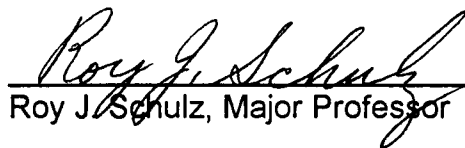
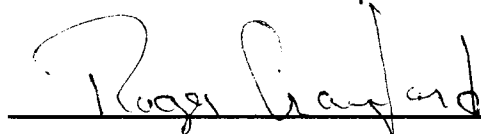


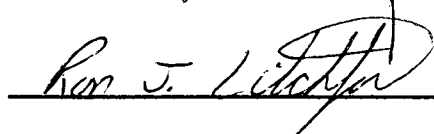
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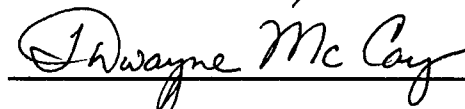
I am submitting herewith a dissertation written by Robert Wood McAmis entitled " A Numerical Study Of Fuel Droplet Ignition." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Mechanical Engineering.

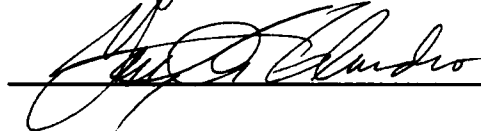

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A NUMERICAL STUDY OF FUEL DROPLET IGNITION

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Robert Wood McAmis

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ABSTRACT

The fundamental processes governing fuel droplet ignition in an oxidizing environment have been studied using a comprehensive numerical model. The study started with an existing time-accurate one-dimensional droplet combustion model which was modified to become a specific model capable of assessing droplet ignition in a hot oxidizing gas or simple ignition as a result of energy deposition (e.g. a spark) within the gas-phase. The baseline numerical model solves the time dependent one-dimensional spherically symmetric governing equations of mass, momentum, and energy within the gas-phase and is based on the Arbitrary Lagrangian Eulerian (ALE) numerical algorithm for the numerical simulation. This model was modified to include finite droplet thermal conductivity, droplet incident radiation, and simplified energy addition representative of a spark source to investigate the physical processes occurring near ignition. An energy conservation equation for predicting the temperature distribution within the liquid droplet has been added to define the temporal and spatial temperature gradients inside the droplet including the droplet surface temperature. Gas-phase radiation heat transfer to the droplet has been included in the formulation. Ignition criteria have been defined and implemented in the assessment of droplet ignition. Model results have been compared with analytical theory. In addition, the model has been demonstrated by comparing its predicted results to experimental data, and the comparison is good. As a result, the model has been validated over a limited range of hydrocarbon fuels for various gas-phase ambient conditions, based on appropriate chemical kinetic reaction mechanisms. The effects of droplet finite thermal conductivity, incident

radiation and chemical kinetics on ignition processes have been assessed. Results show that finite thermal conductivity and radiation heating of the droplet reduce ignition delay. In addition, the numerical results in the present study show that the assumption that droplets have infinite conductivity and no radiation effects may produce results which underestimate ignition delay. Physical flow field parameters have been defined which correlate very well with ignition. Chemical kinetics have a profound effect on ignition delay, which was shown numerically using a detailed chemical kinetic mechanism for methanol in air. This calculation showed that experimental pre-exponential and activation energy values must be better defined for use in modeling ignition of hydrocarbon diffusion flames. The potential usefulness of the model for spark and laser ignition are discussed.

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NOMENCLATURE

a	Stoichiometric coefficient of the reactants
afm	Mass evaporation rate
A	Pre-exponential frequency factor in the Arrhenius rate expression
Ar	Arrhenius Number, $E_a/(R_u T_{max})$
b	Stoichiometric coefficient of the products
B	Spalding transfer number
C	Concentration
C_p	Specific heat
d	Droplet diameter
D	Diffusivity
Da	Damkohler number (ratio of diffusion time to reaction time)
E_a	Activation energy divided by R_u
F	Moles of fuel
g	Gibbs Free Energy (h-Ts)
h	Enthalpy
i	Oxidizer-to-fuel mass ratio
I	Internal Energy
k	Reaction rate
k_f	Forward reaction rate
k_b	Backward reaction rate
K_c	Equilibrium constant based on concentration
K_p	Equilibrium constant based on pressure

L	Ratio of specific latent heat of evaporation and specific combustion heat release
Le	Lewis Number (ratio of rate of diffusional energy transport to rate of diffusional mass transport, α/D)
m	Mass
O	Moles of oxidizer
p	Pressure
Pr	Prandtl number (ratio of rate of momentum transport to the rate of energy transport, ν/α)
Q	Heat source term
r	Droplet radius
R_u	Universal gas constant
s	Entropy
Sc	Schmidt number (ratio of rate of momentum transport to rate of mass transport, ν/D)
t	Time
T	Temperature
u	Velocity
W	Molecular weight
X	Distance
Y	Species mass fraction
α	Thermal diffusivity
β	Evaporation coefficient
δ	Dirac Delta Function
X	Species mole fraction
ϵ	Absorption coefficient

ϕ	Equivalence ratio
η	Temperature exponent
λ	Thermal conductivity
μ	Dynamic viscosity
ν	Kinematic viscosity
θ	Parameter : $T'_{\infty} - T'_s + L$
ρ	Density
σ	Stefan-Boltzman constant
Σ	Stress tensor
τ	Nondimensional time
ω	Nondimensional droplet radius
ψ	Accumulation parameter used to define ignition
Δh_c	Heat of combustion
Δh_r	Heat of reaction
Δh_v	Heat of vaporization

Subscripts

b	Backward reaction rate
B	Boiling point
c	Related to chemical generation
d	Droplet surface
F	Fuel
f	Forward reaction rate
g	Gas
i	Ignition
I	Internal Energy

k	Species index
l	Stoichiometric equation reaction index
L	Liquid
N	North node point
o	Oxidizer
p	Physical delay
P	Discretized Node
rad	Radiation
s	Droplet surface
S	South node point
st	Stoichiometric
wb	Wet bulb temperature
0	Initial condition
∞	Infinity

Superscripts

c	Chemical source term
m	Time index
'	Nondimensional
"	Area Flux
""	Volumetric Flux

CHAPTER I

STATEMENT OF THE PROBLEM

1.1 Existing Research Needs of Conventional Aerospace Propulsion Systems for Ignition Models

Although the liquid rocket engine and turbine engine have very different roles, these propulsion systems have similar requirements for advanced, optimized combustors. Both rocket and gas turbine combustors adequately inject liquid propellant streams such that fast, efficient breakup, atomization, evaporation, mixing, and combustion occurs. Although some bi-propellant liquid rocket engines use gaseous fuels, most current systems use heterogeneous fuels, that is at least one liquid and one gas propellant. Most turbine engines use a liquid fuel, typically JP-4, JP-5, or JP-8, sprayed into a swirling air flow inside a perforated combustion chamber.

One issue common to both the liquid rocket engine and the turbine engine is ignition, flame spreading and subsequent flame holding in the vicinity of the fuel source within the combustor. Ignitability of liquid fuels within the combustor at varying operational conditions is of critical importance. The ignition characteristics of liquid rocket engine systems varies with propellant supply pressure, propellant supply velocity, propellant supply temperature, propellant injectant pattern, ignition source location, ignition source level and duration, combustor geometry, and initial combustor temperature and pressure. Significant effort has been devoted to environmental testing of full scale rocket

and jet engine propulsion systems to study, characterize, or validate their ignition processes.

Techniques for establishing ignition within liquid rocket engines vary with the on-board propellant supply system and the propellants used. Additionally, the ignition process may comprise a sequence of events leading up to and including pre-burner ignition instead of simple ignition of the main combustion chamber fuels. For example, the ignition sequence for a typical turbopump-driven liquid rocket engine cycle consists of the following steps: (1) turbine pumps are started using supply line pressure or pressurization from a solid propellant start cartridge, (2) propellant supply system pressure builds up to a preset level, (3) propellant is discharged into the gas generator (i.e., turbine hot gas supply), (4) gas generator propellants are ignited, (5) main combustion chamber propellant discharge valves open and allow propellant flow into the main combustion chamber, and (6) the main combustion chamber fuels are ignited.

Ignition in rocket chambers is typically a two-stage process. A spark energy source ignites either a gaseous mixture of fuel and oxidizer (e.g., RL10) or a fuel-lean multiphase mixture enclosed in a separate combustion chamber producing a torch directed into the main combustion chamber centered in the injector plate. Ignition of the main combustion chamber mixture then occurs from the torch.

Ignition in gas turbine engine combustors is required during routine ground level startup and for non-routine relighting at altitude. Turbine engine combustor ignition is accomplished when fuel injected into an established air stream is lighted off by a spark ignition source. A critical issue for turbine engines, also related to transient ignition and combustion, is flame stability.

Flame stability assessments require that flame holding and flame lift be investigated. Like ignition, the processes that govern flame spread also govern flame stability.

Ignition of heterogeneous fuels has historically received and continues to receive research attention. Prior to 1961, the H-1 rocket engine using propellants RP-1/LOX (used in the Saturn and Atlas vehicles) was tested at AEDC¹ to determine ignition characteristics at altitude. In 1967, the Lunar Module Ascent and Descent Engines using propellants N₂O₄/AZ50 were tested² to define ignition characteristics at altitude. Later, in 1970, the J-2S engine, using propellants LOX/LH₂, was tested at AEDC³ in part to investigate ignition behavior at altitude. More recently, NASA has investigated requirements for Space Shuttle Main Engine (SSME) altitude starts. The SSME has not previously demonstrated altitude start capability. Furthermore, the USAF continues to substantiate ignition light / no-light altitude-Mach number conditions for the F100 and F110 engines and will perform these tests for the F119 engine.

In summary, commercial companies and government agencies still have a strong requirement for assessing and modeling ignition in liquid rocket and gas turbine engines. Therefore, a fundamental study of the physical processes which influence and control ignition in systems with heterogeneous propellant mixtures is required. At present, computational technology has progressed to the point that a comprehensive numerical simulation of ignition is possible, under certain restrictions, which can serve as a predictive tool⁴ for the assessment of ignitability. It is the intent of the present research study to establish such a numerical model and use it to develop an understanding of the basic fundamentals of fuel droplet ignition. This knowledge may then be applied

¹ Numbers refer to similarly numbered references in the Bibliography.

to overall combustor systems including those with multiphase sprays to predict or assess their ignition and flame holding behavior.

1.2 Proposed Study of Hydrocarbon Fuel Droplet Ignition

Droplet ignition represents the fundamental ignition process within conventional spray combustion systems. Droplet ignition has been studied experimentally for many years and droplet ignition theories are diverse and widespread. Ignition theories have commonly employed quasi-steady burning assumptions with simplified one-step chemical kinetics to represent complex multi-step chemical reaction processes. Quasi-steady theories do not account for all physical processes occurring prior to ignition. A few time-accurate schemes have been proposed, however, details of their development are insufficient to gain adequate knowledge of their full capability. Therefore, the relative importance of heat transfer and mass transfer processes on ignition is not well understood.

Two simplifications routinely used in theoretical approaches to ignition modeling are the assumptions of infinite droplet thermal conductivity and one-step chemical kinetics. The lack of a detailed droplet temperature model in the theoretical formulation is often justified by the assumption that, in the experimental environment, radiation will provide additional heat to the droplet or internal flow circulation will maintain the droplet internal temperature near that at the droplet surface. As a result, theoretical models based on infinite conductivity, without radiation, have been assumed capable of providing reasonable predictions of ignition delay. Attempts have been made to adjust one-step chemical kinetic mechanisms using semi-empirical exponential or pre-

exponential corrections to match experimental data. However, these corrections force predictions to remain within empirical regions beyond which results have not been substantiated.

Therefore, a need exists to establish and demonstrate a computer model of ignition which is truly time accurate and which may be used in conjunction with detailed physical sub-models to assess the importance of the above described simplifications in a droplet ignition and combustion process. Such an approach would provide an easy mechanism for evaluating parametric variations in submodels as the empirical knowledge base of physical submodels improves, for example, chemical kinetic mechanisms. The inclusion of appropriate chemical kinetic models is important for both autoignition and forced external ignition processes, such as spark and laser inductions. However, the feasibility of applying detailed chemical kinetic mechanisms to numerical simulations has not been sufficiently demonstrated.

Much work has been performed to examine thermal droplet ignition both experimentally and theoretically. The importance of ignition is obvious; the complexities are not. Ignition of droplets is known to be affected by liquid droplet properties as well as the ambient conditions. Most work related to thermal ignition has identified a weak link in developing adequate theory, namely, the finite rate chemical reaction mechanism. Similarly, advances in laser ignition now provide the potential for an ambient environment to possess significant atomic and electronic species, as well as ionized species that can affect the ignition process. For example, the production of radicals will be sensitive to molecular oxygen in the path toward ignition.

Positive ions or negative ions (electronically excited ions) in the oxidizing environment may be produced in the electric spark plasma, plasma jet, laser

induced spark, or laser photochemical pyrolysis. In addition, ions have been measured in cool flames of hydrocarbon fuels preceding ignition.

With this in mind, it appears logical to begin to lay the foundation for a critical examination of detailed issues of hydrocarbon fuel droplet ignition based on a rigorous mathematical simulation which incorporates complete models of heat, mass, and chemical kinetic transfer processes.

1.3 Scope of Study

The objective of this research was to establish an appropriate numerical model of single droplet ignition processes for hydrocarbon fuel droplets, and use the model to study the relative effects of heat and mass transfer on ignition of a fuel droplet in a hot oxidizing environment. This study began with acquisition of a model for droplet combustion developed by Los Alamos in 1980. Next, improvements were made as necessary to increase overall model applicability to predict fuel droplet ignition. As part of the research study, the existing code was installed on both a personal computer and a workstation. In addition, an input file and output files were established to facilitate analysis, execution and graphical postprocessing. A baseline model was established and evaluated by comparing model-predicted results to quasi-steady theory for droplet evaporation and burning. Shortfalls were identified in the baseline model and modifications were made. After the model was validated with quasi-steady results, numerical experiments were performed to validate the full, time-dependent features of the model. Proper evaluation required the definition of an ignition criteria in order to compare model results with available test data. Once validated, the model was used to assess the effects of heat and mass transfer

processes on ignition. Specifically, the relative importance of droplet finite conductivity and absorbed incident radiation on ignition processes was evaluated. In addition, the feasibility of using a detailed chemical kinetic mechanism in the model was studied using methanol fuel in air. Results obtained using the liquid droplet ignition model show that detailed chemical kinetics should be used in theoretical models for autoignition, electric spark, laser induced spark, or photochemical laser ignition. All of the results of this study are based, however, on a numerical model of a single spherically symmetric fuel droplet in a stagnant ambient oxidizing environment. Future research must address the effects of convected multi-droplet environments on ignition processes.

1.4 Method of Approach

The first goal of the research was to establish a computational technique to numerically study single droplet ignition. The computational fluid dynamics (CFD) code, CON1D,⁵ was acquired and made operational on a local computer host. Developed by the United States Department of Energy's Los Alamos National Laboratory, this code is a one-dimensional version a family of multiphase codes used to compute spray combustion phenomena: this family includes the time-dependent two-dimensional CONCHAS-SPRAY,⁶ and three-dimensional KIVA II⁷ codes, and the Rocketdyne derived version called the ARICC⁸ code. CON1D solves the time-dependent finite-differenced equations of motion of a spherical liquid droplet surrounded by a chemically reactive mixture that forms the (infinite) ambient environment.

Based on a literature review, limitations and restrictions in the physical models were identified. As a result, the energy and heat flux equations for finite droplet conductivity and droplet incident radiation were reformulated and incorporated into a modified version of CON1D.

The model's capability for predicting quantitative ignition characteristics was verified through comparisons with experimental data existing within published literature. Calculated results of ignition delay were compared to experimental data. For this initial application, one-step chemical kinetics was assumed. This allowed timely verification of the code capabilities and enabled the study to proceed toward other objectives.

The effects of droplet finite thermal conductivity and absorbed incident radiation on ignition delay were assessed for several hydrocarbon fuels. The overall methodology was developed for application with detailed chemistry to predict spark-induced ignition of selected hydrocarbon fuel droplets. This study was accomplished by modeling the kinetics of the hydrocarbon fuel, methanol, reacting in air. A detailed chemical kinetic mechanism, including reaction rates for atomic species, were available for this mixture. The effect of this detailed mechanism on predicted overall heat and mass transfer processes and on subsequent ignition was assessed in comparison to a simple or reduced mechanism. Comparison of the calculations with detailed experimental data was not made because of the lack of data. However, shortfalls and existing needs for experimental data were briefly defined.

As a final product of this research, this investigation provided a computational methodology to assess parametric effects of various physical conditions on ignition of liquid fuel droplets in a highly reactive oxidizing environment. An extension of this tool to account for the effects of high ambient

pressure and multicomponent hydrocarbon fuels is briefly discussed. The potential usefulness of the numerical droplet ignition model for application to predicting multi-dimensional flow ignition and laser ignition is also briefly discussed.

1.5 Outline of the Dissertation

The organization of the dissertation is as follows. First, a detailed survey of the literature on ignition is presented. This search is quite comprehensive and serves to assess the status of ignition modeling and experimental ignition research performed relative to droplet and spray ignition of laboratory and practical combustors. As a result of this literature survey, specific limitations of ignition models are defined and the focus of the dissertation is resolved. Next, the conservation equations and numerical approach of the baseline droplet combustion model is reviewed. Then, improvements to the ignition model are defined. With these modifications complete, the numerical model results are compared with quasi-steady combustion theory and experimental data. In addition, the effects of droplet conductivity and incident radiation of ignition processes are evaluated. Next, alternate ignition criterion are defined by observing parametric variations during ignition. Then the effects of detailed chemical kinetics are evaluated. As a demonstration, the numerical simulation is applied to calculating spark ignition. Finally, research conclusions and recommendations for continued work are addressed.

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Complexities in Combustor Flow Fields

Combustion processes within complex flow environments such as those generated by an injector in a liquid rocket engine combustor chamber (Fig. 2.1)* are heavily dependent on many physical laws derived from the conservation of mass, momentum and energy, including chemical kinetics and complex vortical flows. There is a close coupling (Fig. 2.2) between the rapid chemical kinetic rates which vary with temperature and the dynamics of an expanding premixed system or the dynamics of turbulent mixing in an unmixed system. Therefore, the combustion processes may be dominated either by the molecular chemical kinetics or fluid dynamics. Ignition processes within the combustor are sensitive to turbulence and kinetics which occur at the same time scales as that of ignition.

To fully assess the current status of ignition research in combustor and injector systems, a wide range of literature was reviewed. Ignition in droplets, droplet arrays, sprays, laser-induced systems, and practical combustion systems were dominant areas of research. The relevant historical work related to ignition within turbine engine or liquid rocket engine combustors can be grossly divided into the following categories: (1) Practical Combustor Modeling, (2) Droplet

* Figures are found in Appendix A.

Combustion, (3) Premixed Ignition, (4) Droplet Ignition, (5) Spray Ignition, and (6) Chemical Kinetics.

2.2 Practical Combustor Modeling

Significant research on the ignition of injectant fluids has been accomplished primarily in support of three practical systems: turbine engines, liquid rocket engines, and internal combustion engines. Theoretical models have evolved from steady-state and quasi steady-state theories, to uncoupled gas-liquid phase-transient and fully-coupled-transient formulations of the governing equations.

Combustion within turbine engine combustors⁹ can occur over a wide range of static pressures and temperatures. Therefore, design and performance analysis requires a firm understanding of reaction kinetics, fuel atomization, and turbulent mixing.¹⁰ Experimental studies on turbine engines were performed as early as 1953 to determine the fuel volatility characteristics on minimum spark energy for a single tubular combustor.¹¹ Additionally, studies were conducted to assess combustor lighting as a function of pressure, temperature, velocity, and geometry.^{12, 13} Before practical finite-difference, Navier Stokes-based combustor models existed, combustor models were based on droplet evaporation, stirred-reactor theories,¹⁴ multi-step kinetics and turbulent mixing.^{15 - 18} Mellor reviewed modular and finite difference gas turbine combustor models.¹⁹ Finite difference formulations have been attempted as well.^{20 - 23}

The designs of the first German A-2 rockets in 1934 were accomplished through an understanding of the fundamental laws of nature but primarily through experimental trial and error. The first theoretical combustor models

were largely hypothetical because of the limited capability to investigate the complex flow regimes in a spray combustor. Nonetheless, the fundamental processes of spray combustion in a liquid rocket engine combustor were known to exist²⁴ at an early date. Pertinent issues of droplet combustion,^{25, 26} spray combustion,²⁷ carbon formation,²⁸ combustion stability,^{29 - 34} and ignition³⁵ were being investigated as early as 1946. Many one-dimensional models for heterogeneous combustion have been proposed.^{35 - 45}

Initial models of rocket combustor operation were based on evaporation-limited droplet combustion theory. These were beneficial in estimating the combustor length required to achieve complete droplet spray evaporation.^{46 - 52} Sutton and Hines developed a three-dimensional model describing two phase flow behavior within a liquid rocket engine combustor.⁵³ A similar approach was proposed by Webber and Gaubatz.⁵⁴ However, these approaches were limited in that they neglected turbulence and did not consider droplet-gas coupling, real gas effects, or dense flow regime behavior.

JANNAF proposed a methodology for assessing liquid rocket engine chamber pressure, thrust, and attendant specific impulse.⁵⁵ The methodology is based on an analytical model of a rocket engine in which the major hardware sections (reservoir, feed system, and thrust chamber) are defined in terms of control volumes with interfaces between these volumes. The approach is limited to steady-state, axisymmetric internal flow nozzles, small scale viscous effects, vacuum performance, and noncondensing liquid or solid species. Furthermore, injector influences on combustor performance, such as atomization, vaporization, and mixing, are not included.

Historically, simulations of rocket combustor flows^{56 - 66} have decoupled the critical fluid flow processes. While these codes are adequate for predicting

thrust, the numerical methodologies used are those available prior to recent advances in large-scale, finite difference modeling. Recent attempts in combustor modeling^{67, 68} have utilized finite difference schemes for solutions of the fluid-dynamic equations and coupled them with rigorous models for chemical kinetics and combustion. However, droplets are often treated as an additional species of the continuous medium and characteristics of the spray must be supplied to the model as inputs.

Partial⁶⁹ and full Navier Stokes solvers have been developed to assess heterogeneous flows.^{7, 70 - 72} KIVA-II⁷ is a comprehensive solver in a series of multi-dimensional codes that have been produced by the Department of Energy's Energy Conversion and Utilization Technologies program for the assessment of internal combustion engines. KIVA-II solves the unsteady equations of motion for a turbulent, chemically reactive mixture of ideal gases, coupled to the equations for a single-component vaporizing fuel spray. The gas-phase solution procedure is based on a finite volume method called the Arbitrary Lagrangian Eulerian (ALE) method.

The liquid rocket engine (LRE) community has used KIVA-II as the basic combustor flow solver and has incorporated combustor simulation enhancements by including improved models of atomization, combustion, and two phase fluid modeling.

Significant progress modeling liquid rocket engines has been made by NASA Marshall through contracts to Rocketdyne and the University of Tennessee. The latest contribution to modeling complex flows in LRE combustors having coaxial injectors has been developed by Liang^{73 - 78} for application to the Space Shuttle main engines with coaxial injectors. The code, named the Advanced Rocket Injector Combustor Code (ARICC), was derived

from the KIVA-II flow code and incorporates the following features: Lagrangian tracking of droplets, full chemical kinetics, a fractional volume-of-fluid (VOF) description of liquid jet injection, and turbulence. Code success has been demonstrated with applications to Space Shuttle combustor hardware.^{71, 79 - 81}

Concurrent with Liang, experimental and theoretical work has been accomplished for combustors having like-on-like impingement-type injectors discharging two separate liquids.^{82, 83} Larosiliere and Jeng⁸³ developed a model using KIVA-II as the basic flow solver and incorporated appropriate changes to account for (1) two liquid species, (2) impingement and coalescence of two continuous liquid streams, (3) breakup of liquid streams, (4) droplet combustion, and (5) droplet and chamber wall interaction. Note that the effect of the liquid volume on the gas phase was not accounted for in this model.

Theoretical modeling of ignition processes within practical combustors using finite difference techniques is limited. Nonetheless, applications of finite difference techniques to simple systems have been accomplished by Aggarwal et al.^{84 - 86} Ignition is often a process which is assumed to occur regardless of the given heat and mass transfer processes.

2.3 Historical Issues in Droplet Combustion

Droplet combustion in a quiescent atmosphere is a diffusion controlled process and can therefore be classified as a type of diffusion flame. The rate at which the droplet evaporates and burns is controlled by the rate of heat transfer from the flame front to the fuel surface and the oxidizer diffusion rate from the ambient environment to the flame front. As with gaseous diffusion flames, chemical processes are assumed to occur so rapidly that the burning rates are

determined solely by mass and heat transfer rates (Fig. 2.3). Although this assumption is not reasonable in many physical systems, it provides a basis for evaluation. The basic droplet model was formulated in 1952 by Godsave²⁵ and Spalding²⁶ as a first step to understand physical processes which contribute to the size change of a liquid drop in a spray. This model prescribes that the droplet diameter squared decreases linearly with time. Droplets in laminar convective streams do not behave like those in quiescent atmospheres. In fact, the droplet burning rate in laminar convected streams follows a $d^{3/2}$ burning rate law.⁸⁷

Significant work has focused on the affect of initial droplet temperature and environmental pressure on droplet combustion behavior.^{88 - 96} Comprehensive reviews of droplet combustion have been conducted by Williams,⁹⁷ Faeth,⁹⁸ Law,⁹⁹ and Sirignano.¹⁰⁰

2.4 Fundamentals of Premixed Ignition

Ignition is a transition from a nonreactive to a reactive state in which external stimuli lead to thermochemical runaway followed by a rapid transition to self-sustained combustion. Ignition is a function of many parameters which include mixture composition, pressure, pressurization rate, duration of heating, total energy deposited in the system, initial radius of energy deposition, ambient oxidizer concentration, velocity of the convective stream, turbulence scale and intensity, thermal transport properties of the material being heated, catalysts, and inhibitors.^{87, 101 - 106} In any theoretical model formulation, a definition of the onset of ignition must be established and care must be taken to assure

comparability to experimental data. In some cases, pressure is used as a measure of the extent of reaction.

