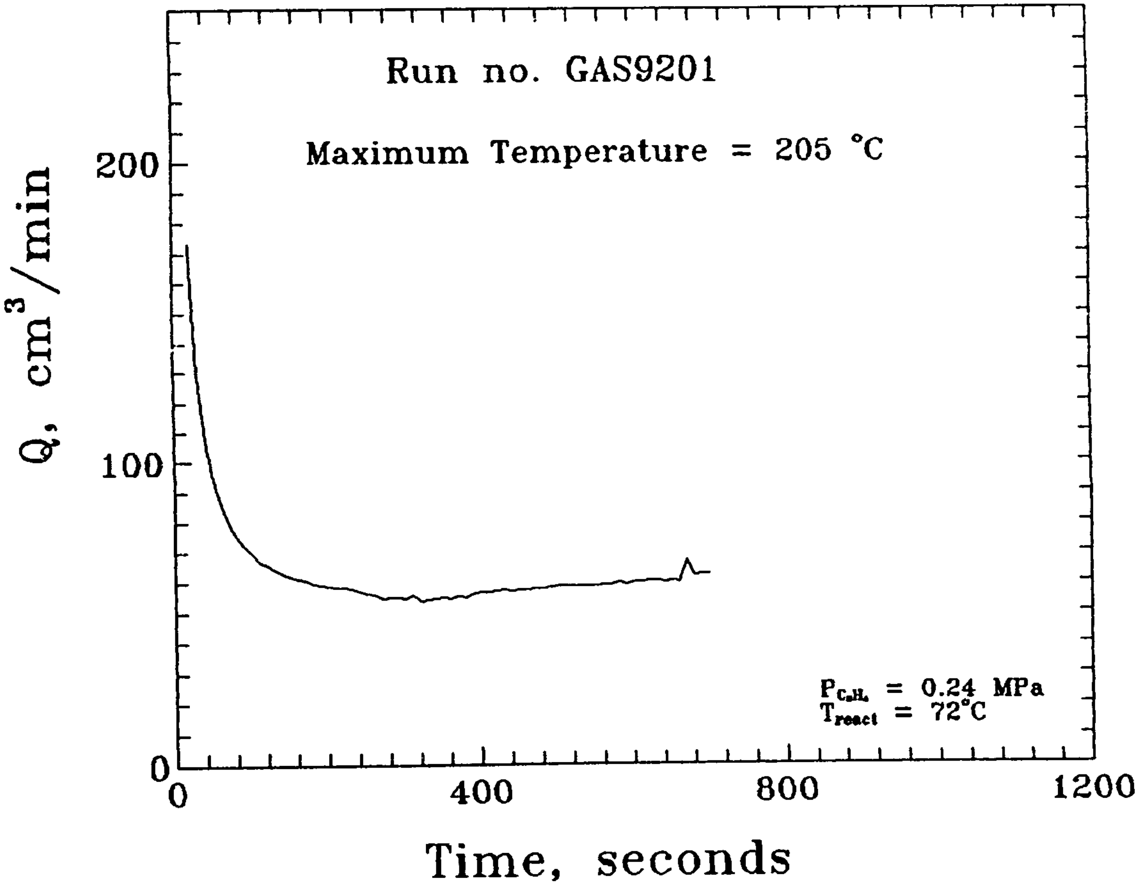


Figure D.2

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED

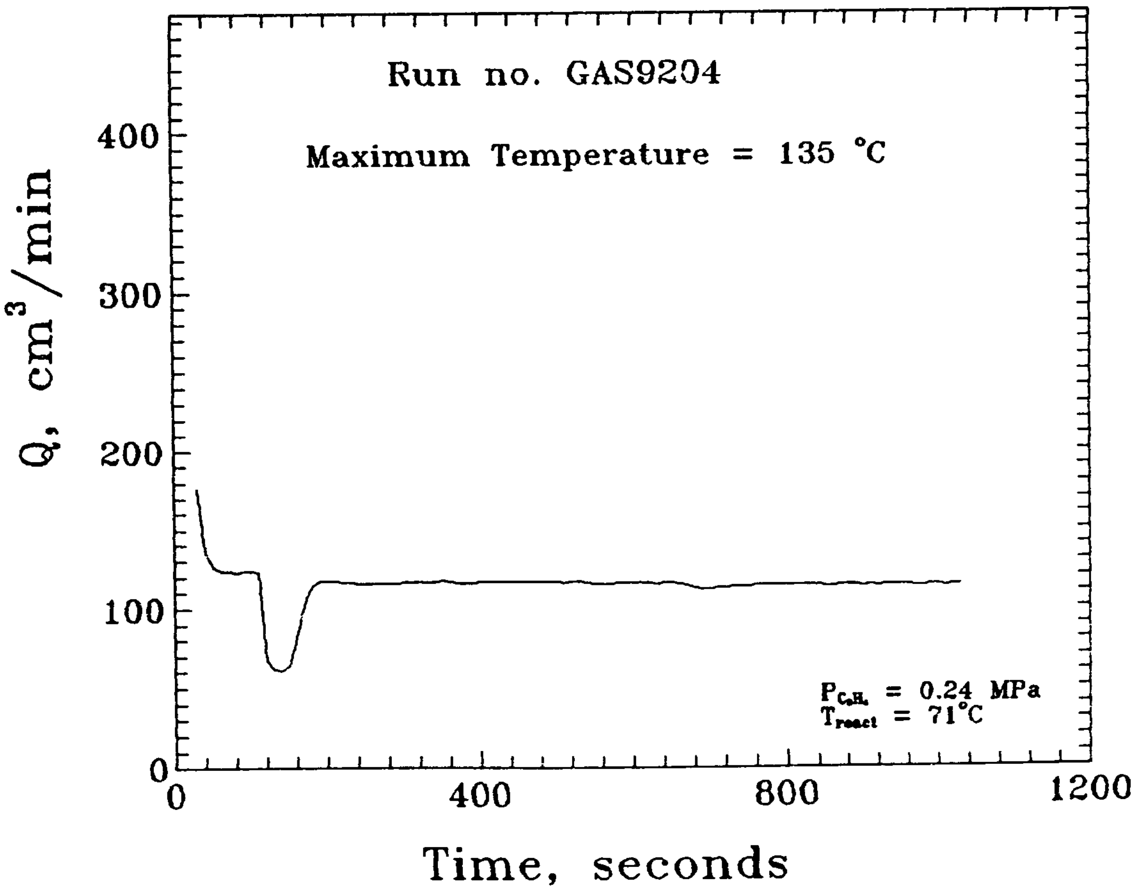


Figure D.3

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED

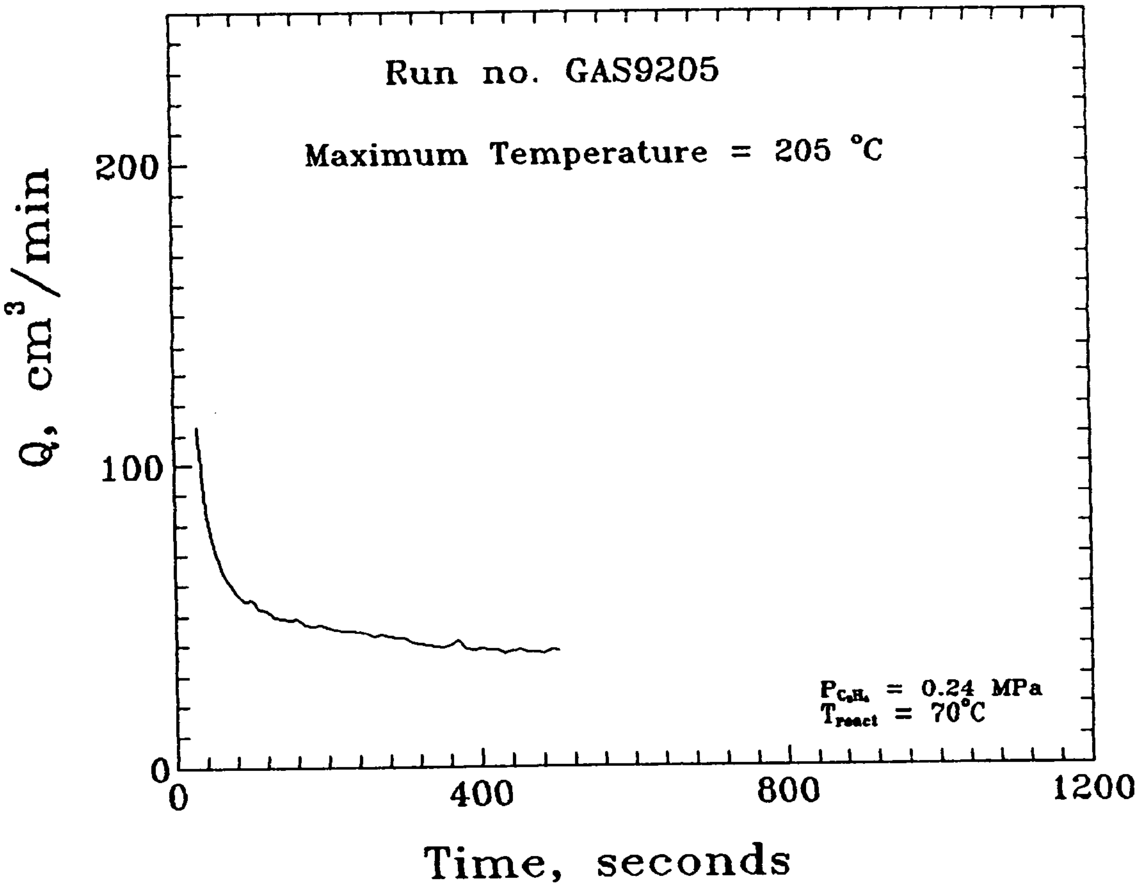


Figure D.4

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED

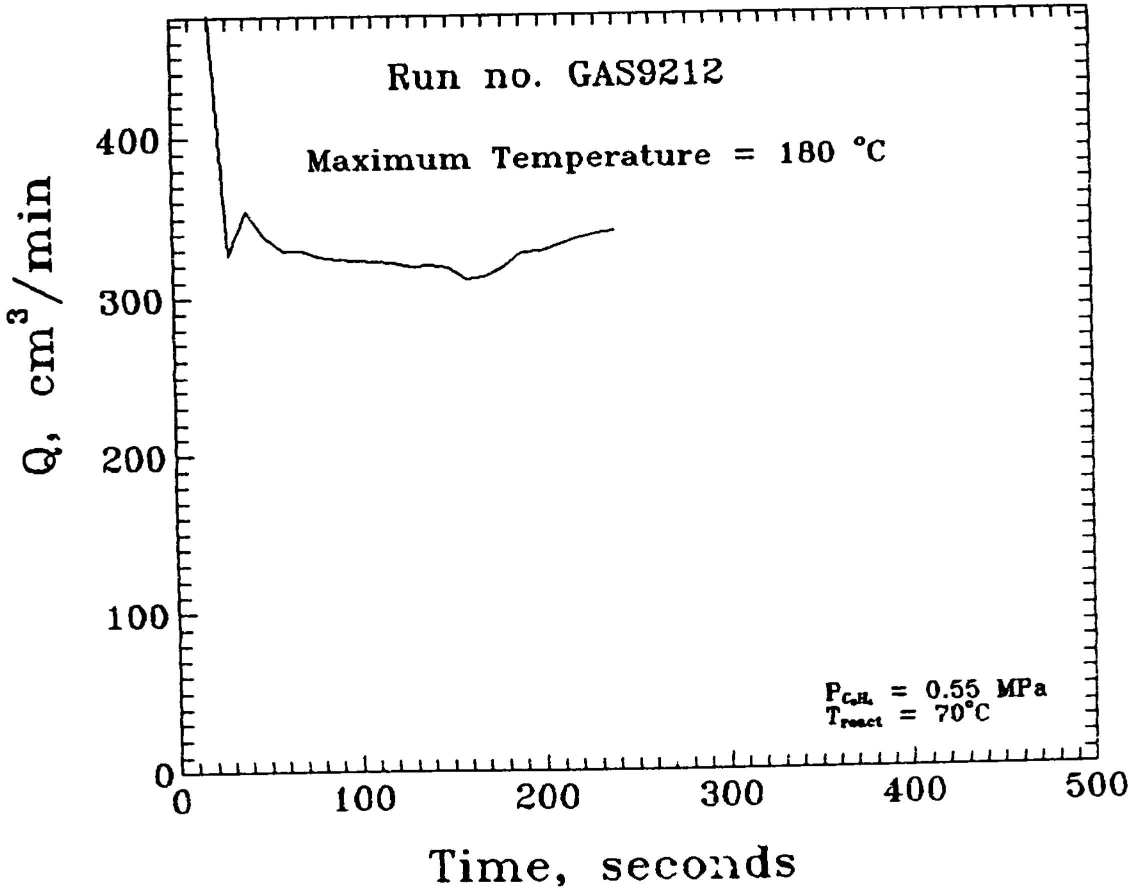


Figure D.5

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED

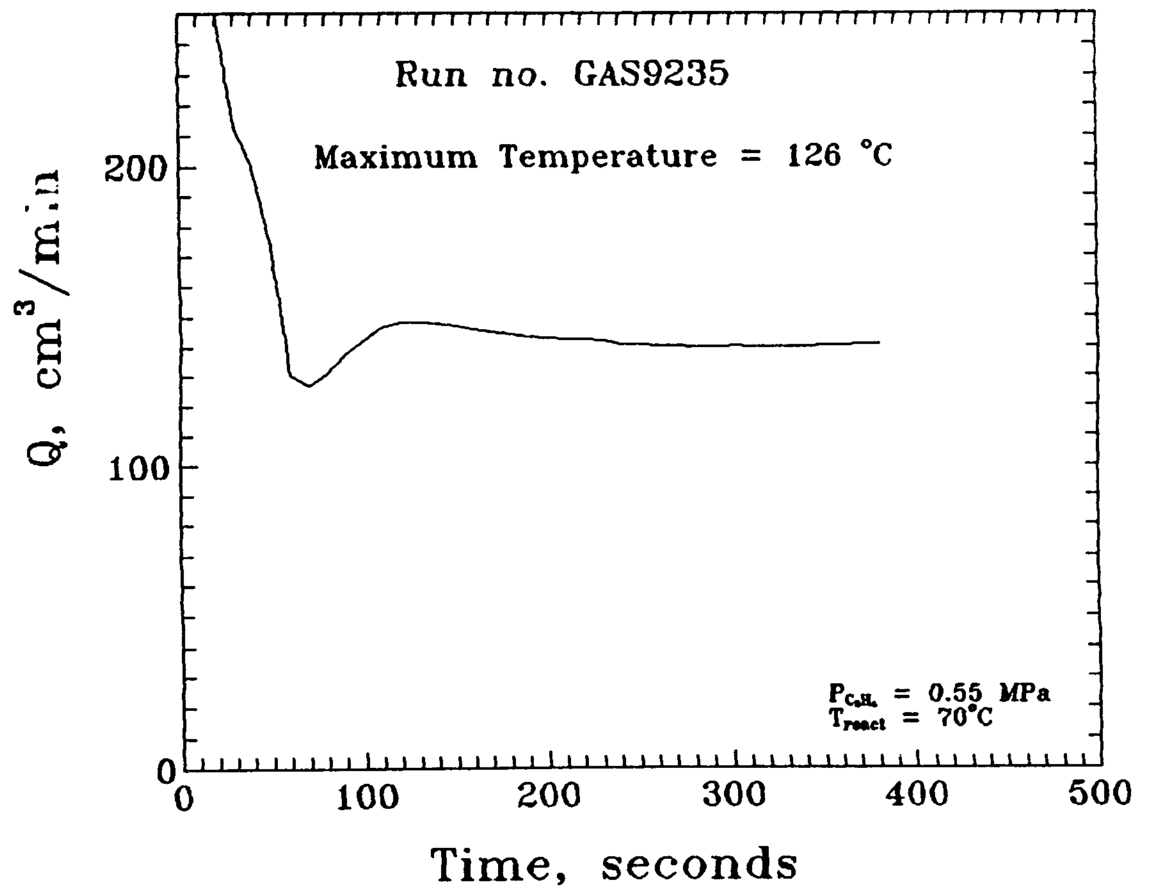
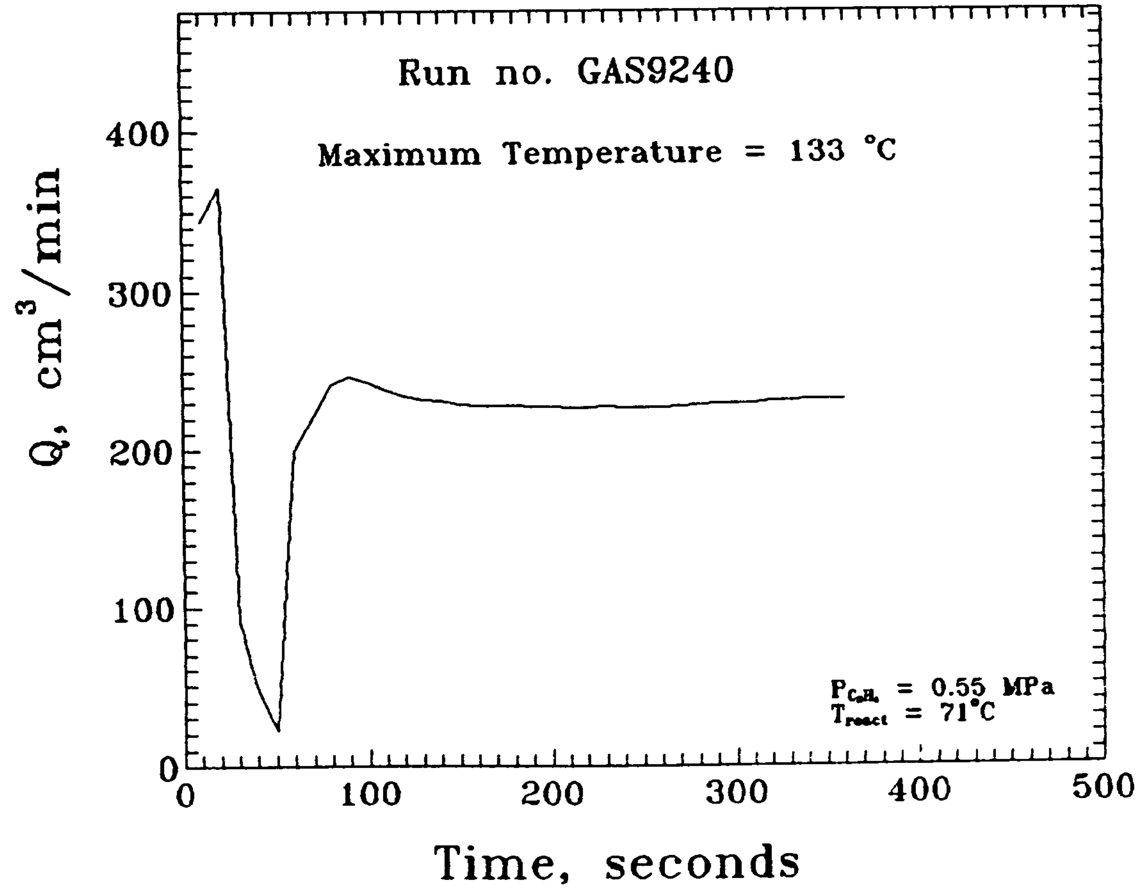


Figure D.6