Ignition is accomplished in three ways: (1) spontaneous chain ignition, (2) spontaneous thermal ignition, and (3) forced ignition. Semenov introduced the spontaneous chain ignition theory in 1927 and the thermal ignition theory in 1928.¹⁰⁷ Spontaneous chain ignition occurs for a premixed combustible mixture when the temperature of the surroundings is increased sufficiently to allow the rate of chain branching, k_b , to exceed the rate of chain termination, k_t . As observed by Semenov, during the initial period of a chain reaction, the chain carrier concentration increases exponentially with time when $k_b > k_t$.

Thermal ignition occurs when the rate of thermal energy released by chemical reaction is greater than the rate of thermal energy dissipation typically to the surrounding system (i.e., storage vessel walls).

Forced ignition is a concept which provides an energy input into an established reactive mixture. Mechanisms used to initiate forced ignition include sparks, pilot flames, flowing hot gases, and hot metal parts. The spark is the first and most prevalent form of forced ignition and has been studied extensively due to its application within the internal combustion engine.^{102, 108} The literature indicates that the ignition of a reactive mixture by a spark is a function of spark electrode gap,^{109, 110} spark intensity,^{111 - 121} spark duration,¹²² spark kernel,^{123 - 127} and initial conditions of the reactive mixture.^{128 - 135}

Much of the work performed investigating ignition of premixed gases provides the basis for understanding heterogeneous or non-premixed mixture ignition.

2.5 Droplet Ignition Theory, Simulation, and Experiment

2.5.1 Overview

General reviews of droplet combustion, including droplet ignition, have been written by Williams,⁹⁷ Faeth,^{98, 136} Law,^{99, 137} and Sirignano.¹⁰⁰ These reviews and much of the contemporary theoretical and experimental work have focused on autoignition of hydrocarbon droplets in air as a function of droplet diameter and ambient pressure and temperature. Droplet ignition may be categorized as thermal (autoignition) or chemical (usually forced with spark, plasma, or laser). Chemical ignition differs from thermal ignition in that the oxidizing environment contains radicals which promote reactivity of the fuel and oxidizer, thus shortening the chemical delay compared to the thermal droplet ignition.

As indicated by Faeth,¹³⁶ the primary objective of droplet ignition studies has been to determine the time required for a stable envelope flame to appear after the droplet has been exposed to an oxidizing environment. The ignition of a droplet is typically considered to be a two-stage process consisting of the droplet heat up followed by a chemical delay for the reaction occurring in the gaseous mixture between the vapor phase of the inflammable liquid and the oxidizing environment. Although these two stages can overlap, a two stage model is often used.¹³⁸ The first stage, droplet-heat-up, is a function of heat transfer processes of conduction within the droplet and convection and radiation at the boundary. The second stage, gas phase chemical reaction, is a function of molecular composition of the fuel and the temperature at which the reaction is taking place. Chemical reaction between the fuel and oxidizer begin before the end of the

physical delay period (i.e., droplet heat-up) and, therefore, the two periods overlap in time. As a result, the rate of droplet ignition is a function of both heat and mass diffusion and chemical kinetics and is ultimately controlled by the one which is dominant in the consumptive environment.

In general, early ignition models^{96, 139 - 143} incorporated the following assumptions: one-step global kinetics, quasi-steady gas phase (i.e., the gas phase structure adapts instantly to imposed boundary conditions at the drop surface and the surroundings), and spherical symmetry with no forced or natural convection effects.¹³⁶

Law established a fundamental technique for predicting ignition employing asymptotic analysis at the limit of large activation energy.¹⁴² This analysis was based on the quasi-steady assumption allowing the gas phase to be separated from the analysis of droplet heat-up. As described by Faeth,¹³⁶ the gas phase analysis yields the droplet gasification rate as a function of Damkohler number at fixed ambient conditions for various fuel vapor mass fractions at the droplet surface (Fig. 2.4). The Damkohler number is defined as the ratio of a characteristic diffusion time and characteristic reaction time. The locus of ignition is determined by conditions where the tangent to the gasification rate curve is vertical. Using these results, ignition delay can be determined by computing the droplet heat-up time and adding to it the time required to reach the locus of ignition conditions. As shown by Faeth,¹³⁶ the trajectory of the droplet heat-up process can also be plotted as a function of the Damkohler number. For example, as the droplet heats up, the surface film concentration of fuel increases while the Damkohler number decreases, since the droplet diameter becomes smaller due to evaporation. Assuming a high Damkohler number, the droplet reaches the ignition locus before heat-up is complete and a

stable envelope flame is formed. For low Damkohler numbers, the droplet reaches its wet bulb state having a fuel vapor concentration below the ignition locus and continues to evaporate through its lifetime without igniting.¹³⁶

Autoignition of a fuel droplet in a hot oxidizing environment involves the following mechanisms: heat-up of the droplet due to convective heat transfer from the ambient environment to the droplet surface; internal heat-up due to conduction heat transfer within the droplet interior; droplet vaporization and fuel vapor accumulation in the vicinity of the droplet surface; and chemical kinetic reactions of the species involved. Autoignition of a hydrocarbon involves a two-step process at low temperatures and pressures just above atmospheric. The first stage begins with the start of reaction to cool flame conditions. The second stage extends over a period from the sudden but small temperature rise in the cool flame reaction to the sudden and large temperature rise in the explosive reaction. At high temperatures, autoignition of a hydrocarbon may proceed as a one-step process without the presence of the cool flame.

Spark ignition of a fuel droplet in an oxidizing environment involves the following mechanisms: an electric spark generates a region of high temperature, heat is transferred to the surrounding ambient environment, temperature in the adjacent layers of ambient gas rises and invokes chemical reactions assuming the mixture is flammable, a combustion wave is formed and propagates radially outward from the original source. Continued propagation of the flame is contingent on generating sufficient heat to compensate for heat loss occurring in the surrounding unburned gas. Development of the spark kernel itself is associated with numerous phenomena which include very fast transformation of energy from the spark electrodes, electron avalanche, streamer formation, radiation, photoionization, electron and positive ion collision, ionization, thermal

ionization, dissociation, fast diffusion, chemical reactions, and formation and emission of a shock wave.¹⁴⁴ Droplet ignition in this environment is contingent on sufficient initial temperature to provoke and maintain proper evaporation to provide a combustible gaseous mixture through which the spark kernel can propagate.

Plasma Jet Ignition (PJI) is typically accomplished through the generation of a plasma in a small containment volume using an electric spark. Upon generation, the plasma jet is directed into a larger combustion chamber containing a reactive mixture. Ignition within the main chamber is accomplished as a result of chemical chain branching due to the existence of radicals within the plasma jet. These radicals are controlled by controlling the gas composition in the preplasma mixture.

Laser ignition is not a sufficiently descriptive term to denote mechanistic processes. At least four types of laser ignition are in use: (1) thermal ignition, where gases are heated by the laser to the autoignition temperature, (2) photochemical ignition, where single or multiphoton photolysis is used to create a pool of reactive radicals throughout the activated volume, (3) nonresonant spark ignition, where sparks are formed by dielectric breakdown of gases in the laser focal volume, and (4) resonant spark ignition, where atomic and molecular resonances are involved in the efficient multiphoton ionization production of seed electrons to initiate gas breakdown. The two most common processes used to ignite liquid fuel sprays are photochemical ignition and laser induced spark (LIS) ignition. With the exception of the shock wave effects on the droplet boundary induced by LIS, these processes are operative on the gaseous ambient mixture. LIS is primarily a thermochemical process where the generated spark kernel and the shock wave provide sufficient heat to ignite the

mixture. LIS ignition is more successful in a gaseous mixture than when focused on the droplet.¹⁴⁵ Photochemical ignition involves the generation of oxidizer radicals to precipitate chemical reactions with the fuel.

2.5.2 Droplet Ignition Modeling

Theoretical models have been developed which concentrate on each stage of ignition.^{137, 142, 146 - 150} To properly account for the influences of finite-rate chemistry on ignition, several approaches have been used. Known chemical reaction rates may be employed in the full set of conservation equations. The complexities of diffusion flame problems have led researchers to simplify chemical kinetics and employ a one-step approximation to reactions. With simplified kinetics, two perturbation methods have been used to improve understanding and to quantitatively match experimental data. These are the Damkohler-number asymptotics and activation-energy asymptotics. The Damkohler number is the ratio of a diffusion time to a reaction time. Activation-energy asymptotics appear to be more useful for the study of ignition. Activation-energy asymptotics lead to results valid for all Damkohler numbers, and therefore results of Damkohler-number asymptotics may be extracted from those of activation-energy asymptotics.

Ignition and extinction of a diffusion flame around a droplet have been represented in terms of the maximum flame temperature and the Damkohler number as derived from the mass and energy conservation equations. As the Damkohler number is increased, the system moves along the lower branch (Fig. 2.4) until it reaches ignition, at which point the solution must jump to the upper branch representative of diffusion burning. As the Damkohler number is

decreased, the system moves along the upper branch until the solution must jump to the lower branch at the point of extinction.

In most thermal ignition analyses of a fuel droplet, it is typically assumed that a spherically symmetric droplet is resident in a hot oxidizing environment. As a result, heat and oxidant species are transported radially inward toward the droplet surface while fuel vapor is transported radially outward. At sufficiently high temperatures, reaction between fuel vapor and oxidant will begin. Typically, a one-step chemical reaction is used as an approximation to the actual multi-step reactions. Gas phase quasi-steadiness is typically used since liquid surface boundary and thermodynamic properties change at a rate much slower than the gas properties.

Fendell¹⁵¹ examined the effects of simplified chemical kinetics on the analytical description of ignition and extinction of initially separated reactants. Perturbation techniques were applied to the exact conservation equations for combustion near frozen and near equilibrium conditions. Results were defined in terms of the Damkohler similarity group, Da , the ratio of the time for a fluid particle of reactant to traverse the combustion zone to the time for a reaction-inducing collision to occur. Small values of Da indicate diffusion dominance while large values indicate reaction dominance. Specifically, for small Da , the reactants convect heat away without releasing the energy stored in their chemical bonds. For large Da , a narrow region of chemical activity exists. For infinite Da , the region is reduced to a surface of discontinuity (e.g., the thin-flame kinetics of Burke and Schumann). For intermediate Da , analysis showed that a numerical solution describing the burning of moderate intensity joins the upper and lower asymptotic limits. Fendell suggested that the sudden transition of the system between the asymptotic limits for Da accounted for ignition and

extinction. As Da increased from zero, the system ignited when it jumped from the weak branch to the strong branch. Likewise, as Da decreased from a large value, the system was extinguished when it jumped from the strong branch to the weak branch.

Physically, the nonexistence of solutions implies that the chemical reaction rate cannot balance the heat transport rate.¹³⁷ Therefore, beyond the ignition point, chemical heat is generated so fast in the reaction region close to the hot, oxidizing ambient environment that it cannot be transported away in a steady manner. This leads to an increase in the reaction zone temperature and further increase in the reaction rate. Arrhenius kinetics provide sensitive high speed feedback to the process.

Peskin and Wise¹⁴⁰ developed a linearized flame surface model which accounts for finite rate chemical kinetics. Nonlinear chemical reaction rates were approximated, allowing the solution of modified conservation equations over the entire range of reaction rates. With this approach, temporal mass burning rates were computed providing evaporation rates at both the evaporative limit (no reaction) and at the infinite reaction rate limit (the classical droplet burning case). Ignition was defined as a rapid transition from kinetic to diffusional combustion occurring at a temperature defined by the following relation:

$$T_i = \frac{Ea/R_u}{\ln(C_1/C_2)} [Y_{o,\infty} + 1] \quad (2-1)$$

where Ea is the overall activation energy, C_1 and C_2 are nondimensional reaction parameters, and Y_o is the oxidizer concentration. - This model provides a continuous description of droplet behavior from the kinetic to the diffusion

controlled region but can only be used in the qualitative sense because in the vicinity of ignition it underestimates the extent of chemical reaction. In going from evaporation to combustion, the system will pass through a characteristic value of reaction rate at which heat is no longer required from the environment but rather is supplied to it. This corresponds to a transition from kinetics-controlled to diffusion-limited regime.

Peskin et al.¹⁴¹ continued to apply this theory to fuel droplets in an oxidizing environment. Variations in the ambient concentration of the oxidizer with temperature showed a lower limit for oxidizer concentration below which ignition cannot occur at any ambient temperature. This model also showed that for a given reaction rate there existed a lower limit temperature for ignition at any ambient oxygen concentration. Plotting the mass burning rate as a function of ambient temperature, there existed regions where a discontinuous change in the rate occurred corresponding to the transition from kinetic controlled combustion to diffusional controlled combustion. This discontinuity was interpreted as ignition.

Faeth and Olson¹⁵² developed an ignition model solving the governing equations of mass, species (fuel and air only), and energy in the boundary layer surrounding the liquid droplet by both direct integration and numerical integration. Direct integration resulted in a solution which was a function of transient conditions at the droplet surface. This procedure required that properties be assumed constant, thus introducing significant error. Results obtained using numerical integration were more reasonable. Ignition was determined by tracking an undefined intermediate species, ψ , and assessing its value compared to one. Above a value of one, ignition was said to have occurred.

$$\psi(r, t) = \frac{X_i(r, t)}{X_{i,c}} = \int_0^t C_1 p^{C_2} \phi^{C_3}(r, t) \exp\left[\frac{-Ea}{R_u T_g(r, t)}\right] dt \quad (2-2)$$

where C_1 , C_2 , and C_3 are empirically derived values for the specific fuel under investigation.

Kassoy and Williams¹⁵³ substantiated the analysis technique of Peskin et al. in the near-equilibrium limit using matched asymptotic expansions of the classical equilibrium equations defining the diffusion zone of a nonpremixed system. Perturbations away from chemical equilibrium were used to model finite rate chemistry with a one-step reaction and appropriate corrections. Diffusion zone perturbations were achieved with variable nonunity exponential decay corrections (known as model reaction orders) to the one-step finite rate equation in use. Results indicated that the model reaction orders could be thought of as parameters related to the flame zone combustion efficiency. Furthermore, results showed that this model supports qualitative physical events of droplet evaporation, mass diffusion, and combustion. However, the lack of rigor toward chemical kinetics prevented good agreement with quantitative data.

Polymeropoulos and Peskin¹³⁹ solved the mass and energy conservation equations for a single symmetric droplet assuming one-step chemical kinetics. Boundary conditions defined at the droplet surface and at a large distance from the droplet formulate a boundary value problem for the fuel mass fraction with the mass burning rate as an eigenvalue. Ignition was defined by the discontinuous change (increase) in mass burning rate as ambient temperature increases. Polymeropoulos' work reinforced the concept that kinetic rates were controlling the ignition process up to the ignition point. This work differs from the previous work of Peskin et al. in that it concludes that ambient temperature

decreases with increasing oxidizer concentration but so slowly that the variation would probably not be observed experimentally. At very low oxidizer concentrations or with fuels exhibiting different combustion kinetics, the effects of oxidizer concentration would be more pronounced. At ambient temperatures above the ignition temperature, diffusional rates control. At the ignition point, the fuel is consumed more rapidly and there is little fuel and oxidizer left outside of the relatively narrow reaction zone. This formulation predicts intermediate results which are physically unattainable.

Rosser and Rajapakse¹⁵⁴ considered the thermal stability of a reacting spherical shell and defined a critical droplet diameter below which the droplet would only evaporate, without ignition. Modeling results indicated the critical diameter would decrease with increasing temperature. This study showed a strong dependence of ignition temperature on fuel concentration and reaction order and a weaker dependence on oxidizer concentration.

Ledwell and Brzustowski¹⁵⁵ developed an analysis for droplet burning with convection by incorporating an empirical flame shape. The burning rate was the cumulative effect of (1) the droplet evaporation in an infinite stagnant gas at the adiabatic flame temperature, (2) an increase in evaporation caused by steepening of fuel concentration gradients existing in the presence of a flame in a stagnant medium, and (3) the contribution of ambient convection.

Two different approaches have been used to define the evaporation and ignition of a droplet in a hot oxidizing environment (i.e., autoignition of droplets due to heat transfer from the ambient). The first approach used approximations of the temperature in the diffusion zone.^{96, 140} A second approach^{151, 153} solved the exact conservation equations by a singular perturbation technique, using the

Damkohler number as either the small or the large parameter. Perturbations in the mass evaporation rate and other parameters of interest were obtained.

Crespo and Linán¹⁵⁶ analyzed the structure of counterflow diffusion flames by the method of matched asymptotic analysis. This resulted in a mathematical description for the entire range of the Damkohler number. Law¹³⁸ extended this methodology to quasi-steady, isobaric, spherically symmetric flows with condensed phase evaporation during droplet combustion.¹³⁸ One-step chemical kinetics were assumed. Correction factors to the mass evaporation rate were used to compensate for multi-step chemical kinetics. Law defined a reduced Damkohler number as follows:

$$Da_R = Da Y_{o,\infty} \left(\frac{Ar \rho_\infty M_o}{T_\infty} \right) \quad (2-3)$$

$$Da = \frac{L_o^2 / \alpha_o}{\frac{\exp(Ar)}{A \sigma^m \rho_o^{(m+n+1)}}} \quad (2-4)$$

$$M_o = \ln \left(1 + \frac{T_\infty - T_s}{\Delta h_v} \right) \quad (2-5)$$

where Ar denotes the Arrhenius number defined by

$$\frac{E_a}{R_u T_{max}} \quad (2-6)$$

and L_o is the characteristic length of the transport zone immediately surrounding the reaction zone, α_o is the characteristic thermal diffusivity, σ is the stoichiometric mass coefficient of the oxidizer per unit mass of fuel consumed, ρ_o is the density of the oxidizer, A , m , and n are kinetic parameters which are

typically empirically determined, and Δh_v is the specific latent heat of vaporization.

An ignition Damkohler number, $Da_i(\theta)$, can be determined for a given value of the parameter, θ :

$$\theta = (T'_\infty - T'_s) + L \quad (2-7)$$

where the temperatures, T , are dimensionless and L is the ratio of the specific latent heat of vaporization and the specific combustion heat release.

Since the problem is characterized by only θ , the curve $Da_i(\theta)$ can be considered to be a universal function of the ignition Damkohler number for droplets. Knowing $Da_i(\theta)$, the ignitability of a droplet in a given environment can be easily assessed:

$Da < Da_i(\theta)$: no ignition

$Da > Da_i(\theta)$: ignition

For small values of θ , Da_i can be accurately represented by:¹³⁸

$$Da_i = 1.05 \exp(6.40\theta) \text{ for } \theta < 0.35 \quad (2-8)$$

which is representative for systems involving hydrocarbon fuels.

Law expanded on his initial analysis to include corrections to the reduced Damkohler number to account for finite rate kinetics. Under ignition conditions the reactions are less intense, the chemical induction times are longer, the reaction region is broadened, and the one-step overall approximation may be less accurate. Therefore, accurate modeling of ignition events require finite-rate

chemical kinetics and may even require detailed multi-step reaction mechanisms.

Internal droplet heating is typically assumed to be negligible. As a result, droplet heating is represented using a rapid-mixing model which assumes the droplet temperature to be uniform in space but time varying. This assumption is equivalent to infinite internal thermal conductivity and may overestimate the rate of droplet heating for droplets that do not possess significant internal circulation. Faeth and Olson¹⁵² have shown that predicted droplet ignition characteristics depend on the rates of internal droplet heat transfer.

The assumption of spherical symmetry is most realistic for small droplets moving relatively slowly in a gas stream such that chemical reactions primarily take place in regions surrounding the droplet rather than in the wake. Sangiovanni and Kesten¹⁴⁷ have experimentally shown that for this envelope type ignition, the relative gas velocities indeed have only small effects on the ignition process.

Sangiovanni and Kesten¹⁴⁷ developed a cylindrical model for a single droplet to study the nonuniform heating of a continuous droplet. The ignition criterion developed by Faeth and Olson¹⁵² was used: ignition occurs when the concentration of a crucial chain branching intermediate reaches a critical value in the gas phase. Theoretical results indicated that the effect of gas velocity on gas phase axial conduction was insignificant.

Numerical calculations were performed by Sloane¹⁰⁶ on the ignition of methane, oxygen, and argon mixtures due to dissociation of molecular oxygen into ground state oxygen atoms. A one-dimensional fluid mechanics model was coupled with a detailed chemical kinetic model to calculate minimum ignition

energy as a function of equivalence ratio. Increased oxygen dissociation resulted in reduced induction time and increased flame propagation rate.

Rah et al.¹⁴⁹ solved a system of partial differential equations describing the ignition of a single droplet by specifying the droplet surface variation with time using the d^2 law. The model was extended to a monosized droplet array by adjustments to the evaporation rate constant in the d^2 law.

Dwyer and Sanders¹⁵⁷ performed a numerical study of ignition of hydrocarbon and monopropellant droplets. One-dimensional, unsteady solutions were obtained for the full transport equations of mass, momentum, energy and species. A one-step chemical kinetics model was used. Results indicated that the reaction zone and gas phase ignition distance was large for hydrocarbon droplets and small for monopropellant droplets.

Bergeron and Hallett¹⁵⁸ investigated the effects of one-step chemical kinetic models for several hydrocarbon fuel droplets including n-heptane, n-hexadecane, and iso-octane. A numerical model was formed from the one-dimensional symmetric conservation equations of mass and energy. Adjustments to the pre-exponential and activation energy values of the one-step chemical kinetics model were required to match experimental ignition delay times.

In general, the more volatile component of the multicomponent fuels tends to control the ignition process.¹⁵⁹ The addition of a volatile component into a fuel causes an increase in vapor production during the early part of the droplet lifetime leading to earlier reaction. Semi-empirical models for chemical kinetics were formulated and used successfully. A linear combination of component rate constants by mole fraction is one approach to model mixture reaction rates and follows the observation that activation energy varies linearly with composition.

Mawid and Aggarwal¹⁵⁰ investigated the transient combustion of a multicomponent liquid fuel droplet. The numerical results indicated that the concentration of fuel vapor in the inner zone of the flame exceeded that at the droplet surface for certain values of the liquid phase Lewis number (ratio of rate of diffusional energy transport to rate of diffusional mass transport). As a result, the mass vaporization rate was suppressed without extinguishing the flame. Using large activation energy asymptotics, Mawid and Aggarwal⁸⁶ also developed a critical Damkohler number to account for nonunity reaction orders.

Cavanagh and Cox¹⁶⁰ assembled a detailed mechanism for the oxidation of acetaldehyde, an important intermediate in the oxidation of many hydrocarbon fuels. Acetaldehyde exhibits all the characteristic behaviors observed for more complex fuels under low-temperature oxidation conditions (e.g., slow oxidation, cool flames, two-stage, and single-stage ignition).

Makino¹⁶¹ developed an ignition criterion for a fuel droplet in a bounded oxidizing environment composed of both oxidizer and fuel mass fraction. In addition, quasi-steady conditions, spherical symmetry, and one-step chemical kinetics were assumed. The criterion was based on a semi-empirical Damkohler number, and, therefore, it is not readily capable of being incorporated into a time accurate numerical simulation.

Hallett and Ricard¹⁶² developed a model to study the ignition behavior of a single two-component fuel droplet in an oxidizing environment. The model assumed spherical symmetry, no free or forced convection, uniform liquid and gas properties, and negligible reactant consumption prior to ignition. Vapor-liquid equilibrium was modeled using Raoult's law with component vapor pressures from the Antoine equation.¹⁶² Chemical kinetics were modeled assuming a one-step reaction mechanism and the rate constants were adjusted

to match experimental data. The governing equations of mass and energy were solved numerically. The results of the numerical study indicated that the distillation curve of the fuel was no indicator of ignition behavior. However, as has been observed by other researchers, ignition of multi-component fuels is governed primarily by the chemical nature and boiling points of the most volatile constituents of the fuel.

Ruszalo and Hallett¹⁶³ extended the numerical technique of Bergeron and Hallett¹⁵⁹ to analyze the autoignition of single droplets of pure fuels and two-component fuels at high pressures. Droplets exposed to pressures two to three times the critical pressure of the fuel required the inclusion of non-ideal effects such as absorption of air into the liquid phase and changes in the enthalpy of vaporization with pressure. The numerical results indicated that the main effect of high pressure was a substantial reduction in ignition delay time resulting from the acceleration of the chemical reaction rate. Diffusion of air or of fuel species in the liquid phase did not significantly affect the ignition delay. Nonetheless, the physical processes of evaporation and vapor diffusion cannot be neglected and accurate models of vapor-liquid equilibrium and transport properties are essential.

Shuen¹⁶⁴ formulated a model of droplet ignition and combustion based on the conservation equations for both gas and liquid phases, and accounted for variable thermophysical properties, finite-rate chemical kinetics, and liquid-vapor phase equilibrium at the droplet surface. The motivation for the work was to describe droplet behavior during its transition from subcritical to supercritical conditions. Thus, the entire droplet history could be modeled including the transition from the subcritical to supercritical state. Results using n-pentane droplets in air indicated that the ambient gas pressure controls droplet

gasification and burning by affecting fluid transport, gas-liquid interfacial thermodynamics, and chemical reactions. Droplet gasification increased with increasing pressure, probably due to increased heat transfer rates at higher gas-phase densities. Ignition time was arbitrarily defined as the time at which the peak gas-phase temperature exceeded its initial value by 100K. A one-step global reaction mechanism was used. Shuen noted that this assumption may not be very accurate for predicting ignition processes in hydrocarbons. In the subcritical region, the vaporization of liquid fuel dominated the burning characteristics of the droplet. However, the transient diffusion in the gas phase dominated in the supercritical region.

Dwyer and Le¹⁶⁵ solved the one-dimensional heat and transport equations and employed semi-empirical corrections to account for droplet drag, heat transfer, and mass transfer in a convecting environment. Transient fluid properties were defined using an existing database of thermodynamic values. Furthermore, the liquid was assumed to be ideal with a Lewis number of unity. Global chemical kinetics were used and the pre-exponential factor was adjusted to match experimental ignition times at a pressure of 80 atmospheres and droplet velocity of 80 meters per second. Ignition time was arbitrarily defined as the time necessary for the maximum temperature in the gas to become twenty percent greater than the surrounding gas temperature. Parametric results were obtained for mixtures of octane and hexadecane. Results also showed that temperature gradients existed in the gaseous mixture surrounding the droplet, therefore, a flame sheet model, which specifies a thin flame zone, would not be appropriate to model the reaction zone surrounding the droplet.

Fedotov¹⁶⁶ promoted a stochastic model for ignition to account for gaseous mixture temperature fluctuations and the possibility of random

transitions between stable-state regimes and random regimes. Near the region of the ignition limit, it appeared that deterministic analysis should be supplemented with information about the behavior of the fluctuations. However, Fedotov noted that if the intensity of the fluctuations are small, the probability for stochastic ignition would be too small to be observed in practice.

Sher et al.¹⁶⁷ described the breakdown of intervening gas during spark discharge in air. Thermodynamic properties of a plasma at 60,000 K were calculated using concepts of statistical thermodynamics in which molecular dissociation, ionization, and the translational, rotational, and vibrational modes of energy storage in a molecule were considered. For a fixed plasma volume of air composed of 79% by volume nitrogen and 21% by volume oxygen, Sher computed the mixture composition as a function of temperature. The gas molecules, N₂ and O₂, were fully dissociated at 14,000 K where the single atoms (N and O) begin to lose their electrons. Above 25,000 K the mixture was mainly composed of ionized atoms and free electrons. A second ionization occurred when the temperature exceeds 40,000 K. At 50,000 K the free electrons constituted about 70% of the plasma composition on a molar basis.

2.5.3 Droplet Ignition Experimental Results

Experimentally defining the critical parameters leading to ignition of a liquid fuel has been a challenging problem for past and present researchers. Significant experimental work has been performed investigating liquid droplet ignition.^{147, 152, 168 - 174} Generally, ignition delay is defined as the time from droplet introduction into the hot ambient environment to the first visual record of light.

Pressure measurements and sound have also been used to identify droplet ignition.

The importance of ignition in conventional systems was realized by Barrerre and Moutet¹⁷⁵ for impinging injector systems. High speed photography (5000 frames/sec) was used to acquire data from which ignition delay or lag was determined. This delay was described as the time required from propellant flow rate initiation to the visual indication of first light. Furfuryl alcohol and nitric acid fuels were used. Ignition lag was measured as a function of mixture ratio, injectant velocity, and initial fuel injectant temperature. Although this experiment did not sufficiently address fundamentals of droplet behavior, it was representative of the concern for, and need for knowledge of the relative importance of ignition for conventional liquid fuel systems.

Nishiwaki¹⁴⁶ inserted a single droplet suspended from a silica filament into a prepared combustion furnace and a nearly quiescent environment. Droplet evaporation, ignition, and burning were observed using Schlieren photographs. Temporal droplet temperatures were measured using a thermocouple from which the droplet was suspended. Droplet radius as a function of time was deduced from the photographs. Ignition lags of methyl-naphthalene and cetane droplets were observed for various oxygen contents. Ignition lag was defined as the accumulation of the time required to bring the droplet to the temperature at which evaporation begins plus the time required from evaporation initiation to observation of first flame.

Kobayasi¹⁷⁶ investigated the ignition of toluene, nitrobenzene, methylnaphthalene, light diesel oil, kerosene, and heavy oil droplets using relatively low speed photography (64 frames/sec). Liquid droplets 0.035 to 0.085 cm in radius were suspended by a quartz fiber 0.005 to 0.01 cm in radius

and submerged into an electric furnace. Data indicated that ignition occurred at one point in a region of the droplet boundary having appropriate fuel-air ratio and temperature, and then spread circumferentially around the concentric region encircling the droplet.

Linuma¹⁷⁷ investigated the effect of air flow parallel to a one-dimensional droplet array on the flame propagation time. The propagation time between droplets was obtained using Schlieren pictures. Droplet spacing and flow velocity were varied and droplet flame propagation times were recorded. Data indicated that flame propagation time between droplets increased with increasing droplet spacing and decreasing flow velocity.

Masdin and Thring¹⁶⁸ investigated the effects of ambient air velocity, ambient air composition, fuel droplet diameter, and fuel droplet volatility on the evaporation and ignition of kerosene droplets. A fuel droplet suspended on a silica filament was introduced into a furnace operating at the specified conditions. Photographic records of the droplet shadow projected onto a graduated planar scale were recorded and the variations of droplet diameter with time were used to deduce evaporation rate. Ignition delay was defined as the time from droplet insertion into the furnace until the time at which visible light was apparent. Ignition lag was correlated as a function of temperature using the following expression:

$$t_i = C_1 \exp(C_2 / T) \quad (2-9)$$

where C_1 and C_2 were functions of fuel type.

Using a semiempirical analysis, El-Wakil and Abdou^{169 - 171} developed expressions for the total, physical, and chemical delays during autoignition of

several normal paraffinic hydrocarbon droplets in a heated, moving airstream. Octane, decane, dodecane, tetradecane, and hexadecane droplets were introduced into flowing air heated to 1255 K. Droplet radii varied from 0.07 to 0.083 cm. Measurements made included photographs (500 frames/sec.) of droplet time history, liquid droplet temperature, liquid droplet diameter, air flow velocity and temperature.

Results were obtained as functions of liquid droplet temperature, air stream temperature, and number of carbon atoms in the fuel molecule. Results indicated two types of flame depending on the velocity of the air stream. For a low velocity air stream, a diffusion type flame started at the flow stagnation point and enveloped the droplet. For a high velocity air stream, the flame remained detached and its detachment distance was proportional to the air stream velocity. The total ignition delay increased with the number of fuel carbon atoms (i.e. decreased with fuel volatility), decreased with air temperature, decreased with air velocity, decreased with initial liquid temperature, and increased with initial droplet diameter.

The expression for total time delay was linearly proportional to droplet diameter and exponentially proportional to free stream temperature according to the following model equation:

$$\begin{aligned}
 t_i &= 10.3d_o^{0.85} \exp(C_1 + C_2 n) \\
 C_1 &= 20.5 - 35.9(T_\infty / 1850)^2 + 13.2(T_\infty / 1850)^4 \\
 C_2 &= 0.364(7.775 - \ln T_\infty)
 \end{aligned}
 \tag{2-10}$$

where T_∞ is the free stream air temperature in Rankine, d_o is the initial diameter of a droplet in inches, and n is the number of carbon atoms associated with the hydrocarbon fuel.

The physical ignition delay was defined as the time elapsed from the instant the droplet was subjected to the air stream until a fuel vapor air mixture of combustible proportions had formed and diffused out into the droplet boundary layer and was at a temperature equal to the autoignition temperature. Chemical ignition delay began prior to the completion of the physical delay and, therefore, there was always overlap. The empirical correlation for the physical delay was defined by the following equation:

$$t_p = 1.10d_o^{0.5} \left(0.025 + \frac{1}{T_B - 1850} \right) n^{0.465} \quad (2-11)$$

Chemical ignition delay was defined as the time delay from the beginning of perceptible chemical reaction until the first appearance of flame. However, the beginning of the chemical ignition period was difficult to define and proved sensitive to the chemical kinetics of the fuel and oxidizer involved.

Ma and Moore¹⁷⁴ examined a premixed mixture of benzene and n-heptane fuel vapor in air (nitrogen and oxygen) to assess the performance of the mixture relative to knock. Since benzene does not ignite at low temperatures, it is resistant to knock. Ignition was accomplished by flowing this mixture through a heat exchanger.

Faeth and Olson¹⁵² investigated the ignition of single fuel droplets in a quiescent environment using a closed chamber heated to a specified temperature. The effects of natural convection, which were observed on most other single droplet experiments, were eliminated by producing a gravity-free environment. This was accomplished by dropping the closed chamber along a controlled vertical path during which time the droplet was discharged and the

photographic data were obtained. Ignition delay times were recorded as a function of initial droplet diameter, ambient gas temperature, ambient gas pressure, and fuel type (n-hexadecane, denzene, iso-octane, n-heptane). Critical droplet diameters were also recorded. Ignition delay times were correlated with droplet diameter at various ambient air temperatures.

Salooja¹⁷² investigated the ignition characteristics of binary hydrocarbon mixtures as a function of temperature of the original mixture. The ignitability of the mixture was controlled by the ignition characteristics of the more volatile component. Mixtures investigated were mostly in the C₆ to C₈ hydrocarbon range.

Wood and Rosser¹⁷³ studied hexadecane and aniline droplets from 0.005 to 0.015 cm in radius falling freely in a oxidizing atmosphere (air and oxygen) within a furnace near 1023 K. Ignition delay was defined as the time required for a droplet to enter the hot furnace until a visible light was evident. Since the photographic viewing port was not sufficiently large, the droplet could not be viewed during its entire lifetime. Therefore, only photographic data were available during ignition and burning. The initial droplet diameters were determined by replication techniques used at the time of the study. As a result of the moving droplet, data indicated the appearance of a luminous zone in the wake of the droplet. The luminous region followed the droplet but never overtook it and enveloped it. Results showed that the ignition lag depended on the environmental temperature, on droplet spacing in the linear array, and on the chemical nature of the fuel. Ignition appeared to be independent of the initial droplet size if the droplets were large enough to ignite.

Cullis and Foster¹⁷⁸ investigated the ignition behavior of binary mixtures. Their work, focused on the heavy hydrocarbon, n-decane, showed that the

ignition tendency of this straight-chain alkane can be reduced by blending with branched alkanes (e.g., trimethylhexane). These experimental results agreed with experimental findings for lower weight hydrocarbons in that the ignition tendency of a binary mixture is controlled by the more volatile fuel component.

Sangiovanni and Kesten¹⁴⁷ examined the ignition behavior of monosized, linear fuel droplet arrays with emphasis on the interaction of individual droplets. Ignition delay times were measured for furfuryl and butyl alcohol fuels as a function of droplet spacing and droplet velocity for droplets of 0.01 and 0.015 cm in radius. Results indicated that the effect of droplet interaction on the ignition process became more important for small droplets, low gas phase temperature, and fuels of low volatility. Furthermore, the influence of forced convection on droplet heating was reduced since each droplet travels in the wake of the preceding droplet.

Kashiwagi et al.¹⁷⁹ investigated the ignition mechanism of n-decane and 1-decene liquid pools under high intensity radiation using a CO₂ laser. Pictures revealed the formation of a radial wave, a central surface depression, and bubble nucleation, growth, and bursting of the droplet.

Using n-heptane, n-hexadecane, and acetone fuels, Saitoh et al.¹⁸⁰ reported that ignition time increases as the droplet diameter decreases at the region near the ignition limits. Furthermore, experiments indicated that ignition occurred more rapidly as the droplet diameter increased if the initial droplet temperature was high. Ignition times obtained in these experiments were slightly longer than those reported by Faeth and Olson.¹⁵² This slight difference is attributed to the variation in technique used by each experimenter to suspend the droplet in its quiescent environment.

Rah et al.¹⁴⁹ measured the ignition delay time from photographs of a monosized droplet stream between an atomizer tip and the ignition point. The droplet stream was surrounded by a laminar flow of helium and oxygen. Results of ignition delay were defined as a function of ambient environment temperature and oxygen concentration.

Bergeron and Hallett¹⁵⁹ suspended droplets on a quartz fiber and provided heat by moving a furnace over the droplet. Ignition was defined using photodiodes at the time light was emitted from the droplet. Initial droplet sizes were determined photographically upon insertion into the furnace. Results of ignition delay were correlated with initial droplet diameter and initial ambient air temperature.

It is postulated¹⁸¹ that in conventional diesel engines, the ignition delay is mainly controlled by chemical pre-ignition processes rather than physical processes, even at low ambient temperature. In an attempt to improve cold starting, ignition delay measurements were made on a full scale internal combustion engine using diesel fuel with various additives. The intent of the additives was to provide additional free radicals to the fuel to improve ignition.

Using suspended droplets introduced into a hot furnace at a prescribed temperature, Takei et al.¹⁸² studied the ignition delay of pure n-heptane, pure n-hexadecane, and mixtures of the two fuels. The total ignition delay was composed of the time required for physical droplet heat-up to a wet-bulb temperature and time required for the reaction. For example, the ignition delay of large droplets or fuel droplets with large latent heat values was primarily controlled by droplet heat-up. However, small droplets vaporize quickly and therefore ignition delay becomes controlled by chemical reactions. Hexadecane exhibited an increase in ignition delay time with increasing diameter because it

possesses a large latent heat and droplet heat-up dominates the ignition delay. Heptane exhibited a decrease in ignition delay with increasing droplet diameter because it possesses a low latent heat value and was therefore reaction controlled.

Recent experimental work by Furutani et al.¹⁸³ using n-heptane has indicated that ionization of species occurs prior to final hot ignition in systems under rapid compression. This evidence suggests that ions may participate in the preflame oxidation reactions which are prerequisite to ignition. Without this mechanism of ion kinetics, ignition may not occur. Therefore, it may represent a form of "go" or "no-go" ignition. Ionization has long been known to occur in the flames of hydrocarbon fuels.^{184, 185}

2.5.4 Laser Ignition

In general, laser ignition of reactive gases can be divided into four categories: (1) thermal ignition, (2) photochemical ignition, (3) nonresonant spark ignition, and (4) resonant spark ignition. Thermal ignition uses a laser to increase the kinetic energy of the target molecules. Molecular bonds are eventually broken by collisions and chemical reactions take place. Photochemical ignition supplies energy through single or multi-photons to dissociate molecules into highly reactive radical species initiating rapid chain reactions toward ignition. Photochemical ignition requires a close match between the laser excitation wavelength and the target molecule's absorption wavelength to result in dissociation. Photochemical ignition requires only a small amount of laser energy, typically less than a millijoule for O_2+H_2 mixtures.¹⁴⁵ Photochemical ignition can be used to ignite mixtures at lower

pressures and close to the flammability limits. Nonresonant spark ignition describes the process where sparks are formed by dielectric breakdown of gases in the laser focal volume. Resonant spark ignition describes the process where atomic and molecular resonances are excited in the multiphoton ionization production of seed electrons.

Differences exist between electric spark and laser spark ignition processes. Electrodes required to produce an electric spark become contaminated, providing a source for catalytic effects of ejected matter on ignition kinetics. Additionally, the electrodes are a heat sink serving as a quenching source to the expanding spark kernel. Laser ignition is a simple alternative to electric spark ignition, offering more flexibility and longer life with less maintenance.

The capability to place a laser-induced spark within three-dimensional space at a controllable energy level and energy disposition rate is an apparent benefit for turbine engine, liquid rocket engine, and hypersonic vehicle combustor operability. In addition, non-intrusive ignition, optical flame holding, reduction of ignition delay time, reduction in minimum ignition temperature, and enhancement of combustion reaction rates may result from photochemical ignition. Photochemical excitation of conventional fuels or oxidants increases the overall reaction rate by several orders of magnitude, thereby decreasing ignition delay times compared to the thermal delays, and potentially eliminating the problem of incomplete combustion due to extremely short residence times for supersonic or hypersonic combustors.

Photochemical ignition is the most commonly used method of laser ignition. This technique is based on the fact that photons of selected wavelengths are capable of in-situ photodissociation of stable molecules into

reactive radicals. The presence of radicals accelerate the reactions leading to ignition. For example, energy absorbed by oxygen molecules in the wavelength region below 245 nm. results in their photodissociation to oxygen atoms. These atoms produce other reactive radicals through chain branching. Continued reaction of the radicals with fuel molecules releases heat. The temperature rises, leading to ignition.

Single and multiphoton processes are used to promote ignition. In some cases, a sensitizer such as nitrogen dioxide is added to an explosive gaseous mixture and the subsequent photodissociation of this species produces a pool of free radicals that initiates the reaction of the host mixture.

Lee and Dnystautas¹⁸⁶ explored the minimum ignition energy required to ignite detonable and nondetonable flammable mixtures using a Ruby laser. Weinberg¹⁸⁷ described the use of plasma-generated radicals to enhance ignition of lean mixtures thus improving emission characteristics. Plasmas were generated using hydrogen, nitrogen, water, and methane and the plasma radicals were injected into a closed cylindrical chamber filled with a highly-stirred mixture of 5% by volume methane in air. The plasma jet was constructed between two electrodes of an electric spark.

Dabora¹⁸⁸ studied the direct interaction of a liquid droplet with a high-powered laser. The Ruby laser was focused on droplets with 0.075 to 0.10 cm radius using two pulses at 50 to 100 microseconds. Liquids used included water, nitromethane, propyl nitrate, and heptane in either air or oxygen ambient gas.

Lavid et al.^{189, 190} irradiated combustible mixtures with ultraviolet light to produce ignition in which the only photoabsorbing species was molecular oxygen. Molecular oxygen absorbs most strongly in the vacuum ultraviolet

region of 130 to 175 nm, where one of the oxygen atoms produced is in an electronically excited state. Therefore, Lavid used two wavelengths emitted by argon fluoride: 157 nm emitted by fluorine and 193 nm. The effects of photodissociated oxygen on the ignition of gaseous hydrogen and oxygen and hydrogen-air mixtures at various equivalence ratios and pressures were investigated. Results indicated that fuel-lean mixtures of hydrogen and oxygen having equivalence ratios near 0.6 to 0.8 were more favorable for photochemical ignitions than other mixtures. Perhaps the increased concentration of molecular oxygen results in higher atomic oxygen upon irradiation. In contrast, the minimum energy for spark ignition was found to occur at an equivalence ratio near 1.0.

Lavid and Stevens¹⁸⁹ proposed a model of the photon absorption, subsequent dissociation, chemical kinetics of the reactant mixture, and heat loss to the surroundings. An extensive chemical reaction mechanism was defined for hydrogen and oxygen reactions. The mechanism included electronically excited state species. Photodissociation was accomplished assuming a unimolecular reaction in which the dissociation rate was a function of the concentration of the absorbing species and the spatial and temporal incident spectral irradiance.

Lavid et al.¹⁹¹ also examined the ignitability of premixed $\text{H}_2 + \text{O}_2 + \text{NO}_2$ mixtures using NO_2 as the photosensitizer. Results indicated that as temperature of the mixture increases, sensitized ignition improved. However, a plateau was reached beyond which ignition did not occur. This was attributed to NO_2 converting to non-absorbing $\text{NO} + 1/2 \text{O}_2$. In the absence of irradiation, autoignition of $\text{H}_2 + \text{O}_2$ was suppressed.

Vosen et al.¹⁹² studied plasma jet ignition of lean premixed methane-air mixtures to determine the effect of different plasma gases on flame kernel

development. Nachshon et al.¹⁹³ used an argon fluoride excimer laser to study the rate of photochemical dissociation of molecular oxygen needed to ignite H_2+O_2 mixtures at different temperatures and equivalence ratios. Attention was focused on the role of the excited oxygen atom, $O(1D)$, in the kinetics. Nachshon categorized laser induced ignitions as follows: (1) spark ignition by plasma breakdown, (2) dissociation of species into free radicals, and (3) combination of plasma breakdown and selective photodissociation. Results were obtained for minimum atomic oxygen concentration required for photochemical ignition as a function of initial mixture temperature and equivalence ratio. In addition, minimum laser energy required for photochemical ignition was obtained for a constant temperature mixture as a function of equivalence ratio.

Kumar et al.¹⁹⁴ studied the effects of ionizing radiation on the ignition of H_2+O_2 mixtures at a hot surface. Witriol¹⁹⁵ described a theoretical technique to simulate laser spark ignition of reactive gases, solving the equations of continuity of individual droplets, of motion, and of energy.

Liou¹⁴⁵ used a Neodymium:YAG laser with a wavelength of 1064 nm. to initiate ignition in gaseous H_2+O_2 , gaseous O_2+CH_4 , and gaseous O_2 + liquid RP-1. The laser was focused through windows in the combustion chamber. The gaseous fuels were injected through straight orifices using three separate patterns: (1) one orifice, (2) three orifices, and (3) five orifices. The O_2 + liquid RP-1 fuels were injected through impinging triplet and pentad elements. Ignition delay was measured as a function of oxidizer-to-fuel ratio. In addition, minimum laser pulse energy required for ignition was defined as a function of oxidizer-to-fuel ratio.

2.6 Spray Ignition Theory, Simulation, and Experiment

Ignition characteristics of sprays in practical systems is of significant importance. Practical applications of sprays require that the ignition process be understood and, in applications such as turbine engines and liquid rocket engines, be optimized. Defining the controlling processes which influence the ignition of sprays is much more difficult than that for a single droplet. Nonetheless, the basis for experimental and analytical research of spray ignition has been the ignition of individual droplets, droplet arrays and droplet groups. Droplet interaction¹⁹⁶ and fuel vapor existing within the region of and surrounding the spray affect heat and mass diffusion processes, which affect ignition.

Although ignition criteria can be formulated based on empirical correlations¹⁷⁵ and probabilistic statistical analysis,^{197, 198} experimenters have long attempted to understand physical processes controlling spray ignition. The initial investigations of heterogeneous spray ignition examined fuel sprays in turbine engine combustors^{199, 200} and hypergolic bi-propellant fuels.²⁰¹ The first fundamental studies of ignition were concerned with stagnant mixtures or with flowing air streams into which a gaseous fuel was injected.¹²² Significant advances in the understanding of spray ignition were accomplished by experiments by Rao and Lefebvre²⁰² using kerosene fuel sprays in a flowing air stream. These experiments indicate that the minimum spark energy for ignition increased with increasing droplet diameter and air flow velocity.

Based on the experiments of Rao and Lefebvre, the spray ignition process was described in the following manner. The spark produces a spherical volume of gas and liquid (i.e., spark kernel) having a temperature sufficiently high to evaporate all the liquid droplets within it. If the rate of heat released by

fuel combustion within the kernel exceeds the rate of heat loss by thermal conduction at the surface of the volume, then the spark kernel will grow. However, if the rate of heat release is less than the rate of heat loss, the spark kernel will dissipate and combustion will not propagate. The minimum ignition energy is the amount of energy required from an external source which will produce a spark kernel capable of unaided propagation.

Benson²⁰³ proposed that the ignition delay of a fuel spray in an oxidizing atmosphere of high pressure and temperature was composed of two parts: (1) the time required to reduce the velocity gradient at the spray tip below the critical velocity gradient for ignition, and (2) the time required for an ignition reaction to occur at the given velocity gradient. The time required to reduce the velocity gradient sufficiently for ignition was the dominant process. The theoretical critical velocity gradient was a function of ambient gas pressure, temperature, oxygen concentration, and fuel properties.

Ballal and Lefebvre^{204, 205} developed a theoretical model for predicting minimum ignition energy of liquid sprays assuming that chemical reaction rates were infinitely fast and that the sole criterion for ignition was an adequate concentration of fuel vapor in the ignition zone. Peters and Mellor²⁰⁶ developed a similar model. Ballal and Lefebvre²⁰⁷ demonstrated good agreement of their model to experimental data over a range of pressure, equivalence ratio, droplet size and fuel volatility. These experiments used hydrocarbon fuel ejected from a simplex nozzle into an established air stream. Ignition was accomplished by a spark. Available data included minimum ignition energies as a function of pressure, velocity, turbulence intensity, equivalence ratio, mean drop size and fuel volatility. The model was refined to include finite chemical reaction rates and the presence of fuel vapor in the ignition zone.^{207, 208}

Continued experimental work examined spray ignition as a function of the droplet environment (i.e., within the combustion chamber), such as subatmospheric pressure^{196, 209} and high pressure and temperature.^{210, 211} Generally, these results indicated that the minimum ignition energy increased with decreasing pressure and temperature.

Damkohler-number asymptotics and activation-energy asymptotics which were employed to investigate droplet burning were extended to spray ignition. Activation-energy asymptotics appeared to be more useful for the study of ignition. However, activation-energy asymptotics may lead to results valid for all Damkohler numbers, and therefore results of Damkohler-number asymptotics may be extracted from those of activation-energy asymptotics.

Law and Chung¹⁴³ extended the ignition criterion derived for droplets¹⁴² and applied it to sprays assuming that the conditions surrounding the droplet were similar to those of all droplets in the spray. Similar to the approach for assessing droplet ignition, the spray system Damkohler number is computed and compared to a numerically determined ignition Damkohler number. The criterion was derived assuming a one-step, overall, irreversible reaction between fuel and oxidizer.

Aggarwal et al.^{84, 85, 212, 213} performed numerical studies using an Eulerian approach for the gas phase and a Lagrangian approach for the liquid phase. Aggarwal modeled monodisperse and polydisperse streams ignited by a vertical hot plate in the vicinity of the droplet stream. The occurrence of ignition was defined by the condition of zero heat flux at the hot surface; this marks the initiation of a propagating flame into the mixture. The numerical studies of both monodisperse and polydisperse sprays by Aggarwal suggested (1) the existence of an optimum droplet size as a function of equivalence ratio to minimize ignition

delay time, (2) the dependence of ignition delay time on the hot wall temperature is of the Arrhenius type, (3) the dependence of ignition behavior on initial fuel composition (e.g., heavy hydrocarbon), and (4) the numerical solution must be resolved on the scale of the spacing between droplets in order to adequately represent the physics of multi-droplet ignition processes.