RATE BEHAVIOUR AFTER THERMAL RUNAWAY OCCURRED



APPENDIX E

Correlation to Estimate the Value of Specific Heat of Ethylene Gas ($C_{p,ethylene}$) as a Function of Temperature and Pressure

The isobaric specific heat capacity of ethylene gas available in the literature ("Ethylene- International thermodynamic tables on the fluid state", No. 10, Blackwell Scientific Publications), assuming ideal gas behaviour, is as follows:

$$\frac{C_{p,o}}{R} = 4.0 + \sum_{i=1}^{12} u_i^2 \frac{e^{u_i}}{(e^{u_i} - 1)^2} \qquad \text{(E.1)}$$

where

$$u_i = \frac{a_i}{T} \qquad \text{(E.2)}$$

Data:

R = 8.314 J/gmol.k

a(1)	4353.91
a(2)	2335.23
a(3)	1930.92
a(4)	1471.93
a(5)	4464.7
a(6)	1778.39
a(7)	1365.45

a(8)	1356.82
a(9)	4469.02
a(10)	1188.48
a(11)	4300.67
a(12)	2077.68

The above correlation was corrected for variations in temperature and pressure by comparing then estimated values with the experimental observations given in the handbook. The correction was made for the range of temperatures (273 to 425 °k) and pressures (0.5 to 3.5 MPa), encountered in the experiment.

The final correlation obtained is as follows:

$$\frac{C_{p,ethylene}}{R} = \frac{C_{p,o}}{R} + 0.17*P + \frac{5.5}{T^2} \qquad \text{(E.3)}$$

The computer program developed, is given at the end of the section.

```
                PROGRAM CPG
C.................................................
C       Program used to obtain correlation of specific
C       heat of gas as a function of Pressure and
C       Temperature for the range of operation of reactor.
C
C       The ideal gas heat capacity relation is taken and
C       and correction based on deviation from
C       experimental values is done.
C
C       CPG...... Specific heat capacity at constant
C                 pressure of ethylene gas
C                 (ref. IUPAC handbook for ethylene)
C       CVC2..... heat capacity at constant volume
C                 = CPG - R
C.................................................

        REAL *8 B(12), X(12), SUM,SUM1,TMP,P,CPG,R
        REAL *8 MWC2,C1,C2
        INTEGER I,J,N

        OPEN (8,FILE='CPG.DAT',STATUS='UNKNOWN')
        OPEN (9,FILE='CPG.OUT,STATUS='UNKNOWN')

        READ(8,*) P,C1,C2
        WRITE(9,*)P,C1,C2
        READ(8,*)(B(I),I=1,12)
          R=8.315D0
          MWC2=28.05D0

                    DO 45 N=1,7
                       SUM1=0.0
                         TMP=320 + N*20.0

                    DO 55 J=1,12
                      X(J)=B(J) /TMP
                          SUM1=SUM1 + ((X(J) **2.0)
     *  *EXP(X(J))/((EXP(X(J))-1.0)**2.))
55      CONTINUE
      CPG = (4.0 + SUM1 + C1*P + C2/(TMP**2.0))*R
       WRITE(9,*)TMP,CPG
45        CONTINUE
                    STOP
                    END
```

APPENDIX F

Calculation of External Surface Area of the Reactor

Data:

1. Outer diameter of the reactor vessel (D) = 14 cm
2. Thickness of the wall = 1.4 cm
3. Distance from the base to the upper flange (h) = 11.5 cm

Calculations:

(a) Surface area of the cylindrical surface = $\pi . D . h$

= 505.8 cm^2

(b) Surface area of the base = $(\pi/4) . D^2$

= 153.9 cm^2

(c) Surface area of the top flange exposed to oil bath = 70.4 cm^2

Total external surface area available for heat transfer = 730.1 cm^2

APPENDIX G

Estimation of Heat Transfer Coefficient of the Oil Bath (h_o) Assuming Only Natural Convection

Data:

1. Length of cylinder (L) = 11.5 cm
2. Density of liquid (Dow corning 200 fluid) (ρ) = 0.964 g/cm^3
3. Volume coefficient of thermal expansion (β) = 0.00096
4. Temperature difference ($\triangle$T)=T_{wall} - T_∞ = 1°C
5. Kinematic viscosity (v) = 10^{-4} m^2/s
6. Specific heat of the oil (C_p) = 1472.8 J/kg.k
7. Thermal conductivity (k_s) = 1.55 J/m^2.s.k

$$N_{GR} = \frac{L^3\ \rho^2\ g\ \beta\ \Delta t}{\mu^2} \qquad \text{(G.1)}$$

$= 99940.325 < 10^9$

Therefore, the following correlation is used:

$$N_{nu} = 0.683\ N_{GR}^{0.25}\ N_{PR}^{0.25}\ [\frac{N_{PR}}{0.861\ +N_{PR}}]^{0.25} \qquad \text{(G.2)}$$

$N_{nu} = 37.5$

$$N_{nu} = \frac{h_o\ L}{k_s} \qquad \text{(G.3)}$$

Therefore,

h_o= 569.3 J/m^2.s.k

APPENDIX H

Details of the Reactor Model Equations

Final form of the six coupled first order differential equations solved numerically using the Runge-Kutta-Fehlberg (4th and 5th) order method, with variable step size.

The differential equations for mass of polyethylene (m_{PE}), volume of the gas phase (V_g) and radius of the growing polymer particle (r_p) were solved in the original form.

The change in internal energy (ΔU_R) during the polymerizarion reaction was related to the heat of reaction (ΔH_R) by the following thermodynamic transformation:

$$\Delta U_R = \Delta H_R - [P + (\frac{\partial u}{\partial v})_T] \Delta V \tag{H.1}$$

Assume change of internal energy is independant of volume

Therefore,

$$\Delta U_R = \Delta H_R(T) - P\Delta V \tag{H.2}$$

$$= \Delta H_R(t) - \Delta nRT \tag{H.3}$$

Here, Δn represents the change in moles of ethylene in the gas phase during the reaction. Since the product is in the solid phase,

$\Delta n = -1$

To relate $\Delta H(T_R)$ to $\Delta H(T)$:

where

T_R = reference temperature (298.16 °k)

T = Reaction temperature

$$\Delta H_R(T) = \Delta H_R(T_R) + \int_{T_R}^{T} ((\frac{1}{MR}) C_{P,PE} - C_{P,ethylene}) \, dT \tag{H.4}$$

Here,

MR = ratio of average molecular weight of polyehtylene and ethylene

The feed rate of ethylene (F_g), was related to the independant variables by the following relation:

$$F_g = [\frac{dN_{C_2H_5}}{dt} + \frac{dm_{PE}}{dt}] * (\frac{RT_p}{P_{ethy}}) \tag{H.5}$$

Using the above relations in the modelling equations (5.1-5.6), the six ordinary differential equations could be solved numerically for the initial values of the variables.

APPENDIX I

Computer Program of the Semibatch Reactor

The final form of the six equations to be solved numerically is shown in appendix H. The physical parameters and reaction operating variables required for the integration are presented in table 5.1.

A standard Runge-Kutta-Fehlberg (4th and 5th) order routine with variable step size was employed. The initial conditions of the variables were the initial values used during the experiment.