The experimental work of Sangiovanni and Kesten²¹⁴ used a pilot flame for ignition resulting in a complex flow field of turbulent flame and unburned fuel. The work of Sommer²¹⁵ used a hot plate for ignition resulting in boundary layer effects on these processes. The work of Dietrich et al.²¹⁶ used the collision of two monodispersed droplet streams to create a bidisperse array. Complex coaxial fuel injector geometry representative of the RL10²¹⁷ and a single injector geometry used on a prototype NASA Roll Control Engine²¹⁸ were tested.

The recent experimental work of Hulka and Makel²¹⁹ focused on physical processes occurring downstream of a coaxial injector. This configuration was composed of one coaxial injector with liquid oxygen in the center and gaseous hydrogen in the annulus and background gas generated to represent the effect of multiple injectors. Ignition was accomplished by a spark energy source located in the chamber. To date, data have been limited to flow visualization measurements using a high speed camera (1000 frames/sec) and have defined the general flow characteristics of a reacting, unconfined, liquid oxygen hollow cone swirl spray. Ignition delay times have not yet been measured, however, this data could be acquired on future tests.

Experimental and analytical work have continued to concentrate on ignition of droplet streams,^{214, 220} droplet arrays,^{213, 221} dense droplet regimes,²²² dilute droplet regimes,^{214, 223} multicomponent liquids,^{84 - 86, 224} and swirl-induced

flow.^{225 - 229} Bellan and Harstad²²² have applied the Damkohler ignition criterion to dense sprays with limited success.

Significant theoretical work has been completed by Law, Chung, and Aggarwal investigating ignition in dilute monodisperse and polydisperse sprays, and in dense sprays. The ignition criterion of Law, based on a critical Damkohler number, has been the basis for many theoretical ignition criteria with variations for multicomponent and dense sprays. However, the utility of an ignition criterion based on a single Damkohler number depends on a priori knowledge of critical Damkohler numbers obtained from experimental data. Therefore, a fundamental approach to assessing ignition could be developed which depends on solving the system of mass, momentum and energy conservation equations, interconnected by physical submodels for thermal and chemical properties, and transport rates, consistent with the expected processes of atomization, vaporization, mixing, and chemical kinetics.

2.7 Chemical Kinetics of Hydrocarbon Fuels

Accurate modeling of ignition processes requires that the reactant chemical kinetics be adequately represented at some level of complexity. The mathematical representation of finite-rate chemistry is termed a reaction mechanism. Over the past few decades, the details of specific reaction mechanisms have followed advances in measurement theory toward improved measurements of species production rates and rates of reaction. It may be generally said that the true path for a reaction is not known; however, a mechanism may be derived based on physics and mathematics which are

representative of the current state of existing data and state-of-the-art measurement systems.

An adequate reaction mechanism is one which meets the needs of the system in question. The depth of adequacy is not well defined. Simple one-step reaction mechanisms well calibrated to the fuel and oxidizer system of concern may be adequate for the purposes of an intended model. On the other hand, reaction models with various levels of detail may be required, as is expected for cool, fuel-rich flames and fuel-lean flames.

The reaction mechanism for hydrogen and oxygen has long been established. Nonetheless, variations exist in the number of reactions within a proposed mechanism. A generally applied mechanism reported in the literature is represented by 19 reactions and 8 species.²³⁰ Mechanisms using 33,²³¹ 37¹¹¹ and 62²³² reactions have also been proposed for application to the $H_2 + O_2$ or $H_2 + \text{air}$ reaction over a temperature range of 300 to 2500 K.

Westbrook and Dryer²³³ established reaction mechanisms for many hydrocarbons based on a hierarchical system of fundamental reactions. This system uses the basic reaction mechanism of $H_2 + O_2$ and progressively builds the reaction mechanism from the lighter to the heavier hydrocarbons. For many fuels, oxidation produces intermediates which are also primary fuels. Each mechanism for the subsequent heavier hydrocarbon includes the defined mechanism for the former lighter hydrocarbon. In this manner, reaction mechanisms were built for complex hydrocarbons.

Since most single-droplet ignition data were acquired using heavy hydrocarbons such as octane and heptane, reaction mechanisms for use in the present study were sought for these fuels. A variety of reaction mechanisms was found to exist, each differing in specific detail and number of reactions.

Axelsson et al.^{234, 235} proposed a mechanism for n-octane and iso-octane having 70 species and 500 reactions. Westbrook²³⁶ proposed a mechanism for iso-octane and n-heptane having 212 species and 765 reactions. Cowart²³⁷ proposed a mechanism for h-heptane, n-octane, and iso-octane having 324 species and 1303 reactions. Comprehensive mechanisms for n-pentane,²³⁸ and n-heptane^{239, 240} were also cited in the literature.

In an attempt to establish mechanisms for practical application in multidimensional models, reduced mechanisms have been contrived. The Shell Knock Model²⁴¹ was developed to study the autoignition of fuel blends such as iso-octane and n-heptane. The model was formed with 15 generalized reactions using a representative chemical entity for a general carbon atom skeleton structure of undefined length and makeup.²⁴² The reaction mechanism was descriptive for both low and high pressure chemistry and simulated the two-stage ignition process which is exhibited for most alkanes at initial temperatures below approximately 600 K. Two stage ignition is composed of an initial period beginning with the start of the reaction to observance of a cool flame, and a second period which extends from the sudden but definite temperature rise in the cool flame reaction to the sudden and large temperature rise in the explosive reaction. The initial mechanism was improved^{243, 244} using 19 reactions and demonstrated^{245, 246} for iso-octane and n-heptane blends. In addition, Westbrook and Dryer²³³ established equivalent one-step and two-step mechanisms for many hydrocarbons. These mechanisms have been routinely employed in theoretical single-droplet ignition studies.

Furutani et al.¹⁸³ proposed 19 positive-ion formation reactions for the production of ions in cool flames of heptane/air mixtures under rapid compression at temperatures near 600 K.

Reaction mechanisms for methanol, in a temperature range of 1000 to 2180 K having 25 species and 84 forward reactions, were proposed by Westbrook and Dryer.²⁴⁷ In addition, Gutheil²⁴⁸ demonstrated a methanol mechanism having 23 species and 84 forward reactions with application to spray ignition. Although the mechanisms of Westbrook and Gutheil are similar, significant differences exist in species and reactions used.

2.8 Remaining Challenges in Droplet Ignition Theory

This literature review is quite comprehensive; however, proper assessment of droplet ignition required that many branch fields be investigated. Basic droplet evaporation affects droplet ignition which affects droplet combustion which, in turn, affects evaporation. Therefore, one physical event may not easily be separated from the other in either experimental investigations or theories. In addition, droplet ignition theory is the result of early theories devoted to premixed gases. The application of droplet ignition theory to multiple droplets and sprays has led to a better understanding of the droplet ignition theory. Finally, the application of these theories to practical systems has defined limitations for their use. In summary, droplet ignition theories have evolved from many aspects of the combustion field and work is continuing in separate fields to solve similar problems.

Significant progress has been made toward understanding droplet ignition over the past decades. Nonetheless, a structured numerical approach has not been formed which will allow advanced knowledge of chemical kinetics, gas-vapor thermochemistry, and numerical formulations to be employed and assessed as they become available. A multipurpose numerical solver capable of

predicting ignition of fuel droplets in an ambient stagnant oxidizer would provide a basis for the fundamental understanding and assessment of physical processes involved in ignition theory, as well as provide a numerical laboratory for the implementation of new and developing hypotheses such as liquid-gas interface physics and chemical kinetic reaction mechanisms.

In addition, the literature is unclear on the effects of simplifying assumptions such as neglecting incident radiation, droplet finite conductivity, and one-step chemical kinetics on droplet heat-up, evaporation and combustion. Although most of the literature supports the fact that detail, in general, is required for fundamental representation of ignition events, little substantiation has been forthcoming related to these effects.

As a result of the literature survey, it appears that a significant contribution to droplet ignition physics and ignition modeling would be made by establishing a fundamental, validated numerical capability to assess droplet ignition, from which, improvements could be readily made, and the overall value of various submodels and thermo-physical data could be assessed. With this tool, the effects of droplet incident radiation, droplet finite conductivity, and one-step chemical kinetics on droplet ignition can be assessed. This is the primary focus of the present research.

CHAPTER III

APPROACH

3.1 Methodology Overview

In the present study, the approach to establishing, verifying, and applying a numerical model to investigate heat and mass transfer processes which occur prior to and during ignition was multifaceted. The baseline numerical model, CON1D,⁵ was ported from a Cray™ operating system to a personal computer operating system and the input and output were modified to streamline execution and graphical display of computed results. The existing physical models within CON1D were assessed for application to ignition events, and shortfalls were identified and corrected. This assessment used existing literature to establish a baseline for an adequate ignition model. With this accomplished, the model results were compared to classical quasi-steady droplet burning theory and ignition theory. Ignition delay, droplet regression rate, flame radius, droplet life time, and droplet flame temperature were predicted. Next, the model was validated over a limited range using the data of Faeth and Olson¹⁵² and Saitoh et al.¹⁸⁰ These data define the ignition delay of droplets from the time the droplets are introduced into a hot furnace until autoignition. These simulations used the one-step chemical reaction mechanism proposed by Westbrook and Dryer.²³³ Prior to validation, the affects of the model grid density and numerical boundary were assessed. The validation process produced the definition of an ignition criterion such that simulated ignition delay may be compared to experimental

values. During the validation process, variations of physical parameters during ignition were examined for use in a unique ignition criterion. Then the effects of droplet conductivity and incident radiation on ignition were investigated. The model was demonstrated for application to a detailed chemical kinetic mechanism using methanol fuel in air. Lastly, the model was demonstrated for application to predicting flow fields subsequent to spark ignition. In the present research study, predicted results using one-step and multi-step chemical reaction mechanisms were compared. The general outcome of the study was a droplet ignition model that showed close agreement with experimental data and provides insight to the physical and chemical mechanisms which control diffusion and reaction processes leading to ignition.

3.2 Analytical Model of Quasi-Steady Droplet Combustion and Ignition

For this investigation, it was instructive to review the analytical solutions for (1) quasi-steady droplet evaporation, combustion and (2) droplet ignition. Two distinct approaches have been used for quasi-steady combustion and droplet ignition.

The analytical solution of droplet evaporation with or without combustion in terms of the B transfer number assumes that chemical reactions are occurring sufficiently fast to prevent fuel species from reaching the outer boundary and oxidizer species from reaching the fuel droplet surface boundary. Essentially, it is assumed that kinetics may be finite but much faster than diffusion. Another assumption is that the Lewis number is equal to one, where, the Lewis number

is the ratio of the rate of diffusional energy transport to the rate of diffusional mass transport.

The analytical study of ignition involved the solution of the governing equations of mass and energy for a spherically symmetric droplet in an oxidizing environment. The outcome of this formulation provides a Damkohler number which may be used to define the ignition limits of any given system.

Godsave²⁵ and Spalding²⁶ first solved the symmetric conservation equations to describe droplet evaporation in a non-burning and burning environment. The development of an analytical solution of droplet evaporation typically employs these assumptions: (1) spherical symmetry without forced or natural convection, (2) flame sheet approximation to combustion: chemical reaction rates are faster than gas-phase diffusion rates producing a thin reaction zone acting only as a sink for reactants and a source for heat, (3) gas-phase specific heat, and thermal conductivity are constant; Lewis number is one, (4) gas-phase quasi-steadiness: the gas phase adapts instantly to imposed boundary conditions at the droplet surface, (5) single component fuel droplet with constant temperature and constant fluid properties, (6) constant pressure, (7) relation between the gas phase and droplet surface is defined using the vapor pressure correlation for the pure liquid in terms of the Clausius-Clapeyron equation, while the liquid surface was insoluble to surrounding gas, and (8) radiation is neglected. Faeth¹³⁶ noted that these assumptions become invalid at pressure below one atmosphere and above the fuel critical point and for droplets near 1 mm in diameter or less.

With these assumptions defined, the time dependent conservation equations of mass, fuel species, oxidizer species, and energy can be written for a burning droplet as follows:

$$\frac{\partial p}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho r^2 v) = 0 \quad (3-1)$$

$$r^2 \frac{\partial}{\partial t} (\rho Y_F) + r^2 \rho v \frac{\partial Y_F}{\partial r} = \frac{\partial}{\partial r} \left(r^2 D \frac{\partial Y_F}{\partial r} \right) + r^2 \dot{\rho}_F \quad (3-2)$$

$$r^2 \frac{\partial}{\partial t} (\rho Y_o) + r^2 \rho v \frac{\partial Y_o}{\partial r} = \frac{\partial}{\partial r} \left(r^2 D \frac{\partial Y_o}{\partial r} \right) + r^2 \dot{\rho}_o \quad (3-3)$$

$$\frac{\partial}{\partial t} (\rho C_p T) + r^2 \rho v \frac{\partial (C_p T)}{\partial r} = \frac{\partial}{\partial r} \left[r^2 \frac{\lambda}{C_p} \frac{\partial (C_p T)}{\partial r} \right] + r^2 \dot{Q} \quad (3-4)$$

The momentum equation is typically ignored in analytical theory since radial pressure gradients are not significant in most instances. The solution to these equations has been documented in most elementary combustion texts.²⁴⁹ For completeness, a solution is documented in Appendix B. Some pertinent results to this research include the flame standoff distance

$$\frac{r_f}{r_s} = \frac{\ln(1+B)}{\ln(1+(F/O)_{st} Y_{o,\infty})} \quad (3-5)$$

The variation of droplet surface area with time (evaporation rate) is

$$\beta = \left[\frac{d(d^2)}{dt} \right]_s = \frac{8\lambda}{\rho C_p} \ln(1+B) \quad (3-6)$$

Therefore, the total droplet vaporization time is

$$\tau = \frac{d_{s,o}^2}{\beta} \quad (3-7)$$

The flame temperature at r_f is

$$T_{\text{flame}} = \frac{1}{C_p} \left\{ \frac{\Delta h_{r,F} \left(\frac{F}{O} \right)_{st} Y_{o,\infty} + C_p (T_\infty - T_s) + \Delta h_v}{1 + \left(\frac{F}{O} \right)_{st} Y_{o,\infty}} - \Delta h_v \right\} + T_s \quad (3-8)$$

Analytical ignition theory has been developed primarily to assess ignition limits. Theoretical ignition delay models are semiempirical and typically incorporate constants which are representative of one-step Arrhenius type kinetics. However, theory focused on predicting ignition limits has evolved from a mathematical and physical background to develop relationships to assess “yes” ignition or “no” ignition for a given fuel immersed in a hot oxidizing environment.

The goal of ignition limit theory is to analytically study the familiar “S-shaped” curve (Fig. 2.4) which results from plotting the Damkohler number versus a relevant parameter such as gasification rate or maximum flame temperature. Recall that the Damkohler number is the ratio of a characteristic reaction rate and characteristic diffusion rate. A brief description of the S curve is appropriate. The S curve represents the progress of a vaporizing droplet which is initially chemically frozen ($Da = 0$) moving toward chemical equilibrium ($Da = \infty$). As Da increases from zero, chemical reactions begin and the gasification rate, for example, increases slightly. As progress continues, the chemical reactions occur so fast that the resultant released heat cannot be transported away. As a result, temperature in the reaction zone increases and the Arrhenius kinetics responds, further increasing reactivity. Ignition is said to

have occurred at this point corresponding to the upward inflection in the lower portion of the S curve.

Law^{137,142} has used the approach developed by Linān²⁵⁰ to define the diffusion flame structure in droplet burning. This approach reproduces the S curve using large activation-energy asymptotics with the inverse of the Arrhenius number as the small parameter of expansion. The formulation of the governing equations assumes spherical symmetry, quasi-steady conditions, isobaric combustion and one-step chemical kinetics. In general, asymptotic ignition analysis solves the governing equations in a nonreactive outer region and a reactive inner region between the flame zone and the droplet surface. The reactive region is assumed to be very thin such that outside of this region all chemical activity ceases. The solution to the inner region is matched with the solution to the outer region using the temperatures obtained at the common boundary. The resulting equation and boundary conditions were solved numerically resulting in an ignition Damkohler number as a function of a heat transfer parameter.¹³⁷ Radiation was neglected and gas-phase transport properties were assumed constant. Details of the solution methodology may be found from Law.^{137, 142}

System ignition is resolved by comparing the calculated system Damkohler number with a critical ignition Damkohler number resulting from the analysis by Law. A system Damkohler number, Da , (sometimes referred to as the reduced Damkohler number), may be defined as¹³⁷

$$Da = Da_0 Y_{o,\infty} \left(\frac{\rho_\infty a f m_0 Ar}{T_\infty} \right)^2 \quad (3-9)$$

where afm_0 denotes the mass evaporation rate

$$afm_0 = \ln \left(1 + \frac{T'_\infty - T'_s}{L} \right) \quad (3-10)$$

T is nondimensional and L is the ratio of the specific latent heat of vaporization and the specific combustion heat release. Da_0 is the initial system Damkohler number

$$Da_0 = \left[\frac{l_o^2}{\alpha_o} \right] / \left[\frac{\exp(Ar)}{i^m \rho_o^{(m+n-1)} A} \right] \quad (3-11)$$

where l_o is a characteristic length scale, α_o is the characteristic thermal diffusivity, $\lambda/(\rho C_p)$, and A is the pre-exponential factor.

By tracking the changes in system pressure, temperature, oxidizer concentration, droplet surface temperature, and droplet radius, the system Damkohler number, Da , may be computed and compared with the ignition Damkohler number, Da_i . The criterion states that ignition occurs when $Da > Da_i$. For small values of θ , Law¹⁴² states a good approximation to Da_i is

$$Da_i = \left(\frac{1 + 0.531\theta}{(1 - \theta)^2} \right)^2 \quad (3-12)$$

As previously presented herein, it has also been noted¹³⁸ that for most hydrocarbon fuels, for $\theta < 0.35$,

$$Da_i = 1.05 \exp(6.40\theta) \quad (3-13)$$

Law¹³⁸ has shown good agreement with experimental data of Faeth and Olson,¹⁵² Wood and Rosser,¹⁷³ and El-Wakil and Abdou¹⁶⁹ for calculating ignition limits of hydrocarbon fuels in air. In addition to the limitations inherent with the stated assumptions, the application of this criterion requires that some of the thermodynamic properties (e.g., gaseous diffusivity, pressure, and species mass fraction) and chemical kinetic pre-exponential and activation energy values must be extracted from the experimental data set; therefore, an a priori prediction may be precluded.

3.3 Baseline Physical Model

The physical and numerical models have been described by Janssen and O'Rourke⁵ in detail and are reviewed here for completeness. Amsden's⁶ development of a physical system for spray analysis may also be referred to for additional definition. Nomenclature used herein is identical to that used in the CON1D program to facilitate reference. The purpose of the model is to predict the time required for ignition after the droplet has been exposed to either a high temperature environment or an energetic source such as might be generated by an electric spark, laser induced spark or laser induced photochemical initiation.

Spherical symmetry is assumed and natural and forced convection is neglected. Spherical symmetry was chosen to reduce computational time while focusing on the effects of heat and mass transfer and chemical kinetics on ignition. Theoretical work by Sangiovanni²⁵¹ and experiments by Faeth and Olson¹⁵² showed that convection has only a small effect on the ignition delay time. However, convection can affect the radius at which ignition occurs. The presence of convection may change the ignition mode from an envelope mode to

a wake mode. The effects of an igniter source induced shock wave are also neglected, although it is recognized that the consideration of such an event would disrupt the droplet resulting in unsymmetric deformation.

The droplet liquid temperature is assumed uniform and equal to the droplet surface temperature. Faeth⁹⁸ described the characteristic times for droplet heat-up and evaporation as a function of pressure. The characteristic time for the diffusion of heat within the liquid droplet is defined by D^2/α_F and the droplet lifetime without the combustion can be characterized by the group:

$$\frac{D^2 \Delta h_v}{C_{p,F} \alpha_F (T_{WB} - T_o)} \quad (3-14)$$

At low pressures, the wet bulb temperatures are low and the heat of vaporization is high. For this condition, the droplet heat-up time becomes negligible compared with the droplet lifetime. Furthermore, Faeth notes that liquid-phase properties may be assumed constant for fuels near ambient pressure. However, higher pressures result in reduced liquid densities and can affect droplet properties.

The one-dimensional system of conservation equations for species mass, mixture mass, momentum, and energy are written as follows:

$$\frac{\partial \rho_k}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho_k u r^2) = \frac{1}{r^2} \frac{\partial}{\partial r} \left[\rho D r^2 \frac{\partial}{\partial r} \left(\frac{\rho_k}{\rho} \right) \right] + \dot{\rho}_k^c \quad (3-15)$$

$$\frac{\partial \rho u}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho u^2 r^2) + \frac{\partial p}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \Sigma_\pi) - \frac{\Sigma_{\theta\theta} + \Sigma_{\phi\phi}}{r} \quad (3-16)$$

$$\begin{aligned} \frac{\partial pI}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho I u r^2) + \frac{p}{r^2} \frac{\partial}{\partial r} (u r^2) = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\lambda r^2 \frac{\partial T}{\partial r} \right) + \\ \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} r^2 \rho D \left[\sum_{k=1}^N h_k \frac{\partial}{\partial r} \left(\frac{\rho_k}{\rho} \right) \right] \right\} + \Sigma_{\pi} \frac{\partial u}{\partial r} + \frac{u}{r} (\Sigma_{\Phi} + \Sigma_{\Theta}) + \dot{Q}_c \end{aligned} \quad (3-17)$$

where $k = 1, \dots, N$ species.

The species mass conservation equation has been formulated neglecting the effects of thermal diffusion on species mass diffusion (i.e the Soret effect). Fundamentally, the mass transfer flux would contain concentration, thermal, pressure and forced diffusion terms.⁹⁸ Forced diffusion occurs only for charged species in the presence of an electric field and can be neglected for this analysis.²⁵² Pressure diffusion is small for typical flows and does not exist in the absence of a pressure gradient. Thermal diffusion accounts for generally less than 10 percent of the total diffusion.²⁵³ Fick's Law is employed assuming an effective binary diffusivity for all species. This is appropriate when all species except one are moving at nearly the same diffusion velocity.

The energy conservation equation has been formulated neglecting the effect of mass diffusion on energy diffusion. Fundamentally, the energy flux is composed of a conductive flux, radiative flux, interdiffusion flux due to internal energy gradients within the flow field, and a thermodiffusion flux. The thermodiffusion flux is the flux due to mass diffusion and is termed the Dufour effect. The Dufour energy flux is quite complex and usually of minor importance for multicomponent systems.⁹⁸

The ideal gas equation of state is used:

$$p = \sum_{k=1}^N \frac{\rho_k}{W_k} R_u T \quad (3-18)$$

Transport coefficients for viscosity, diffusivity, and thermal conductivity are defined by the following relations assuming constant kinematic viscosity, Schmidt, and Prandtl numbers:

$$\begin{aligned}\mu &= \rho \nu_0 + C_1 T^{3/2} / (T + 110K) \\ \zeta &= -\frac{2}{3} \mu \\ D &= \frac{1}{Sc} \frac{\mu}{\rho} \\ \lambda &= \frac{1}{Pr} \mu C_p\end{aligned}\tag{3-19}$$

The stress tensor components are given by the following relations:

$$\begin{aligned}\Sigma_{rr} = \Sigma_{\theta\theta} &= 2\mu \frac{\partial u}{\partial r} + \frac{\zeta}{r^2} \frac{\partial}{\partial r^2} (ur^2) \\ \Sigma_{\phi\phi} = \Sigma_{\theta\theta} &= 2\mu \frac{u}{r} + \frac{\zeta}{r^2} \frac{\partial}{\partial r^2} (ur^2)\end{aligned}\tag{3-20}$$

Detailed finite rate chemical reactions are considered for the mixtures and proceed according to the following description for each reaction, l :

$$k_l = A_{\eta} T^{\eta_{\eta}} \exp(-Ea_{\eta} / T) \prod_{k=1}^N \left(\frac{\rho_k}{W_k} \right)^{a_{k,l}} - A_{bl} T^{\eta_{bl}} \exp(-Ea_{bl} / T) \prod_{k=1}^N \left(\frac{\rho_k}{W_k} \right)^{b_{k,l}}\tag{3-21}$$

The chemical source terms are defined as follows:

$$\dot{\rho}_k = W_k \sum_{l=1}^{NK+NE} (b_{k,l} - a_{k,l}) k_l\tag{3-22}$$

$$\dot{Q}_c = \sum_{l=1}^{NK+NE} \dot{\omega}_l Q_l \quad (3-23)$$

$$Q_l = -\sum_{k=1}^N (b_{k,l} - a_{k,l})(\Delta h_F^o)_k \quad (3-24)$$

Boundary conditions are defined at the droplet surface and at infinity. Pressure, temperature, and species mass fraction are specified at a finite radius. Assuming that no gas or vapor species are absorbed into the droplet liquid, interface mass and energy exchange are governed by the following relations:

$$-\rho_L \frac{dr}{dt} \delta_{k,1} = \rho_k \left(u - \frac{dr_s}{dt}\right) - \rho D \frac{\partial}{\partial r} \left(\frac{\rho_k}{\rho}\right) \quad (3-25)$$

$$\lambda \left. \frac{\partial T}{\partial r} \right|_{r_s} = \frac{r_s}{3} \rho_F C_{p,L} \frac{dT_s}{dt} + m \Delta h_v + m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{rr}}{\rho} \right) \quad (3-26)$$

where m is defined as follows:

$$m = \rho \left(u - \frac{dr_s}{dt}\right) \quad (3-27)$$

The relationship between the liquid temperature and the gas phase fuel concentration at the liquid surface is usually obtained from the equilibrium vapor pressure of the pure fuel as a function of temperature. Species temperature and density at the droplet surface are defined using the Clausius-Clapeyron equation:

$$\frac{\frac{\rho_1}{W_1}}{\sum_{k=1}^N \frac{\rho_k}{W_K}} p = p_o \exp \left(\int_{T_o}^{T_s} \frac{\Delta h_v W_1}{R_u T^2} dT \right) \quad (3-28)$$

where the latent heat per unit mass is defined as follows:

$$\Delta h_v(T_s) = h_g(T_s) - [h_{ref} + C_{p,L}(T_s - T_{ref})] \quad (3-29)$$

The implied assumption is that the presence of other gases at the surface does not affect the equilibrium vapor pressure. This is acceptable for pressures near ambient where liquid phase solubility of the ambient gases are negligible.

Liquid density is assumed to be constant and is equal to the initial value defined at the initial droplet temperature. Liquid specific heat capacity and liquid enthalpy are defined at a reference temperature. Thermodynamic enthalpy of the gaseous species is defined as a function of temperature over the temperature range 0 to 5000 K, and is provided in tabular or curve-fit formats.

3.4 Baseline Numerical Model

The governing equations were formed into equivalent finite difference equations in both the spatial and time domains.⁵ The computational domain is divided into one-dimensional volumetric cells beginning one cell deep into the droplet through the gaseous reactive domain (Fig. 3.1). All thermodynamic quantities are computed at cell centers while cell location and velocity are defined at cell left-edge. Thermodynamic quantities of cell 1 are located at the droplet surface, which is the edge between cells 1 and 2. One computational cycle advances each cell quantity by a time step denoted dt , which is determined for each cycle on the basis of stability and accuracy conditions.

The computational cycle is composed of two parts. First, the cell edge moves with the fluid velocity according to a Lagrangian calculation. Second, the computational mesh is updated (or rezoned) to correspond to the new location of the cell edge caused by the motion of fluid relative to the mesh. Transport quantities of chemical species, momentum, and energy calculated in stage one are augmented by the respective fluxed quantities of the volume swept out by the cell edge as it moves from its initial Lagrangian location to its subsequent time step location.

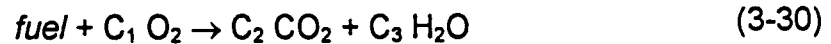
Three rezone options have been provided by Janssen and O'Rourke⁵ to accomplish adaptive remeshing: (1) Eulerian rezone on the gas phase mesh (2) Lagrangian rezone on the gas phase mesh, and (3) user-defined rezone.

Full details of the Lagrangian phase mass, momentum, and energy equations finite differencing may be found in the original CON1D report⁵.

3.5 Chemical Kinetic Mechanisms

Chemical kinetics represent a complex field where researchers are continuing to define both specific intermediate reaction steps and Arrhenius-type reaction rate constants for these steps. Westbrook and Dryer²³³ have established a hierarchical approach to define detailed hydrocarbon reaction mechanisms and proposed simplified one-step and two-step chemical reaction mechanisms for many hydrocarbons. Bergeron and Hallett¹⁵⁸ have shown that adjustments must be made to these models for diffusion flames ignition studies at high temperatures. Nonetheless, one-step mechanisms are usually based on deduced values of pre-exponential and activation energy which will reproduce the desired global thermodynamic results.

One-step mechanisms have been formulated for each fuel investigated (Table 3.1). These mechanisms are based on a typical single-step fuel oxidation reaction of the form



where the stoichiometric coefficients, C_1 , C_2 , and C_3 , are a function of the fuel type. The corresponding rate equation is

$$k_{\text{one-step}} = AT^n \exp(-E_a/T) [X_{\text{fuel}}]^a [X_{\text{oxidizer}}]^b \quad (3-31)$$

where a and b are empirically defined constants from experiments or detailed chemical reactions.²³³

Parametric variations of the constants in the above equation were performed by Westbrook and Dryer²³³ to obtain a set of values for various hydrocarbon fuels which correctly predict maximum flame speed and equivalence ratio at which this maximum occurs, and lean and rich flammability

Table 3.1 One-Step Hydrocarbon Air Reactions.			
Fuel	Reaction	a	b
n-C ₇ H ₁₆	C ₇ H ₁₆ + 11 O ₂ + 11 (3.76) N ₂ → 7 CO ₂ + 8 H ₂ O + 11 (3.76) N ₂	0.25	1.5
i-C ₈ H ₁₈	C ₈ H ₁₈ + 12.5 O ₂ + 12.5 (3.76) N ₂ → 8 CO ₂ + 9 H ₂ O + 12.5 (3.76) N ₂	0.25	1.5
n-C ₈ H ₁₈	C ₈ H ₁₈ + 12.5 O ₂ + 12.5 (3.76) N ₂ → 8 CO ₂ + 9 H ₂ O + 12.5 (3.76) N ₂	0.25	1.5
n-C ₁₆ H ₃₄	C ₁₆ H ₃₄ + 24.5 O ₂ + 24.5 (3.76) N ₂ → 16 CO ₂ + 17 H ₂ O + 24.5 (3.76) N ₂	0.25	1.5

limits in premixed gases. As noted by Westbrook and Dryer, a one-step mechanism has inherent flaws in its application to hydrocarbons. Specifically, at typical flame temperatures of hydrocarbons, significant levels of CO, H₂, and NO exist in equilibrium with CO₂ and H₂O, thus lowering the adiabatic flame temperature approximately one percent. In addition, simplified mechanisms neglect the multi-step oxidation of hydrocarbons which burn in a sequential manner through a hierarchical breakdown of the original fuel molecule into lighter fuel molecules such as methane, C₂H₄, acetylene, C₂H₂, and others. It has been postulated that CO and H₂ are not consumed until all hydrocarbon species have disappeared.

The constants defined by Westbrook and Dryer have been contrived to match maximum laminar flame speed data at the equivalence ratio at which this maximum speed occurs. As a result, it appears that the pre-exponential and activation energy values may not be suitable for simulations in which the local equivalence ratio varies with space and time.

Bergeron and Hallett¹⁵⁸ contrived the pre-exponential and activation energies to match data of ignition delay for several hydrocarbon fuel droplets. These values were significantly different from those of Westbrook and Dryer.

Within the present study, pre-exponential and activation energy values are formed for the one-step reactions based on the work of Bergeron and Hallett.¹⁵⁸ Parametric variations of pre-exponential and activation energy are accomplished by matching the overall species chemical source term for the fuel documented by Bergeron. This source term is calculated using the following relations

$$\dot{\rho}_k^c = W_k k_1 \quad (3-32)$$

$$k_i = A_{f,i} T^{\eta_i} \exp(-E_{a,f,i} / T) \prod_{k=1}^N \left(\frac{\rho_k}{W_k} \right)^{s_{k,i}} \quad (3-33)$$

The intent of demonstrating a multi-step reaction mechanism is to (1) investigate common issues associated with such an application, and (2) investigate the effects of detailed kinetics on ignition events. Because the mechanisms, cited in Chapter 2 section 7, are significant in number of reactions and number of species for heavy hydrocarbons, the demonstration was accomplished using a light hydrocarbon. Methanol is a liquid at normal room conditions and a detailed chemical kinetic mechanism is available for this fuel which, though large, appears manageable. Application of this data set requires determination of backward reaction rates and enthalpy as a function of temperature for all species involved in the reaction set. Two detailed mechanisms for methanol have been proposed by Westbrook²⁴⁷ and Gutheil.²⁴⁸ The mechanism of Gutheil is not wholly defined since thermodynamic properties of several species are not defined. The reactions and species are nearly identical for each mechanism.

The methanol mechanism proposed by Westbrook and Dryer was chosen because thermodynamic properties were available for all species used. This mechanism was validated by comparing selected calculated species concentrations to experimental values in a temperature range of 1000 to 2180 K, fuel-air equivalence ratios of 0.05 to 3.0, and pressures of 1 to 5 atmospheres. In addition, the chemical kinetic model was used to simulate the flame propagation speed of a stoichiometric methanol - air mixture. The reaction rates for each reaction were defined by numerous sources.

This mechanism was used along with the corresponding one-step mechanism for methanol as defined by Westbrook and Dryer.²³³ Their proposed pre-exponential and activation energy values for the one-step mechanism of methanol was used (Appendix C).

3.6 Ignition Criteria

As discussed in the literature survey, Chapter II, ignition criteria have been defined in various ways. Experimentally, ignition was defined using visual records as the event at which first light was recorded. Other experimenters chose to use sound or pressure measurements to define the instant of ignition. Theoretical criteria were originally empirically based, often derived from simple curve fits of experimental data. Peskin et al.¹⁴¹ developed a semi-empirical criterion which implied that ignition occurred upon transition from a kinetically controlled reaction to a diffusionally controlled reaction. As defined in Chapter II, Faeth and Olson¹⁵² developed a criterion based on an accumulating integral:

$$\psi(r, t) = \frac{X_i(r, t)}{X_{ic}} = \int_0^t C_1 P^{C_2} \phi^{K_3}(r, t) \exp\left[\frac{-E_a}{R_u T_g(r, t)}\right] dt \quad (3-34)$$

where C_1 , C_2 , and C_3 are empirically-derived values for the specific fuel under investigation. This criterion precluded specie tracking during the reaction process. Early numerical models did not solve multi-specie reaction kinetic mechanisms, rather, these models used only fuel and air as two generic species. Later models simply used calculated gaseous spatial temperature to define the instant of ignition. Bergeron and Hallett¹⁵⁸ proposed that ignition occurred when

the temperature reached 2000 K, a nominal temperature at which first visible light would occur. Dwyer and Le¹⁶⁵ proposed that ignition occurred when the temperature anywhere in the gaseous field exceeded twenty percent of the surrounding gas temperature.

In general, the ignition criterion employed within a simulation must allow direct comparison to the type of experimental data used to assess first light or ignition. The ignition delays measured in experiments has been derived from visual records of the flame, sound records, temperature histories, or pressure histories. In the present study, data are used whereby ignition delay was assessed as the time from droplet introduction into a hot furnace until the first visual indication of light. Therefore, an ignition criterion must be established which defines the thermodynamic conditions (such as flame temperature) which correspond to the time at which first visible light appears. A proper assessment requires a review of hydrocarbon flame structure.

The hydrocarbon flame is made visible by chemiluminescent radiation. The color of a hydrocarbon diffusion flame is different from that of a premixed flame. Within a premixed flame, the visible emitting species are primarily free radicals, C_2 and CH. The species, C_2 , is formed through a highly exothermic reaction in the formation of carbon. First hydrogen atoms are partially stripped from hydrocarbon molecules by reaction with OH. Second, highly unsaturated carbon groups polymerize, releasing heat, and split off excess carbon atoms. C_2 appears to be very stable. The C_2 bands appear green while the CH bands appear violet blue to the eye. In rich mixtures, the C_2 bands predominate. As the oxygen content is increased, the CH bands become dominant.

The diffusion flame varies from a bright yellow to orange. This color is the result of the formation of soot on the fuel side of the flame. Soot particles reach

the flame temperature as they pass through the reaction zone. Some soot may escape consumption in the reaction zone and appear as black smoke. Non-soot forming flames such as methanol are barely visible and appear similar to their premixed flame counterparts.

Because the onset of visible light in diffusion hydrocarbon flames corresponds to the burning of soot particles in the reaction zone, the ignition criterion can be associated to the thermodynamic conditions within the flame at soot initiation.

The formation of soot within a diffusion combustion flame is a complex phenomena. The tendency for a mixture of fuel and oxidizer to soot is controlled by the separate processes of fuel pyrolysis and oxidation. Initially, fuel pyrolysis produces soot precursors. The relative amount of oxidation of these precursors controls the amount of soot formed. For example, within premixed flames, sooting tendency tends to decrease with increasing temperature. This is because the rate of oxidation of the soot precursors increases faster with temperature than fuel pyrolysis. In diffusion flames, however, soot is formed on the fuel side of the flame where little oxygen is available. In this region, oxidation is controlled by diffusion and cannot compete with the fuel pyrolysis process. Therefore, sooting tendency of diffusion flames tends to increase with increasing temperature.

Sooting tendencies of premixed flames have been shown to correlate well with measured flame temperature or calculated adiabatic flame temperature. Takahashi and Glassman have correlated critical equivalence ratios at which sooting occurs with calculated adiabatic flame temperature²⁵⁴ for many hydrocarbons in air. Harris et al.²⁵⁵ measured flame temperatures near adiabatic

flame temperature values in premixed systems and showed similar results of sooting tendency with equivalence ratio for a few hydrocarbons.

Sooting tendencies of diffusion flames have primarily been investigated using a concentric rectangular configuration with the fuel stream in the center and air in the outer post. The liquid fuels are vaporized to form a gaseous jet in the center post. This experimental apparatus is used to define parametric effects on measurements as a function of sooting height, which is the minimum height at which soot is observed to first break through the top of the luminous flame.²⁵⁶ Early experimental results indicated that soot propensity was dependent on fuel structure and temperature and not on the hydrogen-to-carbon atom ratio of the initial fuel.²⁵⁷ Laser light scattering measurements of soot particle properties²⁵⁸ indicated that temperature exerts the strongest influence on soot formation. Nonetheless, fuel structure defines the rate of pyrolysis and reactive pyrolysis steps and, therefore, significantly affects soot production.

Recent measurements²⁵⁹ of temperature and species concentrations of a methane and air flame revealed that the adiabatic flame temperature was nearly reached and, in fact, was reached when the thermocouple measurements were corrected for radiation. In addition, these measurements showed that soot initiation occurred in the flame region which had the appropriate fuel/air ratio, temperature, and proximity to the radical-rich reaction zone.²⁰

Although fuel pyrolysis leading to the formation of soot is thought to begin in a region on the fuel side of the flame (and thus at a lower temperature than the maximum flame temperature), Gomez et al.²⁶⁰ proposed the adiabatic flame temperature as an appropriate surrogate temperature for correlating soot formation. Logically, the temperature in the sooting region is controlled in part

by heat transfer from the reaction zone which is near the adiabatic flame temperature.

Therefore, it seems justifiable to define the ignition delay as the time required from simulation start (i.e., droplet is at initial conditions and immersed in ambient oxidizer) to the time at which the calculated temperature reaches the stoichiometric adiabatic flame temperature. Note that this criterion is one which will be appropriate for comparison to the experimental data which defines ignition delay as the time to first visible light.

Adiabatic flame temperatures were defined for the reactions listed in Table 3.1 using the NASA SP273 ⁶¹ chemical equilibrium code. They are as follows for the respective fuels: n-heptane, 2232 K; octane, 2230 K; n-hexadecane, 2236 K. NASA SP 273 was used iteratively solving chemical equilibrium at a defined temperature and pressure until convergence occurred at equal reactant and product heats of reaction. Using NASA SP273 provides a technique to account for dissociation as a result of the high flame temperatures. Dissociation, even in small amounts, creates additional species (for example, carbon monoxide, atomic hydrogen) other than water vapor and carbon dioxide which act to lower the overall temperature from values near 2500 K to more realistic values near 2200 K.

Alternative ignition criteria might be based on (1) initial production of product species, (2) change in droplet gasification rate, or (3) change in product species rate. Within this study, pertinent parameters are investigated to define an alternative ignition criterion. A logical criterion should be established to make proper assessments of existing data or perhaps consistent assessments among simulated droplet ignition studies. For example, experimental data of droplet autoignition delay times examined for use in the present study primarily use

visual records of flame initiation to define the ignition event. Therefore, the ignition criterion implemented in the numerical routine should correspond to this physical event. Numerical simulations provide a capability to establish ignition criterion based on continually updated flow fields and droplet surface conditions. Nonetheless, some rational or logical criterion should be defined and used to make proper assessments to existing data or perhaps to achieve consistent assessments among droplet ignition studies. In addition, a criterion could be formed which would be applicable within multi-dimensional codes. Such a criterion would most likely track global variations of thermodynamic properties or species mass fractions. This approach would be more applicable to a complex spray than an approach which monitored individual droplet property variations.

CHAPTER IV

IMPROVEMENTS TO THE IGNITION MODEL

4.1 Shortfalls in the Baseline Model

Literature reviewed in Chapter 2 cited important features required to adequately predict ignition delay times and, most likely, the heat and mass transfer process leading up to ignition. These requirements (Table 4.1) were

Table 4.1 Shortfalls in the Baseline Model for Application to Ignition Systems.		
Requirement for Ignition Model	Historical Approach	Baseline CON1D
1-D Radial Symmetry	✓	✓
Time Accurate	Quasi-Steady	Transient
Variable Droplet Transport Properties	-	✓
Finite Rate Chemistry	one-step	✓
Species Concentration Tracking	-	✓
Spatial Gas-phase Transport Properties	-	✓
Variable pressure Field	-	✓
Radiation Heat Transfer to Droplet	Limited Use	-
Finite Droplet Conductivity	-	-

compared with the baseline model and shortfalls were identified.

The primary shortfalls in the existing or original CON1D code were (1) no radiation heat transfer model, and (2) infinite conductivity was assumed for droplet heat-up. These shortfalls were addressed in the present study.

4.2 Baseline Source Code Modifications Required for Compilation and Execution

Once the source code was received from Los Alamos, numerous modifications were required to eliminate the CRAY™-specific system calls that were embedded in the source file. The code was modified to run on a PC using the Microsoft Fortran Powerstation™ compiler. Compiler specific calls were minimized to maintain a generic source which could be moved, if necessary, to a computationally powerful workstation. One Powerstation™ system call was included to retrieve the date and time, and thus enable solution efficiency to be tracked.

During the present study, two subroutines were added. A matrix solver was added to the chemical equilibrium subroutine, CHEMEQ, to provide a matrix inversion routine for solving the chemical equilibrium equations. However, note this subroutine was not necessarily required for this study of chemical kinetics-controlled processes. A subroutine, EXITPRO, was also added to support abnormal and normal code execution termination. Subroutines TAPERD and TAPEWR were rewritten to allow the solution to be restarted while maintaining problem simulation time accuracy. These routines originally used CRAY™-specific functions to prepare an output file and to read the input file. The output subroutine, FULOUT, was modified to prepare a plottable output file. An ASCII

text file could then be generated and read by Microsoft EXCEL™ to create various time transient plots. In addition, the input subroutine, RINPUT, was modified to accommodate streamlined, user-friendly input. As a matter of record, considerable time was spent defining the units of the input values which were consistent with the source code requirements.

Machine accuracy consistent with a 32 bit compiler was not sufficient for convergence in subroutine PRESIT. This subroutine solved for the Lagrangian pressure of each cell, i , using an iterative procedure. Typically, only 4 iterations have been required to solve these implicit governing equations. The symptom in PRESIT was simply nonconvergence to the specified criteria. This problem was eventually attributed to the roundoff error occurring in the floating point number for the Powerstation™ compiler executing on the INTEL 486™ processing chip. This was corrected by compiling the source in double precision. Problems with machine accuracy were anticipated to some degree since the original version of CON1D was compiled on a CRAY™ computer. This system uses 64 bit words compared to 32 bit words used by the Powerstation™ compiler.

4.3 Radiation Heat Transfer Model

In many physical systems using hydrocarbon fuels, radiation heat transfer from existing hot surfaces or flame zones may provide a significant portion of the overall heat load to the droplet. Faeth⁹⁸ noted that for industrial furnace conditions, the ratio of the radiative to conductive heat flux for single droplets burning in an envelope mode was in the range 0.02 to 0.2. Likewise, Hottell et al.²⁶¹ showed that for ambient air temperatures near 1273 K, the ratio of the radiative to conductive heat flux increased from 0.2 to near 1.0 with increasing

droplet diameter. Hottell's predictions are likely high since they are based upon low values of heat conduction. The effect of radiation heat transfer on ignition delay is also important. However, the extent and transient effects of incident droplet radiation are not well documented. Literature indicates that the effects of radiation on transient droplet temperature distribution may be offset by assuming infinite conductivity. That is, a droplet model based on infinite conductivity would produce ignition delay times similar to test data in which radiation was known to exist and probably affect ignition delay.

Of the radiation incident on the droplet surface, only a fraction is absorbed; the remaining is reflected or transmitted. Radiative flux at the droplet surface is defined as

$$\dot{q}'' = \epsilon \sigma (T_{\text{rad}}^4 - T_s^4) \quad (4-1)$$

Multiplying by the surface area of a sphere, $4\pi r^2$, and dividing by the volume of a sphere, $4\pi r^3/3$, the volumetric absorption per unit time of radiation within the droplet is characterized by the following relation:

$$\dot{q}_{\text{rad}}''' = \frac{3\sigma\epsilon(T_{\text{rad}}^4 - T_s^4)}{r_s} \quad (4-2)$$

where the absorption coefficient has been empirically defined as a function of radius by Hottell²⁶¹ with the following relation:

$$\epsilon = 0.658(1 - \exp(-29.2r_s)) \quad (4-3)$$

This relation requires that the radius be specified in centimeters to match experimental absorptivity data..

The additional radiation source term was added to the energy equation describing the temporal and spatial internal temperature distribution of the droplet (see below, section 4.4). As a result, the heat flux to the droplet consists of both conduction from the surrounding gas and radiation from a user-selected source.

The implementation of the radiation flux term into the baseline source code was completed to provide several user-selected options. The flux may be based on (1) T_{rad} equal to a fixed value representative of a solid surface, or (2) T_{rad} equal to the maximum calculated flame temperature. In addition, radiation may be set to zero. All simulations in this study were performed assuming the radiation source was the flame zone at the associated flame temperature.

With a droplet heating model based on finite conductivity, model results, including radiation implemented as described in section 4.4, generally showed a ratio of radiative flux to conductive flux on the order of 0.5 (Fig. 4.1). This is in relative agreement with the indications provided by Faeth and earlier by Hottell.

4.4 Internal Droplet Heat Transfer Model

Heat transferred from the hot gas surrounding the droplet to the droplet surface provides part of the energy for droplet liquid gasification, with the remainder of the transferred energy providing heat to the droplet interior. The liquid near the surface is the warmest, while interior regions are cooler. As time progresses, the entire droplet heats up with the interior regions approaching the droplet surface temperature. During this time, the droplet may be burning with a

regressing surface. Internal circulation is the physical mechanism responsible for modifying the length and time scales of heat transfer within the droplet. Although internal circulation is neglected by the spherically symmetric approach, consideration of the full transient droplet heat-up process provides a more rigorous analysis.

Historically, the general effects of finite conductivity on ignition events have been recognized. However, little information was discovered in the literature regarding investigation of the parametric effects of finite droplet thermal conductivity on droplet behavior during the ignition process.

There are two common approaches to including time varying temperatures within the droplet. The first approach, called the rapid-mixing limit model, assumes that the droplet possesses infinity conductivity. In this case, the entire droplet mass exists at an equal temperature without spatial gradients. Therefore, the heat flux transferred from the gas to the droplet is generally expressed by

$$\dot{q}_s'' = \lambda_g \left. \frac{\partial T}{\partial r} \right|_{r=r_s} = m\Delta h_v + \rho_L C_{p,L} \frac{dT_s}{dt} \quad (4-4)$$

The second approach, the diffusion limit model, assumes finite conductivity exists within the droplet, with the heat flux expressed by

$$\dot{q}_s'' = \lambda_g \left. \frac{\partial T}{\partial r} \right|_{r=r_s} = m\Delta h_v + \lambda_L \frac{\partial T}{\partial r} \quad (4-5)$$

The temperature distribution within the droplet is then defined by solving the energy equation within the droplet subject to these boundary conditions.

Sirignano¹⁰⁰ recommends that the diffusion limit model be employed to provide a more rigorous method of solving droplet heat-up.

Modeling results by Faeth and Olson,¹⁵² neglecting radiation, showed that internal temperature differences within the droplet due to transient heat conduction have an effect on ignition delay for droplets up to 0.10 cm in radius. Specifically, the finite conductivity of a droplet will reduce calculated ignition delay to approximately 60 percent of the calculated ignition delay based on infinite conductivity. Hottell et al.²⁶¹ showed that internal absorption of thermal radiation will tend to make the internal temperature uniform for droplets less than 0.10 cm in radius.

By including finite droplet heat transfer within the baseline model, CON1D, the baseline droplet surface boundary condition had to be appropriately modified. The baseline boundary condition of the gas field at the droplet surface assumed infinite liquid thermal conductivity. Therefore, the boundary condition at the droplet surface (the heat transferred from the gas to the droplet surface) was governed by the following equation, which, for infinite droplet conductivity, is the energy balance equation for the entire droplet.

$$\dot{q}_s'' = \lambda_s \left. \frac{\partial T}{\partial r} \right|_{r=r_s} = \rho \left(u - \frac{dr_s}{dt} \right) \Delta h_v + \frac{1}{3} r_s \rho_L C_{p,L} \frac{dT_s}{dt} + m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{\gamma}}{\rho} \right) - \dot{q}_{rad}'' \quad (4-6)$$

Literally, this states that the heat transferred from the gas by conduction and radiation to the droplet surface is used to effect gasification with the rest being used to heat up a lumped mass of liquid droplet. The kinetic heat terms are small but have been included for completeness.

A more fundamental boundary condition at the droplet surface includes the temperature gradient due to finite thermal conductivity within the droplet.

$$\dot{q}_s'' = \lambda_s \frac{\partial T}{\partial r} \Big|_{r=r_s} = \rho \left(u - \frac{dr_s}{dt} \right) \Delta h_v + \lambda_L \frac{\partial T}{\partial r} \Big|_{r=r_s} + m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{\eta}}{\rho} \right) \quad (4-7)$$

For the finite conductivity case, the radiation term enters the problem by adding a source term to the droplet energy equation.