The computer program developed is given at the end of this section. In this program, the differential equations were integrated from time $t=0$ to the time at which the temperature (gas phase) T_g reached the melting point of polymer (>135°C). The maximum value of solid product (m_{PE}) was also limited to 250 g because during actual experiments, the reactor filled with polyethylene and required stopping of the ethylene feed after the amount of polymer inside the reactor reached about 250 g.

```
                     PROGRAM isoth2
C*********************************************************
C  Six differential equations to be solved for the heat
C  effectsin an semi-batch polymerization reaction of
C  ethylene using
C  Stauffer AA Type 2.1.
C
C  The dependant variables are :
C  VG... volume of the gas (cm3).
C  NPE.. gms of polymer in the reactor .
C  NC2.. gms of ethylene in the reactor .
C  TP.. temperature of the solid phase inside reactor (K)
C  TG.. temperature of the gas phase inside reactor (K)
C  RD.. Radius of the growing solid particle (cm)
C
C  Initial value problem solved using RKF45 subprogram
C
C*********************************************************

      IMPLICIT REAL*8(A-H,O-Z)
      IMPLICIT INTEGER*4(I-N)
      REAL*8 NPE,NI,NS,NC2,MCAT,MWC2,MWPE,CTP,CTG
      REAL*8 NUM,MCAT1,MU,KF,EMF
      REAL*8 KW,LT
      PARAMETER (N=6)
      EXTERNAL F3
      REAL*8 Y(N)

C*********************************************************

      COMMON /PARM1/FREQ,ER,R,MCAT,MCAT1,DENPE
     *MWC2,VEL,CVCAT
      COMMON /PARM2/ CPPE,CVPE,CVI,CVS,CPG,C1,C3
     *RHOGAS,MU,KF,BETA
      COMMON /PARM3/ TMPR,TGI,MWPE,DHR,DELN,NI,NS,PREG
      COMMON /PARM4/ VG1,TG1,POINER,EMF
      COMMON /PARM5/ AHT,NUM,HO,HTC,U
      COMMON /PARM6/ B1,B2,B3,B4,B5,B6,B7,B8,B9
      COMMON /PARM7/ B10,B11,B12
      COMMON /PARM8/ AO,AI,AM,HX,KW,RO,RI,DT,LT
      COMMON /PARA/  RATE,FC2,PINERT,PC2,RK
      COMMON /COUNT/ ISTEP,NDELAY,NPOINT,NTMAX
C*********************************************************
```

```
      READ(5,*) IPRINT
      READ(5,*) A,DA,H,HMXFR,AER,RER
      READ(5,*) VG,NPE,TP,TG,RD
      READ(5,*) FREQ,ER,R,MCAT,MCAT1,DENPE,MWC2,VEL
      READ(5,*) NINT,ISKIP,NDELAY
      READ(5,*) CVCAT,CPPE,CVPE,CVI,CVS,C1,C3
      READ(5,*) RHOGAS,MU,KF,BETA
      READ(5,*) TMPR,TGI,MWPE,DHR,DELN,NI
      READ(5,*) NS,PREG,POINER
      READ(5,*) AHT,NUM,HO,EMF
      READ(5,*) ISTEP1,ISTEP2,ISTEP3,ISTEP4
     *ISTEP5,ISTEP6,ISTEP7,ISTEP8
      READ(5,*)ISTEP9
      READ(5,*)PREG1,PREG2,PREG3,PREG4,PREG5,PREG6
      READ(5,*) PREG7,PREG8,PREG9
      READ(5,*) B1,B2,B3,B4,B5,B6,B7,B8,B9
      READ(5,*) B10,B11,B12
      READ(5,*) AO,AI,AM,HX,KW,RO,RI,DT,LT

C*********************************************************
C       VG1,TP1,RD1 and TG1 are the initial values
C       of VG, TP and TG.

              VG1=VG
              TG1=TG
              TP1=TP
              RD1=RD
C*********************************************************
C       To calculate the initial amount of C2H4
C       in the reactor

        NC2=((PREG-POINER)*VG1/(R*TP1))*MWC2

C*********************************************************

       WRITE(6,350) NINT
350    FORMAT(I6,' Number of lines in file')
       WRITE(6,*) DA,H,HMXFR,AER,RER
       WRITE(6,*) A,VG,NPE,NC2,TP
       WRITE(6,*) A,ER,MCAT,DENPE,MWC2
       WRITE(6,*) NINT,ISKIP,NDELAY,IPRINT
360    FORMAT(1PE11.4,1PE11.4,1X,1PE11.4,1X,6(1PE11.4))
C345   FORMAT(6(5X,I7))
```

```
      Y(1)=VG
      Y(2)=NPE
      Y(3)=NC2
      Y(4)=TP
      Y(5)=TG
      Y(6)=RD


      IF(NDELAY.LE.0) WRITE(6,360) A,(Y(I),I=1,6)
              NPOINT=1
      IF(NDELAY.GT.0) NPOINT=0
              NTMAX=0

C**************  Start of main loop *******************

      DO 10 ISTEP=1,NINT
      CALL RKF45(A,Y,N,F3,DA,H,HMXFR,AER,RER,IFLAG)
          CTP=Y(4) - 273.16
           CTG=Y(5) - 273.16
           IF(IFLAG.NE.1) THEN
      WRITE(6,915) IFLAG,A,Y(1),Y(2),Y(3),CTP,CTG,Y(6)
915           FORMAT(' ',I3,7(D15.6,1X))
              GO TO 100
      ENDIF
      IF(ISTEP.GT.NDELAY .AND. ISTEP/ISKIP*ISKIP.EQ.ISTEP) THEN
          WRITE(6,360) A,Y(2),CTP,CTG,Y(6),FC2,U
           WRITE(7,360) A,Y(2),CTP,CTG,Y(6),FC2,U
             NPOINT=NPOINT+1
      ENDIF
         IF(A .GE. 400)GO TO 111
         IF(Y(4) .GE. 415.)GO TO 111
         IF( Y(2) .GE. 2[illegible].0)GO TO 111
         IF( Y(1) .LE. [illegible])GO TO 111
         IF(ABS((PINERT-PREG)*100/PREG) .LE. 0.002) THEN

       WRITE(6,222)
222    FORMAT(1X,'Pres of inert is > Pres of regulator')

       GO TO 111
                  ENDIF

C*********************************************************
```

```
C       TO CHANGE THE REGULATOR PRESSURE

        IF(ISTEP .GT. ISTEP1)PREG=PREG1
        IF(ISTEP .GT. ISTEP2)PREG=PREG2
        IF(ISTEP .GT. ISTEP3)PREG=PREG3
        IF(ISTEP .GT. ISTEP4)PREG=PREG4
        IF(ISTEP .GT. ISTEP5)PREG=PREG5
        IF(ISTEP .GT. ISTEP6)PREG=PREG6
        IF(ISTEP .GT. ISTEP7)PREG=PREG7
        IF(ISTEP .GT. ISTEP8)PREG=PREG8
        IF(ISTEP .GT. ISTEP9)PREG=PREG9

C*******************************************************

        Y(3)=((PREG - PINERT)*Y(1)/(R*Y(4)))*MWC2

 10   CONTINUE