The energy equation within the droplet must be solved to supply the gradient within the above equation. The fully implicit method used by Litchford and Jeng²⁶² has been employed in the present study to calculate the internal droplet heat distribution as a function of time. This technique uses a nondimensional governing energy equation for the liquid droplet and thus allows the computational grid to vary with each time-step to accommodate the regressive droplet surface. In addition, the implicit method provides an unconditionally stable numerical algorithm required to handle the discontinuity of thermal conductivity across the droplet interface.

The energy equation defined by Litchford and Jeng²⁶² was modified to include (1) a radiation source term representative of the incident radiation volumetrically absorbed by the droplet, (2) a heat conduction term representative of the heat load from the surrounding gas to the droplet, and (3) all spatial terms expressed in droplet radius instead of diameter. The energy equation within the droplet can be expressed as:

$$\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} + \left(\frac{1}{\alpha} \frac{r}{r_d} \frac{dr_d}{dt} \right) \frac{\partial T}{\partial r} + \frac{3\epsilon\sigma(T_\infty^4 - T_s^4)}{r_d \lambda_L} \quad (4-8)$$

This equation can be nondimensionalized as follows:

$$\frac{r_d^2}{r_{d,0}^2} \frac{r_{d,0}^2}{\alpha} \left[\frac{1}{\alpha} \frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} + \left(\frac{1}{\alpha} \frac{r}{r_d} \frac{dr_d}{dt} \right) \frac{\partial T}{\partial r} + \frac{3\epsilon\sigma(T_\infty^4 - T_s^4)}{r_d \lambda_L} \right] \quad (4-9)$$

Rearranging yields

$$\begin{aligned} \frac{r_d^2}{r_{d,0}^2} \frac{1}{\alpha} r_{d,0}^2 \frac{\partial T}{\partial t} &= r_d^2 \frac{\partial^2 T}{\partial r^2} + r_d^2 \left(\frac{2}{r} + \frac{1}{\alpha} \frac{r}{r_d} \frac{dr_d}{dt} \right) \frac{\partial T}{\partial r} + r_d^2 \frac{3\epsilon\sigma(T_\infty^4 - T_s^4)}{r_d \lambda_L} \\ \frac{r_d^2}{r_{d,0}^2} \frac{\partial T}{\partial(\alpha t/r_{d,0}^2)} &= r_d^2 \frac{\partial^2 T}{\partial(r/r_d)^2} + \left(\frac{2}{r/r_d} + \frac{r}{r_d} \frac{r_d}{r_{d,0}} \frac{r_{d,0}}{\alpha} \frac{dr_d}{dt} \right) \frac{\partial T}{\partial(r/r_d)} + r_d \frac{3\epsilon\sigma(T_\infty^4 - T_s^4)}{\lambda_L} \end{aligned} \quad (4-10)$$

Next, defining nondimensional variables:

$$\begin{aligned} \Gamma &= \frac{r_d}{r_{d,0}} \\ \tau &= \frac{\alpha t}{r_{d,0}^2} \\ \omega &= \frac{r}{r_d} \\ \frac{d\Gamma}{d\tau} &= \frac{r_{d,0}}{\alpha} \frac{dr_d}{dt} \end{aligned} \quad (4-11)$$

The nondimensional equation may now be written:

$$\Gamma^2 \frac{\partial T}{\partial \tau} = \frac{\partial^2 T}{\partial \omega^2} + \left(\frac{2}{\omega} + \omega \Gamma \frac{d\Gamma}{d\tau} \right) \frac{\partial T}{\partial \omega} + r_d \frac{3\epsilon\sigma(T_\infty^4 - T_s^4)}{\lambda_L} \quad (4-12)$$

where the following boundary conditions were specified:

$$\begin{aligned} \left. \frac{\partial T}{\partial \omega} \right|_{\omega=0} &= 0 \\ \left. \frac{\partial T}{\partial \omega} \right|_{\omega=1} &= \frac{r_d \dot{q}''}{\lambda_L} \end{aligned} \quad (4-13)$$

$$\dot{q}'' = \lambda_s \left. \frac{\partial T}{\partial r} \right|_s - m \Delta h_v - m \left(\frac{u^2}{2} - u \frac{dr_d}{dt} - \frac{\Sigma_{\pi}}{\rho} \right) \quad (4-14)$$

This equation was discretized using the same method of Litchford²⁶² with the additional source term included in the temporal discretization (Appendix D).

In general, the calculated effect of finite conductivity on droplet surface temperature produced a faster surface heat-up (Fig. 4.2). This phenomena was attributed to the finite value of liquid hydrocarbon thermal conductivity resulting in droplet heat-up within an outer shell of liquid. Therefore, assuming finite conductivity, less mass is involved receiving an equivalent amount of heat from the surroundings than is involved assuming an infinite conductivity model.

4.5 Simulated Spark Addition

A spark energy deposit was simulated by user-provided inputs of spark energy per unit time for a specified time at a specified location within the grid. As is used in both KIVA-II⁷ and ARICC,⁸ the spark energy is continually added until the temperature of the cell is greater than 1600 K. At this point, energy deposition is stopped. This algorithm allows user control over both the spatial and temporal spark energy deposit.

CHAPTER V

NUMERICAL SIMULATION AND VALIDATION

5.1 Validation and Demonstration Plan

The overall goal of the dissertation research was to demonstrate and validate a numerical model of hydrocarbon fuel droplet ignition. As an initial demonstration of the model capability, an iso-octane droplet with an initial radius of 0.12 cm and initial droplet temperature of 285 K was burned in air at an initial temperature of 973 K. A one-step chemical reaction model was implemented assuming droplet finite thermal conductivity and incident radiation from the ambient environment. Typical results obtained from the numerical model include the following: cell center location (Fig. 5.1), droplet radius variation with time (Fig. 5.2), droplet surface and center temperature variation with time (Fig. 5.3), internal droplet temperature profiles (Fig. 5.4), maximum flow field temperature (Fig. 5.5), droplet evaporation rate (Fig. 5.6), ratio of radiative to conductive flux at the droplet surface (Fig. 5.7), and flow field properties (Figs. 5.8 - 5.12) and species mass fractions as functions of both time and space (Figs. 5.13 - 5.17).

Validation requires comparison of code results to analytical theory and to test data. Analytical theory for quasi-steady droplet evaporation and droplet burning in air has long been established and provides general results for droplet diameter as a function of time, droplet lifetime, flame standoff distance, and flame temperature. Analytical theory for droplet ignition has been proposed by Law¹⁴² and validated against data.¹³⁸

In addition, the numerical model was demonstrated with the inclusion of detailed chemical kinetic reactions and spark ignition processes. Methanol was chosen as the fuel to demonstrate detailed chemistry effects because a reaction mechanism was available from the literature which included a reasonable number of species and reactions. However, no experimental data were found in the literature for methanol in air, to compare calculated ignition delay times.

Liquid fuel thermodynamic and transport property data and gaseous product species enthalpy were obtained and incorporated into the numerical model. Specifically, liquid fuel specific heats, densities, heats of vaporization, and thermal conductivities, as well as fuel gaseous specific heats, vapor pressures, and gaseous heats of formation were obtained and included in the model. Reactant and product species enthalpies of formation, molecular weights and enthalpies as functions of temperature over the anticipated simulation temperature range were obtained for the selected hydrocarbon fuels and reaction products.

The model was formed in terms of its data files and validated for the selected hydrocarbon fuels and initial conditions by comparing calculated ignition delays to measured values for autoignition. In addition, the model was implemented with a detailed chemical kinetic mechanism for methanol and air reactions. Separately, the model was applied to predict flow field variations under spark induction conditions.

5.2 Comparison of Simulation to Analytical Theory

5.2.1 Quasi-Steady Combustion Theory

A comparison to quasi-steady theory was necessary to verify the numerical approach used in CON1D for predicting transient droplet evaporation and burning. For this comparison, the ignition event was ignored and the above processes were investigated. Both CON1D and the quasi-steady theory are formed using the basic equations of mass, energy and the relational Clausius-Clapeyron equation. Neglecting radiation and finite droplet conductivity, both techniques should produce similar results.

Analytical theory solutions were obtained using an iterative technique solved within an electronic spreadsheet, for both an evaporating droplet and a burning droplet. The method of solution required the following approach. First, a value of the saturation temperature at the droplet surface was assumed. With this value, the associated vapor pressure was determined from curve fits of data for the specific hydrocarbon fuel (e.g., Appendix E). Knowing the partial pressure of the fuel, the mass fraction of the fuel vapor was calculated from the following relation:

$$Y_{F,s} = \frac{P_{F,s}}{P_{mix}} \frac{MW_F}{MW_{mix}} \quad (5-1)$$

Next, the assumed saturation temperature and calculated fuel vapor mass fraction were substituted into the appropriate energy balance equation for an evaporating and burning droplet²⁴⁹ and a corrected saturation temperature was determined. For an evaporating droplet

$$\frac{C_p (T_\infty - T_s)}{\Delta h_v} = \frac{Y_{F,\infty} - Y_{F,s}}{Y_{F,s} - 1} \quad (5-2)$$

and for a burning droplet

$$\frac{C_p (T_\infty - T_s) + i \Delta h_c}{\Delta h_v} = \frac{i Y_{O,\infty} + Y_{F,s}}{1 - Y_{F,s}} \quad (5-3)$$

where i is the stoichiometric ratio of oxidizer to fuel.

This process was continued until the guessed saturation temperature and calculated temperature were equal. The droplet evaporation rate,

$$\beta = \left[\frac{d(d^2)}{dt} \right]_s = \frac{8\lambda}{\rho C_p} \ln(1 + B) \quad (5-4)$$

the total droplet lifetime,

$$\tau = \frac{d_{s,0}^2}{\beta} \quad (5-5)$$

and the ratio of the flame standoff radius to droplet surface radius were calculated.

$$\frac{r_{flame}}{r_s} = \frac{\ln(1 + B)}{\ln(1 + (F/O)_{st} m_{O,\infty})} \quad (5-6)$$

The B number is defined for an evaporating droplet as

$$B = \frac{C_p(T_\infty - T_s)}{\Delta h_v} \quad (5-7)$$

and for a burning droplet as

$$B = \frac{C_p(T_\infty - T_s) + \dot{m}_{o,\infty} + \Delta h_c}{\Delta h_v + C_{p,L}(T_s - T_L)} \quad (5-8)$$

Quasi-steady theory was compared to CON1D results (referred to hereafter as the simulation results), first assuming an evaporating droplet and second assuming droplet burning. The fuels used included n-heptane, iso-octane, n-octane, n-hexadecane, and methanol. Each droplet was initially 0.07 cm in radius and exposed to air at 950 K during evaporation and 1300 K during burning. Each reaction was a one-step stoichiometric reaction of fuel in air.

The simulation inputs were adjusted to match quasi-steady droplet temperature. These included the droplet temperature and density. In addition, the one-step activation energy value was decreased to assure immediate ignition and achieve burning for nearly the entire simulation. All simulations were completed assuming infinite conductivity and no incident radiation. The flame location was deduced from the location of the maximum temperature node in the solution grid. The ratio of flame radius to droplet surface radius did not change significantly during the first and middle portions of the droplet lifetime as calculated using the simulation.

Analytical model results are shown in Figs. 5.18 through 5.21 for each of the fuels investigated. Analytical model droplet radius variations with time for an evaporating droplet (Fig. 5.18) and burning droplet (Fig. 5.19) are consistent with expectations. Numerical model predicted flame standoff distance differs

significantly from theoretical values for the heavy hydrocarbons (Fig. 5.21). However, the theoretical flame standoff distance of the lighter-weight alcohol compares favorably with the model prediction. Results obtained using CON1D, namely droplet radius and lifetimes, compare quite well to analytical theory (Figs. 5.22 - 5.27). However, the quasi-steady results are highly sensitive to the thermodynamic properties in the boundary layer between the droplet surface and flame zone. These properties include the specific heat capacity, density, and thermal conductivity of the boundary layer fluid. Well defined theoretical evaporation rates may be calculated through judicious choice of the transport properties.

It is well known that predictions of the B number and flame temperature are uncertain and highly dependent on transport properties.⁹⁹ The transfer number, B, represents the ratio of the driving force for gasification to the resistance to gasification. The driving source may consist of both a thermal source and a chemical source. The B number is lower for evaporating droplets than for burning droplets (Fig. 5.27). For burning droplets, the chemical source is much greater. Values obtained in this study for the B number are consistent with those in the literature. Analytical theory computations made using parametric variations of the transport properties within the boundary layer cannot achieve agreement with the numerical model for the location of the flame zone. On the other hand, since experimental values of flame standoff distance ratio are typically on the order of 10 rather than 40 to 50 as calculated by theory, the numerical model predicted values are in good agreement with experiment.

5.2.2 Quasi-Steady Ignition Theory

Law¹³⁸ has examined the strengths and weaknesses of ignition theory through comparison of the theoretical results to the data of Faeth and Olson.¹⁵² Therefore, a comparison to ignition theory will not be reproduced here but only summarized. Specifically, theory was compared to ignition limits and to ignition delay. Ignition limits are readily defined by computing the system Damkohler number, Da (eqn. 3-9), and comparing it with the ignition Damkohler number (eqn. 3-12). Law noted that the comparison to data was good; however, the kinetic pre-exponential factor, identified in equation 3-11, was contrived to match experimental data. In addition, transport properties of the gas phase were assumed constant and at average values.

Comparison to ignition delay required a rapid-mixing model for droplet internal energy distribution wherein the droplet size and droplet surface temperature were computed as functions of time.

$$r_s = \exp \left[-\frac{2}{3} \int \frac{dT_s}{\Delta h_{v,e} - \Delta h_v} \right] \quad (5-9)$$
$$\Delta h_{v,e} = (T_\infty - T_s)(Y_{F,s} - 1)$$

For each time step, the Damkohler number was calculated and compared to the ignition Damkohler number. Chemical reactions were not considered. Fuel vaporization was controlled by prescribed heat input. In general, the comparison to data was poor. Neglecting chemical kinetics and varying transport properties contributed to the poor comparison.

5.3 Details of Autoignition Test Data

Data exist which define autoignition of droplets in air for various fuels as a function of initial droplet radius and ambient air temperature. Two data sets were closely examined in the present study: the data of Faeth and Olson¹⁵² and the data of Saitoh et al.¹⁸⁰ Faeth used a furnace enclosed in an air tight chamber which was dropped prior and during the ignition process to simulate gravity free environment. This procedure attempted to eliminate natural convection effects and thus provide spherical symmetry at the droplet. The fuel droplet was suspended on a bead at the end of a filament with an outside diameter of 280 μm . Ignition was determined by the appearance of light near the droplet. The data are summarized in Figs. 5.28 and 5.29.

Saitoh suspended a fuel droplet on a silica filament with an outside diameter of 150 μm . A furnace on movable rails was transferred over the suspended droplet and droplet diameter as a function of time was recorded using photography and changes in infrared intensity. The shape of the droplet was nearly spherical for large droplets and slightly ellipsoidal for relatively small droplets. An equivalent diameter was used for the small droplets. The data are summarized in Figs. 5.30 through 5.32.

The data for n-heptane differed between the two experiments (Fig. 5.33) while little difference was seen for n-hexadecane (Fig. 5.34). Both natural convection and radiation, which were believed to have been eliminated in the experiments of Faeth, would have shortened the ignition delay when included in the system of Saitoh. Therefore, these mechanisms must be either non-existent or simply insignificant in both experiments. However, radiation heat flux from the furnace walls most likely existed due to the nature of each experiment. Increased

heat conduction to the suspended droplet may have existed in the experiments of Faeth due to the larger filament used. By comparison, the filament used by Faeth provided 3.5 times larger cross sectional area input than did the filament used by Saitoh.¹⁸⁰ Therefore, more heat was conducted into the droplet with the larger filament used by Faeth.

Note also that the Saitoh data clearly exhibits ignition limits of n-heptane fuel at small droplet radii. N-heptane, for example illustrates an increasing ignition delay for smaller drop diameters. This is attributed to the droplet radius approaching the ignition limit, below which ignition does not occur, only evaporation.

As a result of this evaluation, the Saitoh data will be used for comparison with model results. These data include ignition delay times as a function of initial droplet radius and initial ambient air temperature for n-heptane (Fig. 5.30) and n-hexadecane (Fig. 5.32) at an initial droplet temperature of 293 K.

5.4 Liquid Hydrocarbon Fuel Property Data

Liquid hydrocarbon thermodynamic and transport property data have been well documented by Yaws²⁶³ for temperatures below appropriate fuel boiling points. These data include boiling point (Table 5.1), specific heat, heat of vaporization, vapor pressure and density all as a function of temperature. Thermal conductivity as a function of temperature was obtained^{264, 265} for n-heptane, iso-octane, n-octane, n-hexadecane and methanol. Properties are summarized in Appendix E for the representative hydrocarbons used in this study.

Table 5.1. Critical Properties of Selected Hydrocarbons.				
Fuel	Molecular Weight (g/mole)	Freezing Point (K)	Critical Point (K)	Boiling Point (K)
n-heptane	100.203	182.6	540.1	371.6
n-octane	114.230	216.4	569.1	398.8
iso-octane	114.230	165.8	543.8	372.4
n-hexadecane	226.445	291.0	734.3	560.5
methanol	32.042	175.5	513.0	337.8

N-heptane and n-hexadecane are typically chosen fuels for experimentalists because of the disparate properties each possesses and the associated different behavior during droplet heat-up. Therefore, the use of these fuels in this numerical study likewise provides a range of demonstrative capabilities.

5.5 Thermodynamic Properties for Reactant and Product Gaseous Species

The thermodynamic property enthalpy is required to relate temperature and energy for each specie considered in the simulation. Reactant enthalpies were obtained for all fuels: n-heptane (n-C₇H₁₆), iso-octane (iso-C₈H₁₈), n-octane (n-C₈H₁₈), n-hexadecane (n-C₁₆H₃₄), methanol (CH₃OH). For the simulations which used a one-step chemical reaction model, enthalpies were required for the product species: H₂O and CO₂. The detailed reaction mechanism for methanol required enthalpy and Gibbs free energy for 25 species: CH₃OH, CH₂OH, CH₃O,

CH₂O, C₂H₆, C₂H₅, C₂H₄, C₂H₃, C₂H₂, C₂H, CH₄, CH₃, CH₂, CH, CO, CO₂, H, H₂, H₂O, H₂O₂, HO₂, HCO, O, O₂, OH.

Thermodynamic values of enthalpy as a function of temperature have been measured for many hydrocarbons at the Thermodynamic Research Center (TRC) and documented appropriately.²⁶⁶ Measurements were limited by minimum and maximum temperatures. In addition, JANNAF²⁶⁷ has composed thermodynamic tables including enthalpy for typical species up to a range of 5000 K. These tables, however, were limited in the number of species cited and did not include data for heavy hydrocarbons. Lastly, NASA SP273⁶¹ contained curve-fits for many species including lower weight hydrocarbons and a few heavy hydrocarbons. This source was found to be most comprehensive.

All data examined agreed for temperatures below 3000 K. However, differences existed above 3000 K. In fact, little data were available above 3000 K and a curve fit was required to extrapolate enthalpy to 5000 K (a commonly used upper limit). A comparison was made among these data for enthalpy using linear extrapolation, polynomial extrapolation and values for the NASA SP273 curve fits. A linear fit of the last three data points of the TRC data closely matched the NASA SP273 curve fit.

For all simulations executed during the course of this study, enthalpy values were defined using NASA SP273 curve fits where available and TRC data extrapolated to 5000 K using a linear fit of the last three data points.

Enthalpies of species defined in the detailed reaction mechanism for methanol were also computed using the curve fits defined in NASA SP273. In addition, it was necessary to compute specific heat and entropy to obtain Gibbs free energy for all species over an appropriate temperature range for combustion. Detailed properties are listed in Appendix F.

5.6 Numerical Boundary Conditions

Prior to model application, it was necessary to evaluate the effects of the imposed far-field fixed boundary conditions on calculated results, specifically, ignition delay. This was accomplished using both n-heptane and n-hexadecane fuels at droplet radii of 0.08 cm and 0.06 cm, respectively (Table 5.2). The initial droplet temperature for all simulations was 293 K. Ambient air temperatures was 948 K and 973 K for n-heptane and n-hexadecane, respectively. Along with the effects of boundary conditions, the effects of grid density were evaluated (Table 5.2). The goals of these exercises were to establish minimum limits of grid spacing and far-field boundary locations which would not affect calculated results. These values would then be employed as guidelines for the remainder of the study. Note that this evaluation was directed toward the gas-side grid and infinite boundary; the grid density used to define internal droplet nodes was consistently set at 100 nodes in the present study.

Two fuels were chosen which represented those used in this study. N-

Table 5.2. Summary of Simulations Evaluating Grid and Boundary Effects.			
Case	Fuel	Grid Nodes	Ratio of Boundary Radius to Initial Droplet Radius
1	n-heptane	20	20, 30, 40, 50
2	n-heptane	20, 41	30
3	n-hexadecane	20	20, 30, 40
4	n-hexadecane	20, 41, 63	20
5	n-hexadecane	41	20, 30, 40

hexadecane possesses a much higher boiling point and heat of vaporization than the mid-weight hydrocarbons heptane and octane.

In general, the grid density was varied from 20 to 63 nodes and the far-field boundary radius was varied from 20 times the initial droplet radius to 50 times the initial droplet radius. Results obtained for n-heptane using grids with far-field boundaries 20 times the initial droplet radius appeared crowded and otherwise affected by the close boundary. The thermodynamic property variations within this system were influenced by the boundary. With most hydrocarbon fuel droplets burning in air, the flame zone is located from 10 to 12 times the droplet radius. Therefore, the boundary and droplet surface would be equidistance from the reaction zone given a boundary at 20 times the initial droplet radius. Intuitively, this is not adequate, as the numerical results showed.

As the numerical boundary was moved to beyond 30 times the initial n-heptane droplet radius, holding the grid density constant, the effects on calculated ignition delay were eliminated (Fig. 5.35). Droplet surface temperature was unaffected with the exception of variations occurring at ignition. Increasing the boundary distance systematically decreased the overall droplet lifetime (Fig. 5.36), having little effect on surface temperature (Fig. 5.37). The overall evaporation rate did not converge as the boundary radius was increased at a grid density of 41 nodes (Fig. 5.38). At a fixed boundary distance of 30 times the initial droplet radius, increasing the grid density from 20 to 41 nodes had little effect on ignition delay (Fig. 5.39). Droplet lifetime decreased approximately 10 percent with increasing grid density to 41 nodes (Fig. 5.40). Surface temperature was unaffected (Fig. 5.41) while evaporation rate increased approximately 5 percent with increasing grid density from 20 to 41 nodes (Fig. 5.42).

As a result, ignition delay of n-heptane may be best modeled using a fixed boundary distance of at least 30 times the initial droplet radius and a grid density of at least 20 nodes. Computational time was decreased by a factor of four using 20 nodes compared to 41 nodes.

In general, n-hexadecane exhibited different trends from n-heptane. Using a grid density of 20 nodes, no trend of ignition delay toward convergence was observed with increasing fixed boundary distance (Fig. 5.43). Results for droplet surface regression (Fig. 5.44), surface temperature (Fig. 5.45), and evaporation rate (Fig. 5.46) were unique for each fixed boundary condition. In general, the droplet ignition delay and lifetime were extended with increasing boundary distance. However, using a fixed boundary distance 20 times the initial droplet radius, little change in ignition delay was observed with grid density changes from 41 to 63 nodes (Fig. 5.47). In fact, convergence was observed for all investigated parameters (Figs. 5.48 - 5.50). Therefore, a grid density of 41 nodes appeared to be a maximum below which calculated results were significantly affected.

Using a grid density of 41 nodes, the effects of increasing boundary distance on ignition delay were negligible above a boundary distance 30 times the initial droplet radius (Fig. 5.51). However, variations still persisted in droplet regression (Fig. 5.52), droplet surface temperature (Fig. 5.53), and droplet evaporation rate (Fig. 5.54). This was in part attributable to the high heat of vaporization and high boiling point of hexadecane.

As a result, it is concluded in the present study that ignition delay of n-hexadecane may be best modeled using a fixed boundary distance of 30 times the initial droplet radius and a grid density of 41 nodes.

5.7 Comparison of Model Predicted Results to Test Data

The numerical simulation results were compared to the test data of Saitoh for five separate cases (Table 5.3). Ignition in the simulation was defined as the time at which the temperature anywhere in the flowfield exceeded the adiabatic flame temperature for the given reaction. Liquid properties were defined at the initial droplet temperature of 293 K and used appropriately for n-heptane and n-hexadecane. The fixed boundary and grid resolution were applied as defined in section 5.6. Finite droplet conductivity was invoked using a constant value of thermal conductivity at a temperature of 293 K. Radiation was considered using the ambient air temperature and subsequently the maximum flame zone temperature as the source.

One-step reactions were assumed for each fuel:

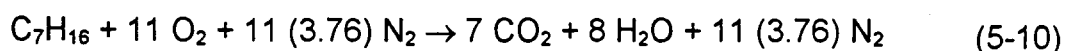


Table 5.3. Summary of Validation Test Cases.				
Case	Fuel	Ambient Air Temperature (K)	Initial Droplet Temperature (K)	Adiabatic Flame Temperature (K)
1	n-heptane	923	293	2232
2	n-heptane	948	293	2232
3	n-heptane	1023	293	2232
4	n-hexadecane	973	293	2236
5	n-hexadecane	1073	293	2236

The pre-exponential and activation energy values of Westbrook were initially used. However, these values resulted in immediate ignition for all cases examined and were unsuitable for application. This conclusion was also reached by Bergeron and Hallett¹⁵⁸ for a similar application of one-step mechanisms with the pre-exponential and activation energy values defined by Westbrook and Dryer.²³³ Therefore, the tactic used by Bergeron and Hallett was employed here: the pre-exponential and activation energy values for each fuel were established based on comparison to a selected set of test data at hand. Although this approach does not provide completely a priori predictions of ignition delay and combustion response, it does provide a tool for prediction within the frame of an established one-step reaction mechanism. Recall that a one-step mechanism is a simple model of an as-yet undefined multiple step, complex mechanism.