 100   CONTINUE

C************  End of main loop ***********************

 111    WRITE(6,910) NPOINT
 910     FORMAT(' ',' # OF POINTS =',I6)

 C       The endfile and close statement should be commented out
 C       when  run on MTS.

 C                 ENDFILE(9)
 C                   CLOSE(9)
                            STOP
                            END


C*********** End of main program ********************

          SUBROUTINE F3(T,Y,YP)



          IMPLICIT REAL*8(A-H,O-Z)
          IMPLICIT INTEGER*4(I-N)
          REAL*8 NI,NC2,NPE,MWC2,MWPE,MCAT,NS,MR,NUM
          REAL*8 HTC,MCAT1,MU,KF
          REAL*8 Y(6),YP(6),X(12),B(12),EMF
          REAL*8 KW,LT

 C*****************************************************
```

```
      COMMON /PARM1/ FREQ,ER,R,MCAT,MCAT1,DENPE,MWC2
     *VEL,CVCAT
      COMMON /PARM2/ CPPE,CVPE,CVI,CVS,CPG,C1,C3,RHOGAS
     *MU,KF,BETA
      COMMON /PARM3/ TMPR,TGI,MWPE,DHR,DELN,NI,NS,PREG
      COMMON /PARM4/ VG1,TG1,POINER,EMF
      COMMON /PARM5/ AHT,NUM,HO,HTC,U
      COMMON /PARM6/B1,B2,B3,B4,B5,B6,B7,B8,B9
      COMMON /PARM7/B10,B11,B12
      COMMON /PARM8/AO,AI,AM,HX,KW,RO,RI,DT,LT
      COMMON /PARA/ RATE,FC2,PINERT,PC2,RK

C*******************************************************
C      B(I) are the coeffecent of the equation to calculate
C      the specific heat of ethylene gas.

        B(1)=B1
        B(2)=B2
        B(3)=B3
        B(4)=B4
        B(5)=B5
        B(6)=B6
        B(7)=B7
        B(8)=B8
        B(9)=B9
        B(10)=B10
        B(11)=B11
        B(12)=B12
C*******************************************************
               VG=Y(1)
               NPE=Y(2)
               NC2=Y(3)
               TP=Y(4)
               TG=Y(5)
               RD=Y(6)
C*******************************************************
      PINERT = POINER*VG1*TG/(VG*TG1)

C*******************************************************
C      CPG.. is the specific heat capacity at const. pressure
C      of ethylene gas. It is calculated using the following
C      equation obtained from curve fitting the exptal values
C      given in the IUPAC handbook.
C      CVC2.. is the heat capacity at constant vol.
C      CVC2 = CPG-R
```

```
              SUM1=0.0
              ATM=1.013E05
      DO 55 J=1,12
       X(J)=B(J)/TG
        SUM1=SUM1+((X(J)**2.0)*EXP(X(J))/
     *         ((EXP(X(J))-1.0)**2.))

55        CONTINUE

     CPG=(4.0+SUM1+(C1*PREG/ATM)+C3/(TG**2.))*

     *        R*(1./MWC2)

     CVC2=CPG-(R/MWC2)
C*****************************************************
C       RK... Rate constant of the polymerization reaction.
C       MR... Ratio of mol.wt of PE and Ethylene

         MR=MWPE/MWC2
          RK=(FREQ*EXP(-ER/TP))*60.00
           RATE=RK*(PREG-PINERT)*MWC2/(R*TP)

         DVGDT=-(RATE*MCAT/DENPE)*1.0E-6
         DNPEDT=RATE*MCAT

        CON=(PREG/(R*TP))*MWC2
         CONI=CPG*(TGI-TG)+(R*TG)/MWC2
          CONIIA=(NPE*CVPE+NS*CVS+MCAT*CVCAT)
            CONIIB=(NC2*CVC2+NI*CVI)
              CONIII=((1/MR)*CPPE-CPG)*(TP-TMPR)

C*****************************************************

C       TO CALCULATE THE SOLID-GAS HEAT TRANSFER COEFF.

C       HTC. is the solid gas htc.(J/cm2.s.K)
C       dp.. is the diameter of the polymer particle (cm)
C       u.. is the relative velocity of the S-G (cm/sec)
C       rho(gas).. is the density of the gas phase (gm/cc)
C       MU(gas).. is the viscosity of the gas phase
                   (g/cm.s)
C       h..is the heat transfer coefficent (J/cm2.sec.K)
C       Kf...is the thermal cond. of the gas phase
              (J/cm.sec.K)
C       VEL... is the relative velocity of S-G
               system(cm/sec)
```

```
C       PR.. is the prandtl no.
C       RHOGAS.. is the density of the gas.
C       MU.. is the viscosity of the gas.
C       DT.... is the diameter of the vessel
C       LT.... is the height of the fluidized bed
             (70% of vessel ht)
C       EMF... is the voidage.
C       BETA... is the shape factor

        PI=3.1415927D0
        DP=RD*2.0
             RE=DP*VEL*RHOGAS/MU
             PR=CPG*MU/KF


C       HTC..calculated using Kunni-Livenspiel
             correlation
C              HTC=0.03*(RE**1.3)*KF/DP

C       HTC...calculated using the Bordulya correlation
C              HTC=0.37*(PR**0.31)*(RE**0.71)*KF/DP

C       HTC..calculated using Zenz-Othmer correlation
               HTC=0.017*(RE**1.21)*KF/DP

C       HTC..calculated using the Ranz Marshall correlation
C              HTC=(2.0+0.6*(RE**0.5)*(PR**0.33))*KF/DP

C       HTC..calculated using the Kettenring correlation.
C              HTC=0.0135*(RE**1.3)*KF/DP

C*****************************************************

C       Q1.. heat transfer between solid and gas phase.
C       AP.. surface area for heat transfer per particle
C       NUM..no. of particles

         AP= 4.0*PI*((RD**2.))
         Q1= -HTC*AP*NUM*(TP-TG)*60.0


C*******************************************************
```

```
C    TO CALCULATE THE WALL HEAT TRANSFER COEFFICENT

C       HI.. is given by the Livenspiel correlation
          HI=0.6*(RE**0.3)*PR*KF/DP*1.0E04

C       HI.. calculated using Van Heerden correlation
C    HI=0.58*(PR**0.5)*((BETA*RE)**0.45)
C    *((CPPE/CPG)**.36)*((DENPE*(1-EMF)/RHOGAS)**0.18)
C       *KF/DP *1.0E04

C    HI.. calculated using the Dow-Jacobs correlation
C       HI=0.55*(RE**0.8)*((DT/DP)**0.3)*((DT/LT)**.65)
C    *(((1-EMF)/EMF)**.25)*(((DENPE*CPPE)
C    /(RHOGAS*CPG))**.25)
C    *KF/DP *1.0E04


C***********************************************************

C    TO CALCULATE THE OVERALL HEAT TRANSFER COEFFICENT

C   U = 1/((1/ho) + Ro +(x*Ao/Kw*Am) +((1/hi) + Ri)*Ao/Ai)

C       ho .. is the outside htc (of the oil bath)
C       hi.... is the inside htc (wall htc)
C       Ro... dirt scale resistance outside
C       Ri... dirt scale resistance inside
C       Ao... outside h.t area
C       Am... mean h.t area
C       Ai... inside h.t area
C       Hx... thickness of the conducting material
C       Kw... Thermal conductivity of the retaining wall.

       HX1 = (HX*AO)/(KW*AM)
        U=1.0/((1/HO)+RO+HX1+((1/HI)+RI)*AO/AI)

C**********************************************************

C       Q.. is the heat transferred from the system
            to the oil bath
C       AHT.. is the area for heat transfer at the wall

        TW = 337.0

        Q = - U*AHT*(TG - 337.0)*60.00
```

```
C       RD.. is the radius of the spherical particle (cm)
C       MCAT1.. is the catalyst on one seed particle (gm)
C       TP..is the temperature of the solid phase.
C       TG.. is the temperature of the gas phase.

            DHRT=DHR+CONIII
             TERM1=RATE*MCAT*CONI
          TERM2=(RATE*MCAT)*(-DHRT+((DELN*R*TP)/MWC2))

 DRDDT= ((RATE*MCAT1)/DENPE)*(1.0/AP)
  DNC2DT=(CON*DVGDT)-(1/CONIIA)*(Q1+TERM2)*(CON*(VG/TP))
    DTPDT=(1/CONIIA)*(TERM2+Q1)
      DTGDT=(1/CONIIB)*(TERM1+CONI*DNC2DT+Q-Q1)

C*********************************************************

C       FC2.. is the flow rate of C2H4 entering
              the reactor (cc/min)
C       PC2.. is the partial pressure of the ethylene gas.

       FC2 =(DNPEDT+DNC2DT)*(R*TP/(PREG-PINERT))*1.E06/MWC2
        PC2=PREG-PINERT

           YP(1)=DVGDT
           YP(2)=DNPEDT
           YP(3)=DNC2DT
           YP(4)=DTPDT
           YP(5)=DTGDT
           YP(6)=DRDDT

                       RETURN
                          END
```

```
      SUBROUTINE RKF45(A,Y,N,DIFEQS,DA,H,HMXFR,ABSER,RELER,IFLAG)
      IMPLICIT REAL*8 (A-H,O-Z)
      IMPLICIT INTEGER*4(I-N)
      INTEGER*4 I,IADJS,IFLAG,MAXEQS,N
      INTEGER*4 ISTEP,NDELAY,NPOINT,NTMAX
      PARAMETER (MAXEQS=6)
C
C     .............................................................
C
C     SUBROUTINE RKF45
C
C     PURPOSE
C        INTEGRATION OF A SYSTEM OF N ORDINARY DIFFERENTIAL EQUATIONS
C        USING A RUNGE-KUTTA-FEHLBERG METHOD.  A FIFTH ORDER RUNGE-
C        KUTTA PROCEDURE IS USED FOR THE INTEGRATION, AND THE LOCAL
C        ERROR IS CONTROLLED BY ADJUSTING THE INTEGRATION STEP-SIZE.
C        THE LOCAL ERROR IS MEASURED AS THE DIFFERENCE BETWEEN THE
C        FIFTH ORDER SCHEME AND A FOURTH ORDER SCHEME.
C
C     USAGE
C        CALL RKF45(A,Y,N,F,DA,H,HMXFR,ABSER,RELER,IFLAG)
C
C     DESCRIPTION OF THE PARAMETER LIST
C
C       A     -ON INPUT THE INITIAL VALUE OF THE INDEPENDENT VARIABLE.
C              ON OUTPUT THE LAST VALUE AT WHICH A SOLUTION WAS
C              SUCCESSFULLY COMPUTED.  NORMAL OUTPUT HAS A INCREASED BY DA.
C
C       Y     -ON INPUT THE VECTOR OF INITIAL VALUES OF THE DEPENDENT
C              VARIABLES.  ON OUTPUT THE VECTOR OF COMPUTED SOLUTIONS
C              AT OUTPUT VALUE OF A.
C
C       N     -NUMBER OF EQUATIONS TO BE INTEGRATED.
C
C       DIFEQS-SUBROUTINE OF THE FORM  F(A,Y,YP)  WHICH ACCEPTS INDEPENDENT
C              VARIABLE A AND A VECTOR OF DEPENDENT VARIABLES Y, AND
C              FURNISHES A VECTOR OF VALUES OF THE DERIVATIVES YP.
C              IN VECTOR FORM THE DIFFERENTIAL EQUATIONS SOLVED ARE:
C
C                   DY/DX = YP   ,    Y(A)=Y
C
C       DA    -INTEGRATION IS TO PROCEED FROM A TO A+DX. DX CAN BE NEGATIVE
```

```
C
C     H      -NOMINAL STEP-SIZE ON INPUT.  ON OUTPUT IT IS REPLACED BY THE
C             OPTIMAL VALUE CURRENTLY BEING USED.  H CAN BE NEGATIVE.
C
C     HMX    -UPPER BOUND ON STEP-SIZE TO BE USED. HMX CAN BE NEGATIVE.
C
C     HMXFR  -MAXIMUM FRACTION OF STEP-SIZE TO BE USED.
C
C     ABSER  -ABSOLUTE LOCAL ERROR TO BE TOLERATED.
C
C     RELER  -RELATIVE LOCAL ERROR TO BE TOLERATED.
C
C            ABS(EST. LOCAL ERROR) < ABS(H)*(RELER*ABS(Y(I))+ABSER)
C
C     IFLAG    1  NORMAL RETURN, INTEGRATION REACHED A+DA
C              2  HMX, H AND DA ARE NOT ALL OF THE SAME SIZE ON INPUT.
C              3  RELER<0, OR ABSER<0, OR RELER+ABSER=0 ON INPUT
C              4  DA IS TOO SMALL RELATIVE TO COMPUTER PRECISION.
C              5  H HAS BECOME INSIGNIFICANT RELATIVE TO A (PRECISION PROB
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C
C     DIFEQS- SUBROUTINE CONTAINING ODE'S TO BE INTEGRATED
C             THE "ACTUAL" NAME OF  DIFEQS  MUST BE DECLARED EXTERNAL
C             IN THE PROGRAM SEGMENT WHICH CALLS RKF45.
C             IT IS CALLED DIFEQS IN THIS SUBROUTINE.
C
C
C     REFERENCES
C        SHAMPINE, L.F. AND R.C. ALLEN, NUMERICAL COMPUTING:
C           AN INTRODUCTION, SAUNDERS, TORONTO, 1973.