Simulation results for case 1 (n-heptane in air at 923 K) compared very well to test data (Fig. 5.55). The simulation matched several important features of the test data. First, simulated absolute ignition delay times (primarily as a result of contrived activation energy values) compared very well across the range of n-heptane drop radii. Second, the simulation indicated that a minimum droplet radius existed below which ignition did not occur, only evaporation occurs. This was evident by the increasing ignition delay times with decreasing droplet radius. Ignition limits were dependent on fuel type, droplet radius, and ambient temperature. Third, the model reproduced the general trend of decreasing ignition delay with increasing droplet radius until a nearly constant value is reached at the largest droplet sizes. The experimental data indicated that ignition delay began to increase again with droplet radius greater than 0.1 cm and, therefore, a minimum ignition delay may exist at some optimum droplet

diameter. The model reproduced this trend only slightly and not with the severity exhibited by the test data. The increasing ignition delay may be attributed to increased internal circulation with larger droplets and associated increase in conduction heat transfer within the droplet, thus producing an effective increase in thermal conductivity above that assumed uniform in this analysis.

To assess the sensitivity of ignition delay on activation energy, the activation energy was increased by 1.6 percent to 12120 K. This value was chosen to match ignition delay test data at the maximum tested droplet radius of 0.12 cm. Significant effects on ignition delay were evident over the entire range of investigated droplet radii especially at the ignition limit. Chemical kinetics certainly plays an important role in ignition models.

The simulation of n-heptane in air at 948 K compared well with test data (Fig. 5.56) using the same one-step reaction mechanism applied in case 1. The simulation trends were certainly more comparable to the data of Saitoh than to the data of Faeth for n-heptane. The sensitivity of calculated ignition delay was made evident by changing the activation energy by only 1.5 percent.

The simulation of n-heptane in air at 1023 K also compared well with test data (Fig. 5.57) using the same one-step mechanism applied in cases 1 and 2. Although the absolute values of ignition delay were slightly higher than test data, all trends were appropriate.

The data of n-hexadecane illustrated different trends than did the data for n-heptane. The ignition limit for n-hexadecane was not reached in the experiments since sufficiently small droplet diameters could not be obtained. Therefore, the data indicate that ignition delay increased with increasing droplet radius. The data did not increase linearly. There appears to be a step increase in ignition delay at a droplet radius of 0.08 cm. This step change may be

indicative of a change in the reaction mechanism. The data of Faeth did not include droplets this large.

Simulation results of n-hexadecane in air at 973 K (case 4) compared favorably with test data (Fig. 5.58). However, the simulation trend of increasing ignition delay with increasing droplet radius was not sufficiently steep. This result may be affected by increasing the liquid thermal conductivity above its specified value (Fig. 5.58) at the initial droplet temperature. This increase may only be justified when internal circulation increases heat and mass diffusion within the droplet. Hexadecane is a more volatile fuel and may exhibit internal vortical flow more readily than n-heptane; however, there is no evidence to support this hypothesis.

Finally, n-hexadecane in air at 1073 K was compared with test data (Fig. 5.59) using the same one-step mechanism used above in case 4. The simulation produced a very reasonable trend of increasing ignition delay with increasing droplet radius. The trend was much steeper than that observed in case 4 and compared well with test data. The test data at 1073 K also indicated a step increase in ignition delay at 0.065 cm. This trend may only be reproduced using a different chemical kinetic mechanism.

In summary, a one-step mechanism with an activation energy of 11925 K provided simulation results which compared well with test data for n-heptane at all operating temperatures, 923 K, 948 K, and 1023 K. Likewise, a one-step mechanism with an activation energy of 13100 K provided simulation results which compared well with test data for n-hexadecane at temperatures of 973 K and 1073 K. Furthermore, general trends of ignition delay variation with droplet radius and ignition limits were reproduced. Small variations in activation energy were shown to have a significant effect on predicted ignition delay times. In

addition, the effects of arbitrarily increased liquid thermal conductivity improves the comparison between model results and experimental data, which may imply that internal circulation exists in large droplets and in volatile fuels such as hexadecane.

5.8 Effects of Droplet Conductivity and Radiation on Ignition Heat and Mass Transfer

5.8.1 Summary of Findings

Because the effects of droplet conductivity and radiation are not well defined in the literature, significant effort was devoted to investigating the effects of their parametric variations on predicted ignition delay, droplet surface regression, droplet surface temperature, droplet internal temperature gradients, and droplet evaporation rates. Therefore, n-heptane and n-hexadecane fuels were used over a range of initial droplet radii and ambient air temperatures (Table 5.4).

For all cases defined in Table 5.4, the initial droplet temperature was 293 K. Droplet density and thermal conductivity were set to correspond to the initial droplet temperature. One-step chemical reaction mechanisms were used with activation energies of 11295 K for n-heptane and 13100 K for n-hexadecane. The grid resolution and boundary conditions were applied as defined in section 5.4 for each fuel. For each case, results were obtained assuming (1) finite conductivity in the droplet and incident radiation, (2) finite conductivity in the droplet without incident radiation, and (3) infinite conductivity with radiation, and (4) infinite conductivity without radiation.

Table 5.4. Summary of Simulations Evaluating Effects of Incident Radiation and Finite Thermal Conductivity.

Case	Fuel	Initial Ambient Air Temperature (K)	Initial Droplet Radius (cm)	Result Figure Numbers
1	n-heptane	948	0.07	5.60 - 5.66
2	n-heptane	948	0.09	5.67 - 5.73
3	n-heptane	948	0.11	5.74 - 5.80
4	n-heptane	1023	0.05	5.81 - 5.87
5	n-heptane	1023	0.07	5.88 - 5.94
6	n-heptane	1023	0.09	5.95 - 5.101
7	n-hexadecane	973	0.06	5.102 - 5.108
8	n-hexadecane	973	0.08	5.109 - 5.115
9	n-hexadecane	973	0.10	5.116 - 5.122

In general, results indicated the following trends:

- (1) Ignition delay decreased significantly when radiation was considered.
- (2) Ignition delay decreased significantly when finite droplet thermal conductivity was considered.
- (3) The effects of finite conductivity on ignition delay did not diminish with increasing droplet radius. However, the effects of radiation on ignition delay did diminish with increasing droplet radius and were nearly negligible for droplets greater than 0.10 cm in radius.

- (4) Assuming infinite conductivity with radiation, ignition delay times were predicted within 10 percent of test data values for droplets larger than 0.08 cm in radius.
- (5) Assuming infinite conductivity without radiation consistently produced ignition delay times which compared poorly to test data for all cases investigated.
- (6) Although radiant energy produces nearly uniform droplet temperature profiles in small droplets, it does so after a time lag. Therefore, the assumption of a uniform temperature profile within smaller droplets may produce results which underestimate ignition delay.
- (7) For n-heptane, differences among the calculated ignition delay times for all models decreased with increasing droplet radius.
- (8) For n-heptane, differences among the calculated ignition delay values for all models, except infinite conductivity without radiation, decreased with increasing ambient air temperature for a given droplet radius.
- (9) For n-hexadecane, differences among the calculated ignition delay times for all models were large for small droplets and increased with increasing droplet radius.
- (10) For finite conductivity cases, temperature gradients within the droplet were flat in the interior and steep approaching the surface. For droplets greater than 0.10 cm, the effect of radiation produced internal droplet temperatures slightly greater than the surface temperature for a short period during the droplet lifetime.

- (11) Droplet surface regression prior to ignition was significant, amounting to approximately 10 percent of the initial radius.

5.8.2 Overview

The ignition delay of n-heptane decreased when either finite droplet conductivity or radiation (Fig. 5.60) was included in the model. These effects were consistent over the n-heptane droplet range of 0.07 to 0.11 cm (Figs. 5.67, 5.74), the n-heptane temperature range of 948 K and 1023 K (Figs. 5.81, 5.88, 5.95), and the n-hexadecane droplet range of 0.06 to 0.10 cm (Figs. 5.102, 5.109, 5.116). For n-heptane fuel, results of cases 1 through 6 showed ignition delays which followed the general trend of test data in that ignition delay decreased with increasing droplet radius to approximately 0.09 cm and then flattened. Likewise, results using n-hexadecane fuel (cases 7 through 9) followed test data trends which showed ignition delays generally increasing with increasing droplet radius.

The effect of radiation and finite conductivity on the ignition delay of n-hexadecane was similar to that of n-heptane at a given droplet radius (Fig. 5.102). However, the effects were not as dramatic as those observed for n-heptane with increasing droplet radius. All solutions, with exception of those with infinite conductivity without radiation, converged toward a single value of ignition delay with increasing droplet radius (Figs. 5.67, 5.74, 5.109, 5.116). Therefore, as ignition delay times decrease, the importance of droplet thermal conductivity and radiation is minimized for larger droplets.

For all cases investigated, droplet regression began well before ignition. In general, droplet radius was reduced approximately 10 percent prior to ignition

for those cases investigated (Figs. 5.61, 5.68, 5.75, 5.82, 5.89, 5.96, 5.103, 5.110, 5.117). Therefore, this fact must be considered in experiments as well as in mathematical models. This observation indicates that fuel vapor accumulation near the droplet surface is significant prior to ignition. As expected, droplet lifetime decreased when either radiation or finite conductivity were considered.

For n-heptane, peak evaporation rate at ignition decreased with increasing droplet radius (Figs. 5.66, 5.73, 5.80). N-hexadecane also exhibited this trend dramatically (Figs. 5.108, 5.115, 5.122). For all cases, the effect of finite conductivity on evaporation rate was small at small droplet radii, yet became significant for large droplets. After ignition, evaporation rates were affected significantly by assumed radiation and droplet conductivity (Fig. 5.108 for example). This is due, in part, to the increased heat input to droplet from hotter surroundings.

5.8.3 Discussion of the Effects of Finite Conductivity on Ignition Delay and Heat and Mass Transfer Processes

This discussion is focused on the comparison of results assuming infinite conductivity without radiation and finite conductivity without radiation. In general, all results showed that ignition delay times were significantly shorter when finite conductivity was assumed. This conclusion is in contrast to the deductions of Bergeron and Hallett,¹⁵⁸ however, it is consistent with previous calculations of Faeth and Olson.¹⁵² The effect of finite conductivity on ignition delay diminished with decreasing droplet radius (Figs. 5.60, 5.67, 5.74) and increasing ambient air temperature (Figs. 5.81, 5.88, 5.95). The effect of finite conductivity on ignition delay was pronounced for n-hexadecane due to its high

wet bulb temperature and associated longer droplet heat-up (Figs. 5.102, 5.109, 5.116).

The effect of finite conductivity on ignition processes was apparent from the results and may be explained as follows. As a result of finite thermal conductivity within the droplet, temperature gradients were produced. Without radiation, these gradients were steep for all droplet radii prior to ignition (Figs. 5.65, 5.72, 5.79). Therefore, heat transferred to the droplet was contained in a volume shell nearest the surface. The center temperature was slow to respond while the surface temperature responded quickly. Assuming finite conductivity, the surface temperature rose faster than when for the case of infinite conductivity. The infinite conductivity assumption allowed the entire mass of the droplet to participate in the heat absorption of conductive flux from the hot surrounding gas. As a result, and the surface temperature was lower.

Temperature gradients near the surface increased with increasing droplet radius (Figs. 5.72, 5.79). Larger droplets represent larger thermal sinks and additional time was required for heat flux to penetrate the droplet interior. Likewise, temperature gradients increased with increasing ambient temperature for the same droplet radius (Figs. 5.93, 5.100). Higher heat flux entering the same mass produced higher surface temperatures. Temperature gradients within an n-hexadecane droplet responded similarly (Figs. 5.107, 5.114, 5.121) with the exception of much longer droplet heat-up times to a high wet bulb temperature near 530 K compared to 360 K for n-heptane. At equivalent times during the simulation, n-heptane droplet center temperatures decreased with increasing droplet radius (Figs. 5.84, 5.91, 5.98). However, the surface temperature was not affected by droplet size (Figs. 5.83, 5.90, 5.97). N-hexadecane behaved differently. Both the center temperature (Figs. 5.105,

5.112, 5.119) and surface temperature (Figs. 5.104, 5.111, 5.118) decreased with increasing droplet radius at equivalent times.

5.8.4 Discussion of the Effects of Radiation on Ignition Delay and Heat and Mass Transfer Processes

Radiation provides additional heat to the droplet which raises the internal temperatures and reduces the gradients within the droplet (for example, compare Figs. 5.71, 5.72). In effect, the radiative flux allows more droplet mass to participate in the overall heat absorption and therefore reduces the surface temperature while increasing the droplet center temperature. Larger droplets of fuels with relatively low boiling points reached internal temperatures greater than the surface temperature for short periods after ignition when the flame zone is driving the radiative flux (Figs. 5.78, 5.99). High boiling point fuels such as n-hexadecane did not exhibit this trend for droplets with radii less than 0.10 cm (Fig. 5.120).

The center temperature of n-heptane droplets responded nearly immediately to radiative flux and begins to rise well before ignition occurs (Fig. 5.63). The center temperature of n-hexadecane, with a lower specific heat, responded slowly to the radiative flux for all droplet radii investigated (Figs. 5.105, 5.112, 5.119). For both n-heptane and n-hexadecane droplets, the difference in center temperature due to radiation was significant.

The wide variation in ignition delay times assuming infinite conductivity with radiation and the same without radiation was caused by the implementation of radiation in the boundary condition specified at the droplet surface:

$$\dot{q}_s'' = \lambda_s \left. \frac{\partial T}{\partial r} \right|_{r=r_s} = \rho \left(u - \frac{dr_s}{dt} \right) \Delta h_v + \frac{1}{3} r_s \rho_L C_{p,L} \frac{dT_s}{dt} + m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{\gamma}}{\rho} \right) - \dot{q}_{rad}'' \quad (5-12)$$

This formulation restricts the radiative flux component to a surface flux rather than a volumetric flux. This provides a higher flux than volumetric absorption. Nonetheless, the effect diminished with increasing droplet radius. Results obtained with the infinite conductivity model at a droplet radii above 0.09 cm compared closely with other model results at air temperatures of 948 K and 1023 K (Figs. 5.67, 5.74, 5.88, 5.95). Therefore, the effects of radiation are not significant for larger droplets with radii greater than 0.10 cm. Radiant absorption tends to produce nearly uniform droplet temperature profiles in smaller droplets during the droplet lifetime. However, prior to ignition, calculations show that substantial temperature gradients exist and affect ignition delay. Therefore, a uniform liquid temperature assumption may not be accurate for small droplets with incident radiation, in contrast to current approaches.

As a response to the early ignition, droplet lifetimes were much shorter for those models considering finite conductivity (Figs. 5.61, 5.68, 5.75). However, the effect of radiation on reducing droplet lifetime was much greater than that of finite conductivity for small droplets (Figs. 5.61, 5.82, 5.89). Assuming finite conductivity, the effect of radiation on droplet surface temperature (Figs. 5.62, 5.83, 5.90) and evaporation rate (Figs. 5.66, 5.87, 5.94) was negligible for small droplets at either 948 K or 1023 K prior to ignition. Effects did exist with larger droplets (Figs. 5.80, 5.101) and also after ignition.

5.9 Observed Parametric Variations During Ignition

Notable patterns were evident in several transient parameters. Specifically, the rate of change of the droplet evaporation rate and the maximum rate of change of the product species density sum. Polymeropolous et al.¹³⁹ noted that the evaporation rate, plotted as a function of ambient temperature, indicated regions where a discontinuous change in the rate occurred corresponding to the transition from kinetic controlled combustion to diffusional controlled combustion. This discontinuity was interpreted as ignition. The rate of change of product density sum is representative of chemical reactivity in the flow field. This term, therefore, is similar to the numerator of the Damkohler ratio and a sudden increase in this parameter is indicative of runaway chemical reaction. Assuming ignition is the time at which the adiabatic flame temperature is reached, all of the defined parameters provide an excellent correlation with the ignition event (Figs. 5.123 - 5.134).

As a verification, the rate of change of the droplet evaporation rate and the rate of change of the product species density sum were calculated for n-heptane and n-hexadecane at several droplet radii and different ambient air temperatures. For all simulations, the initial droplet temperature was 293 K. One-step mechanisms were assumed with activation energies of 11295 K and 13100 K for n-heptane and n-hexadecane, respectively. Finite conductivity and radiation were included in the model.

For example, considering n-heptane in air at 948 K, the rate of change of the product species sum reaches a peak value at ignition (Fig. 5.123). Likewise, the rate of change of droplet evaporation indicates a peak value corresponding to ignition (Fig. 5.124). These conclusions are substantiated by results obtained

at examined initial droplet radii and ambient air temperatures. (Figs. 5.123 - 5.134). Additionally, these conclusions are valid for n-hexadecane fuel at various initial droplet radii (Figs. 5.135 - 5.140). These two parameters are very different in that the evaporation rate is associated with the droplet while the product species sum is associated with the gaseous flow field. In that regard, the product species sum is somewhat generic and may be applicable to defining ignition within a multi-dimensional code where such a parametric variation could be monitored much more economically than individual droplet evaporation rate of change.

5.10 Application of a Detailed Chemical Reaction Mechanism

The detailed reaction mechanism listed in Appendix C defines forward reactions and their associated rates for a methanol + air reaction. Backward reaction rates must be defined for each reaction using the equilibrium constant for the given reaction and the defined forward reaction rate. The equilibrium constant and the reaction rates are related at equilibrium as follows:

$$k_b = \frac{k_f}{K_c} \quad (5-13)$$

This relationship is assumed to hold at all other times as well. Common definitions for the equilibrium constant are⁸⁷ partial pressure equilibrium constant (K_p) and equilibrium constant based on species concentration (K_c). For many species, K_p is defined within the JANNAF tables²⁶⁷ as a function of temperature. With these values, K_p for the reaction may be computed at a specified

temperature. For example, given $\text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{OH}$, the equilibrium constant may be defined as follows:

$$K_p(rX, T) = \frac{K_{p(\text{CH}_3)} K_{p(\text{OH})}}{K_{p(\text{CH}_3\text{OH})}} \quad (5-14)$$

However, K_p was not defined for all species listed in the detailed reaction set. Therefore, K_p was computed using the fundamental relation of Gibbs free energy:

$$g(T) = h(T) - Ts(T) \quad (5-15)$$

where the enthalpy and entropy are both known values calculated using the NASA SP273 curve fits. The equilibrium constants based on partial pressures were then calculated from:

$$\ln K_p = \frac{-\Delta g}{R_u T} \quad (5-16)$$

$$\Delta g = \sum_{k=1}^N b_k \Delta g_k - \sum_{k=1}^N a_k \Delta g_k$$

Then the equilibrium constant based on species concentration is calculated as follows:

$$K_c(x, T) = \frac{K_p(x, T)}{(R_u T)^{\Delta n}} \quad (5-17)$$

where

$$\Delta n = \sum b_m - \sum a_m$$

Finally, the backward rate was calculated by

$$k_b = \frac{k_f}{K_c} \quad (5-18)$$

For most reactions considered, Δn is equal to zero, and K_c is equal to K_p .

The detailed reaction mechanism was used to predict the ignition of a methanol droplet with an initial radius of 0.06 cm, initial droplet temperature of 300 K, and initial air temperature of 1100 K. The high air temperature was chosen to maintain chemical reactions above 1000 K, a minimum limit where the detailed mechanism was applicable. The application of the one-step mechanism proposed by Westbrook²³³ used a pre-exponential value of 3.2 E12 and an activation energy of 15100 K. The application of the detailed reaction mechanism involved 184 reactions and 25 species (Appendix C).

The detailed reaction mechanism required significant computational resources. The number of computational cycles (one cycle is one time step) per calendar minute (cycs/min) observed on several computer platforms were (1) PC 486, 66 megahertz: 270 cycs/min, (2) 33 megahertz workstation: 419 cycs/min, and (3) 150 megahertz workstation: 1235 cycs/min. The simulation of detailed kinetics required a time step of approximately 1.38 E-11 sec for one cycle on all platforms. The time step is variable and a function of the rate of change of species density due to chemical reaction. Assuming the above time step and that ignition may occur prior to 1.0 sec, the completed simulation would have required 72,000,000,000 computation cycles and a total calendar time of 111 years using the 150 megahertz machine. With these computational speeds,

ignition times on the order of 0.1 sec would have required 11 years of calendar time. Execution on a super-computer may halve the calendar time assuming sole source access. Processor parallelization may eventually provide a capability for solution of such problems.

Results obtained for both the one-step and multi-step mechanisms indicate nearly immediate ignition (Fig. 5.141). In the simulation of the one-step mechanism, ignition occurred after approximately 0.00002 sec while ignition, assuming multi-step mechanism, occurred at approximately 0.00029 sec. Stability of the multi-step solution required an average time step of 1.38×10^{-11} sec with excursions to 5.0×10^{-14} sec. Variations between simulation results of droplet regression, droplet surface temperature and droplet evaporation rate were not significant over this time range (Figs. 5.142 - 5.144). For both cases, simulations much beyond ignition were not possible due to numerical instabilities attributed to species chemical reactivity. Species generation in the multi-step case was limited to maximum mass fractions of 0.07 for H_2O and 0.09 for CO_2 . All other specie mass fractions were insignificant.

Although experimental data for methanol are not available, the results do not appear reasonable. Similar results were obtained early in the investigation using n-heptane with a single-step reaction where the values of the pre-exponential and activation energy were those proposed by Westbrook. Specifically, ignition was achieved immediately and, as a result of excessive chemical reactivity, the simulation was unstable shortly after ignition. This experience is similar to that of Bergeron¹⁵⁸ for the application of activation energies proposed by Westbrook. These values are known to have been based on premixed combustion experiments rather than diffusion systems. As a result,

these mechanisms may not be applicable to diffusive systems where heat and mass transfer are important contributors to the developing flame zone.

5.11 Demonstration of Spark Ignition

With the incorporation of a spark energy deposition model, a simulation of burning n-octane was completed with the droplet having an initial radius of 0.065 cm, initial droplet temperature of 285 K, and initial ambient air temperature of 600 K. The low temperature ensured appropriate fuel evaporation without ignition. A one-step chemical reaction was assumed in the model with the pre-exponential and activation energies of Bergeron. Spark ignition was applied at 3.1 seconds and was located in cell 10, half-way through the flow field.

With the application of the spark, ignition was immediately achieved as evidenced by change in slope of droplet regression (Fig. 5.145) and increase in droplet surface temperature (Fig. 5.146). Flow field temperature increases with the increase in chemical reactivity (Fig. 5.147). The energy added to the flow by the spark is shown in Fig. 5.148 as a small increase at cell 10 immediately prior to large energy gradients of combustion. Density, velocity and species mass fractions are also shown (Figs. 5.149 - 5.155).

With a validated chemical kinetic mechanism, this approach could be used to determine minimum ignition energies required for droplet ignition. However, ignition kernel phenomena would not be accurately represented and most likely play an important part in ignition dynamics through plasma kernel droplet interaction and shock wave droplet interaction.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The fundamental processes governing fuel droplet ignition in a hot oxidizing environment (i.e., autoignition) have been studied with a comprehensive numerical model. The study was based on a one-dimensional time-accurate combustion model obtained from Los Alamos National Laboratory and modified by the author for assessing droplet ignition in a hot oxidizing gas or simple ignition as a result of energy deposition within the gas-phase. To improve ignition modeling, finite droplet conductivity and a radiative flux source term were added to the basic model. The model was demonstrated and validated through application to experimental data with and without these added effects.

Hydrocarbon liquid properties and gaseous species thermodynamic properties were defined for all fuels and gaseous species in this research study. As a result, a comprehensive data set of properties was formed for ready access by the numerical model. For the gaseous species encountered in this study, thermodynamic enthalpies as a function of temperature from 0 to 5000 K were compared among several literature sources.

Numerical model results were compared to quasi-steady theory for droplet evaporation and burning. Results of droplet radius variation with time and overall droplet lifetime compared well with quasi-steady theory. The ratio of

flame radius to droplet surface radius obtained from the numerical model did not compare well with analytical theory, however, the numerical model results were consistent with experimental values for hydrocarbons in air.

Validation of the model was accomplished by comparing model results to experimental values of ignition delay as a function of initial droplet radius and initial ambient environment temperature. Experimental ignition delay was defined as the time between droplet introduction into the hot furnace and first recorded visible light. Therefore, an ignition criterion, based on adiabatic flame temperature, was implemented into the numerical model to correspond to the emission of visible light. Using a one-step chemical reaction mechanism for the hydrocarbon fuels, n-heptane and n-hexadecane, numerical model results indicated good agreement with absolute ignition delay values, droplet radius defining the ignition limit for n-heptane, and trend of changing ignition delay times with increasing initial droplet radius. The affects of the numerical grid density and far-field boundary location on calculated ignition delay were found to be significant and a function of the fuel type. These affects were eliminated from the present study by optimizing both the grid density and far field boundary location.