C        FEHLBERG, E., "CLASSICAL FOURTH- AND LOWER ORDER RUNGE-KUTTA
C           FORMULAS WITH STEP-SIZE CONTROL AND THEIR APPLICATION TO
C           HEAT TRANSFER PROBLEMS", COMPUTING 6, 61-71 (1970).
C
C     ..........................................................................
C
      REAL*8 Y(MAXEQS),YTEMP(MAXEQS),TEMP(MAXEQS),R(MAXEQS)
      REAL*8 FUN1(MAXEQS),FUN2(MAXEQS),FUN3(MAXEQS),FUN4(MAXEQS)
      REAL*8 FUN5(MAXEQS),FUN6(MAXEQS)
      REAL*8 DOUT(MAXEQS)
C
      COMMON /COUNT/ ISTEP,NDELAY,NPOINT,NTMAX
C
C     U IS APPROXIMATELY EQUAL TO THE MACHINE PRECISION
C     B IS THE END-POINT OF THE INTEGRATION INTERVAL
C     IADJS IS SET TO 1 WHEN THE END OF THE INTERVAL IS REACHED
C
      U=1.0D-15
      HMX=HMXFR*DA
      HEXP=0.2D0
      HATMPT=0.75D0
      B=A+DA
      IADJS=0
      ASV=A
C
C     CHECK FOR THE ERROR CONDITIONS 2, 3 AND 4
C
      IF(HMX*DA.LE.0.0D0 .OR. HMX*H.LT.0.0D0) THEN
         IFLAG=2
         RETURN
```

```
      ENDIF
      IF(RELER.LT.0.0D0 .OR. ABSER.LT.0.0D0
     *    .OR. RELER+ABSER.EQ.0.0D0) THEN
         IFLAG=3
         RETURN
      ENDIF
      IF(IFLAG.GE.0 .AND. DABS(DA).LE.13.D0*U*DABS(A)) THEN
         IFLAG=4
         RETURN
      ENDIF
C
C     ADJUST THE INITIAL AND THE MAXIMUM STEP-SIZES IF NECESSARY
C
      IF(DABS(HMX).GT.DABS(DA)) THEN
         HMAX=DA
      ELSE
         HMAX=HMX
      ENDIF
      IF(DABS(H).LE.13.0D0*U*DABS(A)) H=HMAX/100.D0
C
C     THIS IS THE BEGINNING OF THE INTEGRATION LOOP.
C     WHEN A PARTICULAR STEP IS ACCEPTED, THE CALCULATIONS FOR
C     THE NEXT STEP BEGINS HERE.
C
 10   CONTINUE
      IF(DABS(H) .GT. DABS(HMAX)) H=HMAX
      IF(DABS(B-A) .LE. DABS(H)*(10.D0*U+1.D0/(HATMPT**HEXP))) THEN
C
C     SET PARAMETERS TO INDICATE THAT THE LAST STEP IS BEING TAKEN
C
         HKEEP=H
         IADJS=1
         H=B-A
      ENDIF
C
C     OBTAIN THE DERIVATIVE VALUES (IN FUN1) BASED ON THE
C     INDEPENDENT VARIABLE=A AND THE DEPENDENT VARIABLES=Y(I)
C
      CALL DIFEQS(A,Y,FUN1)
 20   CONTINUE
C
C     IF A STEP IS REJECTED DUE TO A LARGE ERROR, THE STEP
C     IS REPEATED WITH A SMALLER H STARTING AT THIS POINT.
C
      DO 30 I=1,N
         YTEMP(I)=Y(I)+0.25D0*H*FUN1(I)
 30   CONTINUE
      ARG=A+0.25D0*H
      CALL DIFEQS(ARG,YTEMP,FUN2)
      DO 40 I=1,N
         YTEMP(I)=Y(I)+H*(FUN1(I)*(3.D0/32.D0)+FUN2(I)*(9.D0/32.D0))
 40   CONTINUE
      ARG=A+H*(3.D0/8.D0)
      CALL DIFEQS(ARG,YTEMP,FUN3)
      DO 50 I=1,N
         YTEMP(I)=Y(I)+H*(FUN1(I)*(1932.D0/2197.D0)
     *            -FUN2(I)*(7200.D0/2197.D0)+FUN3(I)*(7296.D0/2197.D0))
 50   CONTINUE
      ARG=A+H*(12.D0/13.D0)
      CALL DIFEQS(ARG,YTEMP,FUN4)
```

```
      DO 60 I=1,N
         YTEMP(I)=Y(I)+H*(FUN1(I)*(439.D0/216.D0)-8.D0*FUN2(I)
     *             +FUN3(I)*(3680.D0/513.D0)-FUN4(I)*(845.D0/4104.D0))
60    CONTINUE
      ARG=A+H
      CALL DIFEQS(ARG,YTEMP,FUN5)
      DO 70 I=1,N
         YTEMP(I)=Y(I)+H*(-FUN1(I)*(8.D0/27.D0)+2.D0*FUN2(I)
     *             -FUN3(I)*(3544.D0/2565.D0)+FUN4(I)*(1859.D0/4104.D0)
     *             -FUN5(I)*(11.D0/40.D0))
70    CONTINUE
      ARG=A+0.5D0*H
      CALL DIFEQS(ARG,YTEMP,FUN6)
      DO 80 I=1,N
         TEMP(I)=FUN1(I)*(16.D0/135.D0)+FUN3(I)*(6656.D0/12825.D0)
     *             +FUN4(I)*(28561.D0/56430.D0)-0.18D0*FUN5(I)
     *             +FUN6(I)*(2.D0/55.D0)
C
C     YTEMP WILL NOW CONTAIN THE VALUES OF THE
C     INDEPENDENT VARIABLES AT THE END OF THE STEP.
C
         YTEMP(I)=Y(I)+H*TEMP(I)
80    CONTINUE
C
C      THE R(I) TERMS ARE THE   (LOCAL ERROR)/H   ESTIMATES
C      FOR EACH OF THE VARIABLES.
C
      DO 90 I=1,N
         R(I)=FUN1(I)/360.D0-FUN3(I)*(128.D0/4275.D0)
     *     -FUN4(I)*(2197.D0/75240.D0)+FUN5(I)/50.D0+FUN6(I)*(2.D0/55.D0)
90    CONTINUE
C
C      DETERMINE THE MAXIMUM RATIO BETWEEN THE ESTIMATED ERRORS
C      AND THE MAXIMUM ALLOWABLE (DESIRED) ERROR.
C
      RATIO=0.0D0
      DO 100 I=1,N
         TR=DABS(R(I))/(RELER*DABS(YTEMP(I))+ABSER)
         IF(RATIO.LT.TR) RATIO=TR
100   CONTINUE
C
C     IF RATIO>1, THEN THE STEP MUST BE REJECTED, AND THE INTEGRATION
C     MUST BE ATTEMPTED AGAIN WITH A SMALLER STEP-SIZE.
C
      IF(RATIO.GT.1.D0) THEN
         IF(RATIO.GT.4096.D0) RATIO=4096.D0
         H=H*(HATMPT/RATIO)**HEXP
         IADJS=0
C
C     IF H HAS BECOME SO SMALL THAT IT IS LESS THAN THE
C     COMPUTER'S PRECISION WHEN COMPARED TO T, THEN RETURN
C     WITH AN ERROR CODE.
C
         IF(IFLAG.GE.0 .AND. DABS(H) .LE. 13.D0*U*DABS(A)) THEN
            IFLAG=5
            RETURN
         ENDIF
C
         GO TO 20
      ELSE
```

```
C
C     IF RATIO<=1, THEN THE REQUESTED ACCURACY WAS ACHIEVED.
C
C     ACCEPT THE VALUES OF THE STEP, AND RETURN IF THE ENTIRE
C     INTERVAL HAS BEEN COMPLETED.  OTHERWISE, PERFORM THE
C     INTEGRATION FOR THE NEXT STEP.
C
         DO 110 I=1,N
            Y(I)=YTEMP(I)
110     CONTINUE
        A=A+H
        IF(IADJS.EQ.1) THEN
           IFLAG=1
           H=HKEEP
           RETURN
        ENDIF
        IF(IFLAG.GE.0) THEN
            IF(RATIO.LT.6.5536D-04) RATIO=6.5536D-04
            H=H*(HATMPT/RATIO)**HEXP
            ELSE
           IFLAG=0
            ENDIF
         GO TO 10
          ENDIF
         RETURN
        END
```