The effects of radiation and thermal conductivity on ignition heat and mass transfer were evaluated through a detailed study of n-heptane and n-hexadecane over a range of droplet diameters and ambient air temperatures. Results showed that ignition delay decreased when either finite conductivity or radiation was included. Assuming infinite conductivity with radiation, ignition delay times were predicted within 10 percent of test data values for droplets larger than 0.08 cm in radius. Assuming infinite conductivity without radiation consistently produced ignition delay times which compared poorly to test data for

all cases investigated. In contrast to previously held beliefs, results indicate that although radiant energy produces nearly uniform droplet temperature profiles in small droplets, it does so after a time lag. Therefore, the assumption of a uniform temperature profile within droplets having a radius near 0.06 cm may produce results which underestimate ignition delay.

Temperature gradients within the droplet were flat in the interior and steep approaching the surface. For droplets with a radius near 0.10 cm, numerical results showed the effect of radiation produced internal droplet temperatures slightly greater than the surface temperature for a short period during the droplet lifetime. Droplet surface regression prior to ignition was significant, amounting to approximately 10 percent of the initial radius.

Parametric variations during ignition were evaluated to serve as alternate ignition criteria. Two parameters showed excellent agreement with the established ignition criterion: (1) the rate of change of droplet evaporation rate, and (2) the rate of change of the product species sum. Each parameter correlated well with the established ignition criterion for both n-heptane and n-hexadecane over the investigated range of initial droplet radii and initial ambient environment temperature.

A demonstration using a detailed chemical kinetic mechanism for methanol in air showed that experimental pre-exponential and activation energy values must be better defined for use in modeling ignition of hydrocarbon diffusion flames. A second demonstration was completed using a simplified spark ignition energy model with an n-octane fuel droplet in air. Results showed spatial and temporal development of the flow field subsequent to the spark energy introduction.

6.2 Recommendations

Extensions of this ignition model are now obvious and may be readily accomplished. First, high pressure phenomena should be evaluated and appropriately incorporated into the model. Sufficiently high pressures may produce supercritical droplets. At these conditions, wet bulb temperatures increase with increasing pressure and the solubility of the liquid by the ambient gas becomes significant. The effects of high pressure on droplet combustion have been studied; however, few details on droplet ignition have been published. Naturally, most combustion devices operate at pressures higher than atmospheric.

Secondly, considerations should be made for multi-component fuels. These practical fuels are mixtures of hydrocarbons. As a result of the mixture, the more volatile components gasify first and therefore liquid mass diffusion becomes significant. Third, detailed chemical kinetic mechanisms may be established for diffusion flames of different hydrocarbon fuels.

In addition, application of the model could be extended to laser ignition by adding a model for distribution of laser energy and appropriate kinetics representative of ionic reactions.

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APPENDICES

APPENDIX A

FIGURES

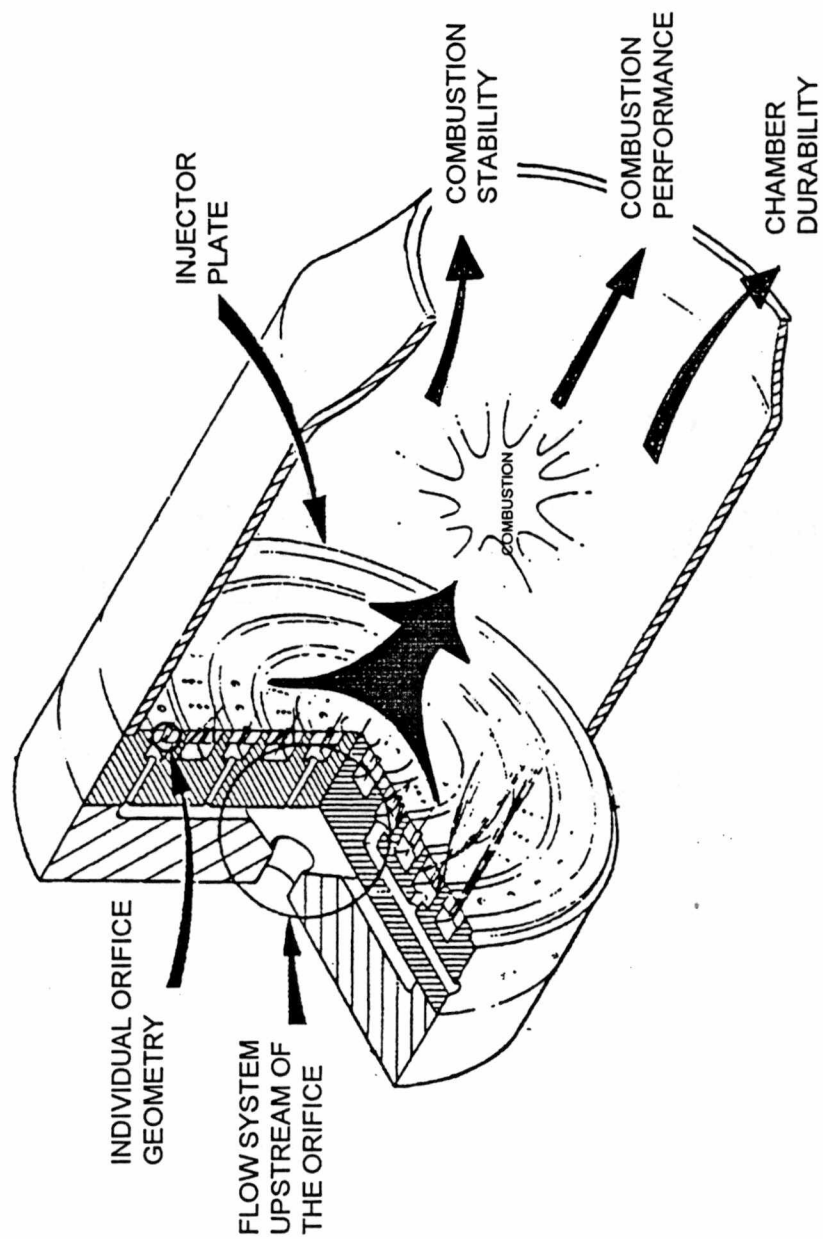


Figure 2.1. Liquid Rocket Engine Manifold, Injector and Combustion Chamber (adapted from NASA SP-8089²⁶⁸).

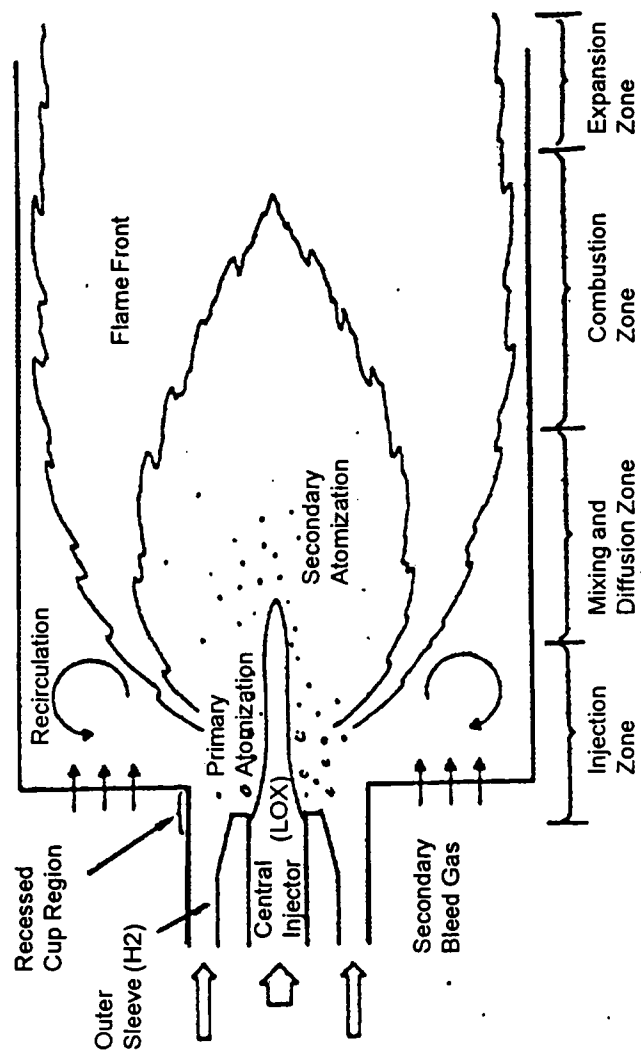


Figure 2.2. Coupled Flow Processes (adapted from Liang⁷⁵).

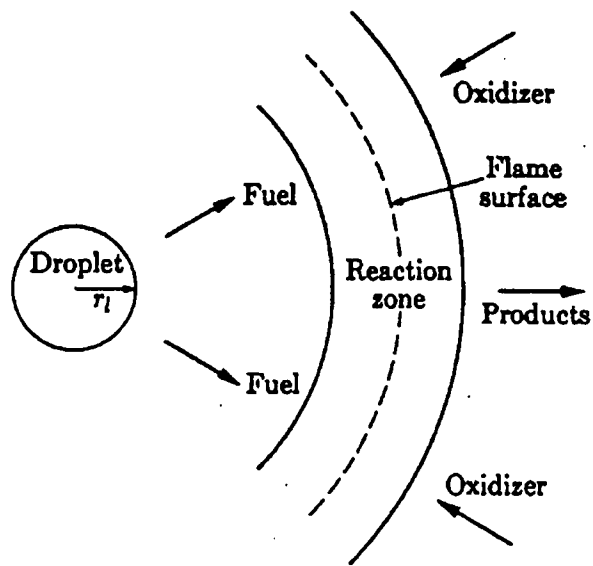


Figure 2.3. Droplet Heat-up and Combustion.

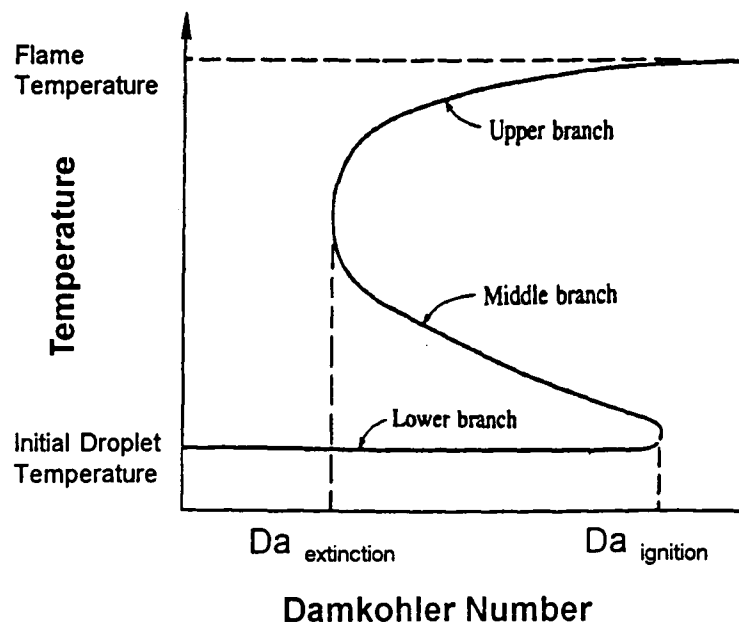


Figure 2.4. Damkohler Number as a Function of Temperature.

NOTES
 Grid Coordinates, Cell Velocity assigned at cell left edge
 Thermodynamic Quantities assigned at cell center

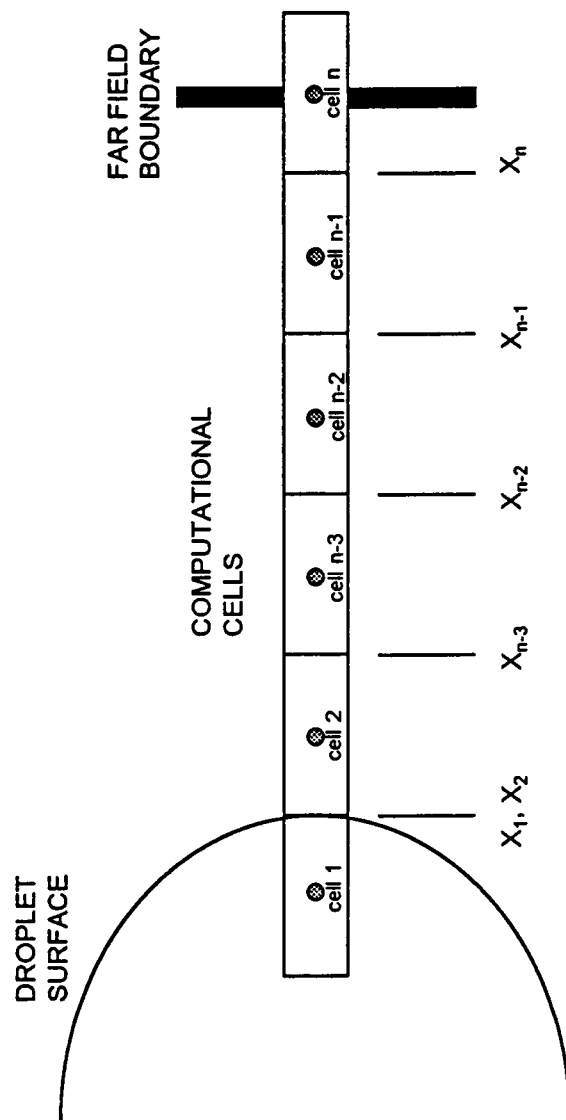


Figure 3.1. Computational Domain Used in CON1D.

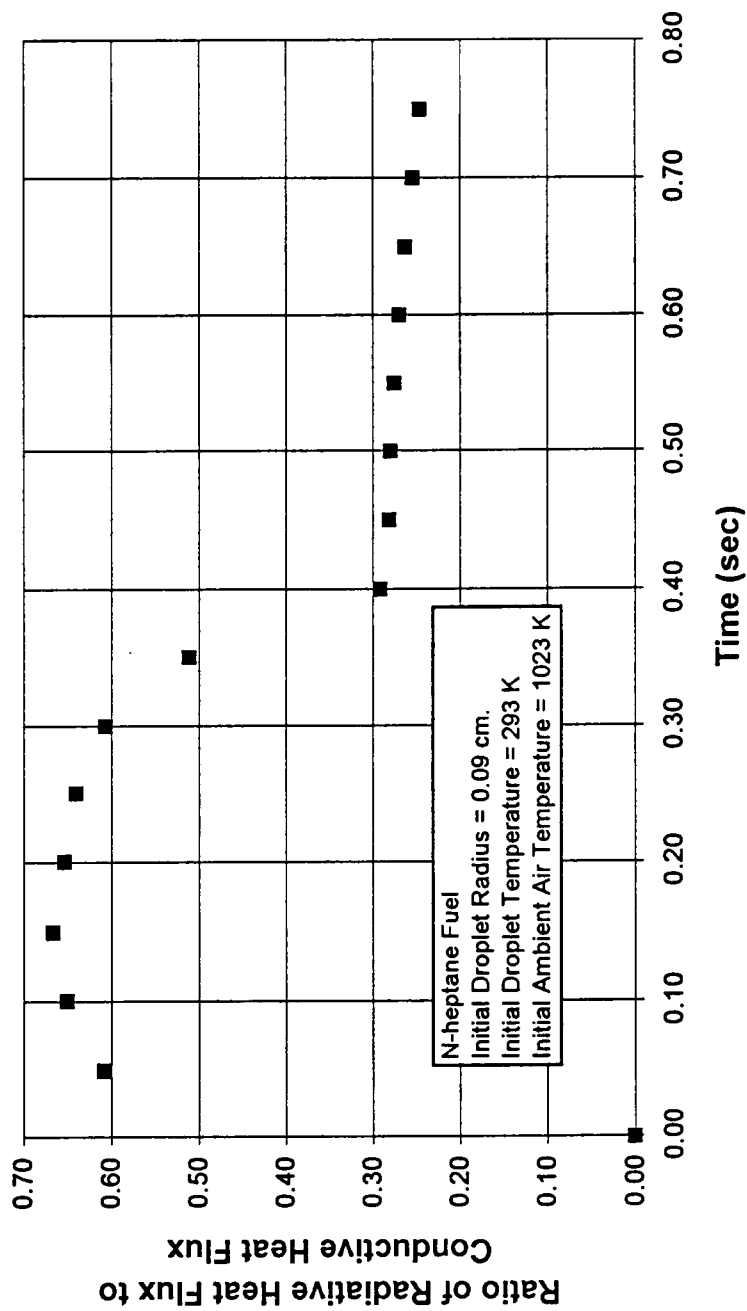


Figure 4.1. Ratio of Radiative Flux to Conduction at the Droplet Surface Typical for Hydrocarbons Investigated in the Study.

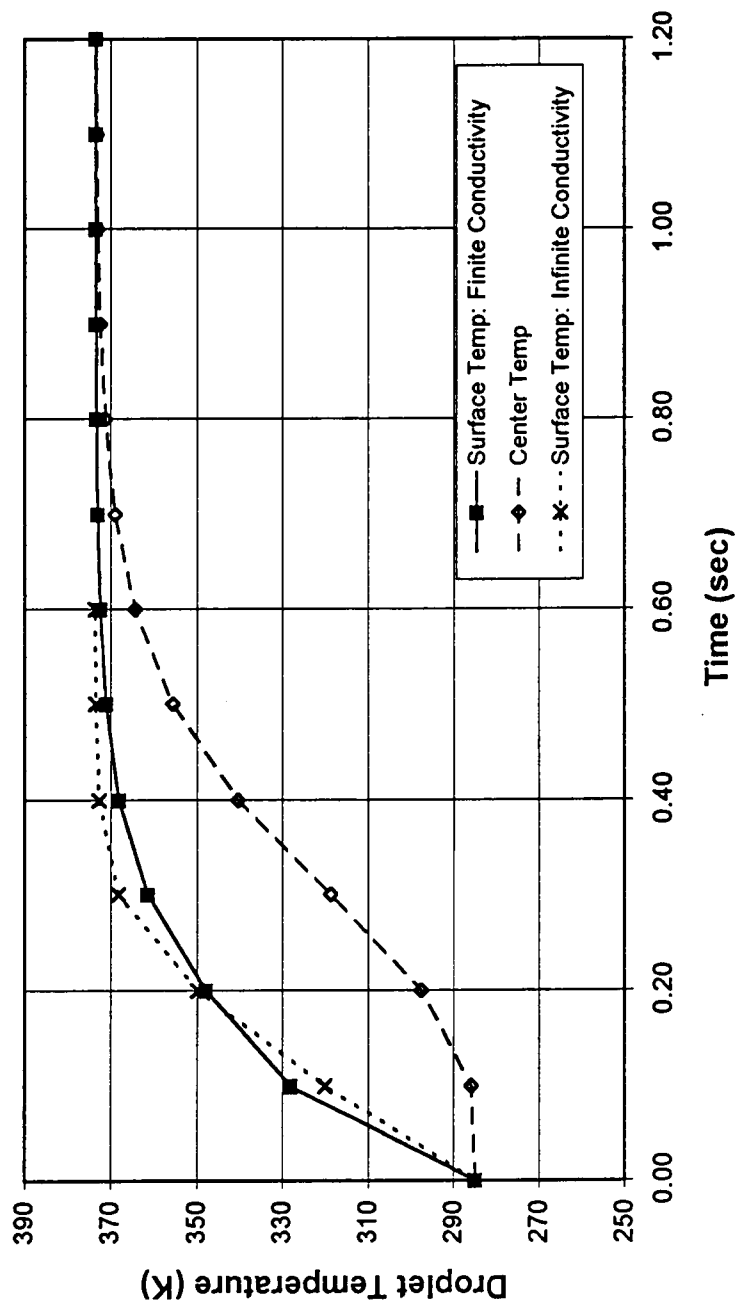


Figure 4.2. Typical Droplet Temperature Profiles Assuming Finite Conductivity and Infinite Conductivity.

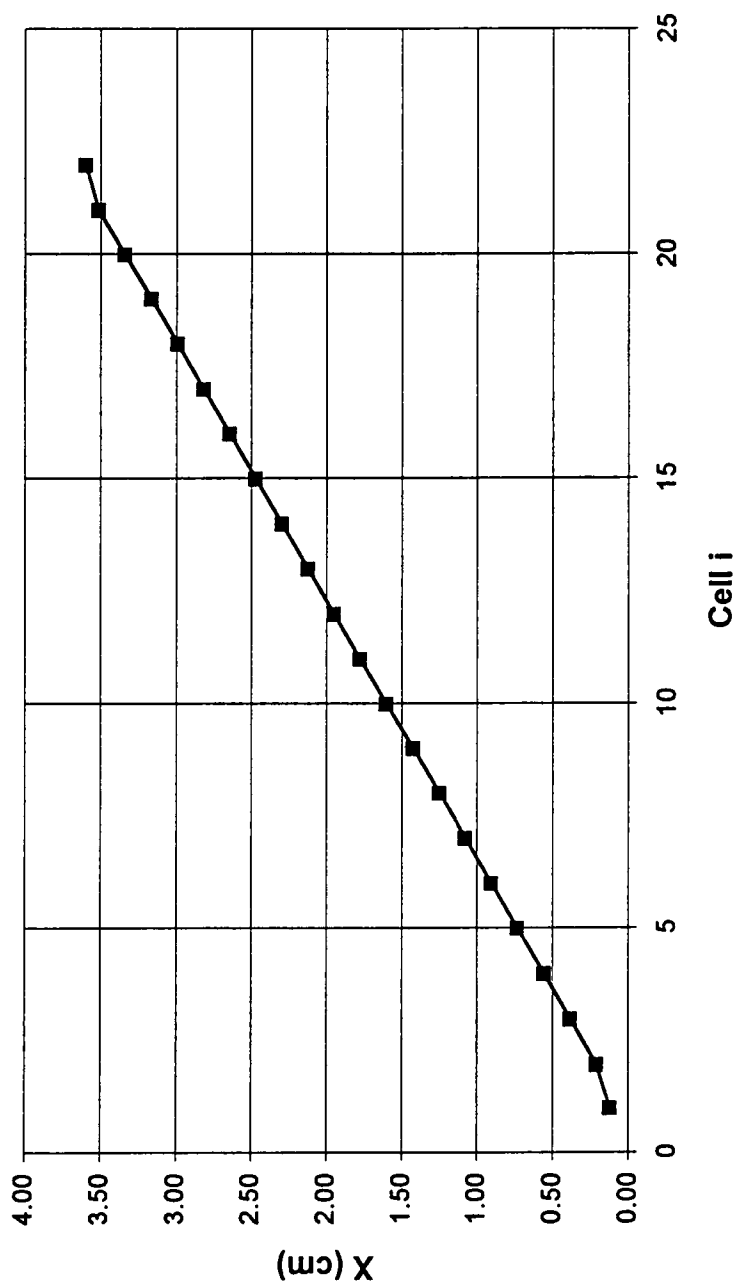


Figure 5.1. Model Results Using Iso-Octane Fuel: Cell Center Location.

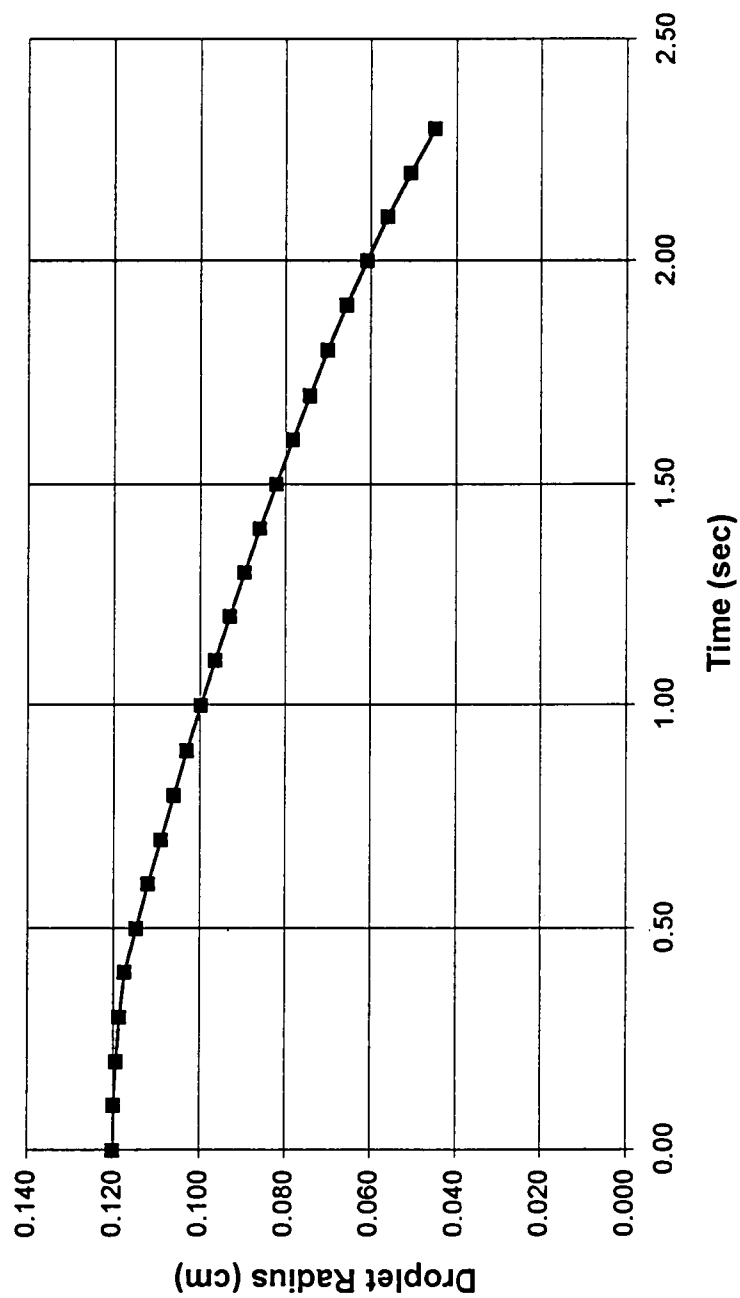


Figure 5.2. Model Results Using Iso-Octane Fuel: Droplet Radius Variation with Time.

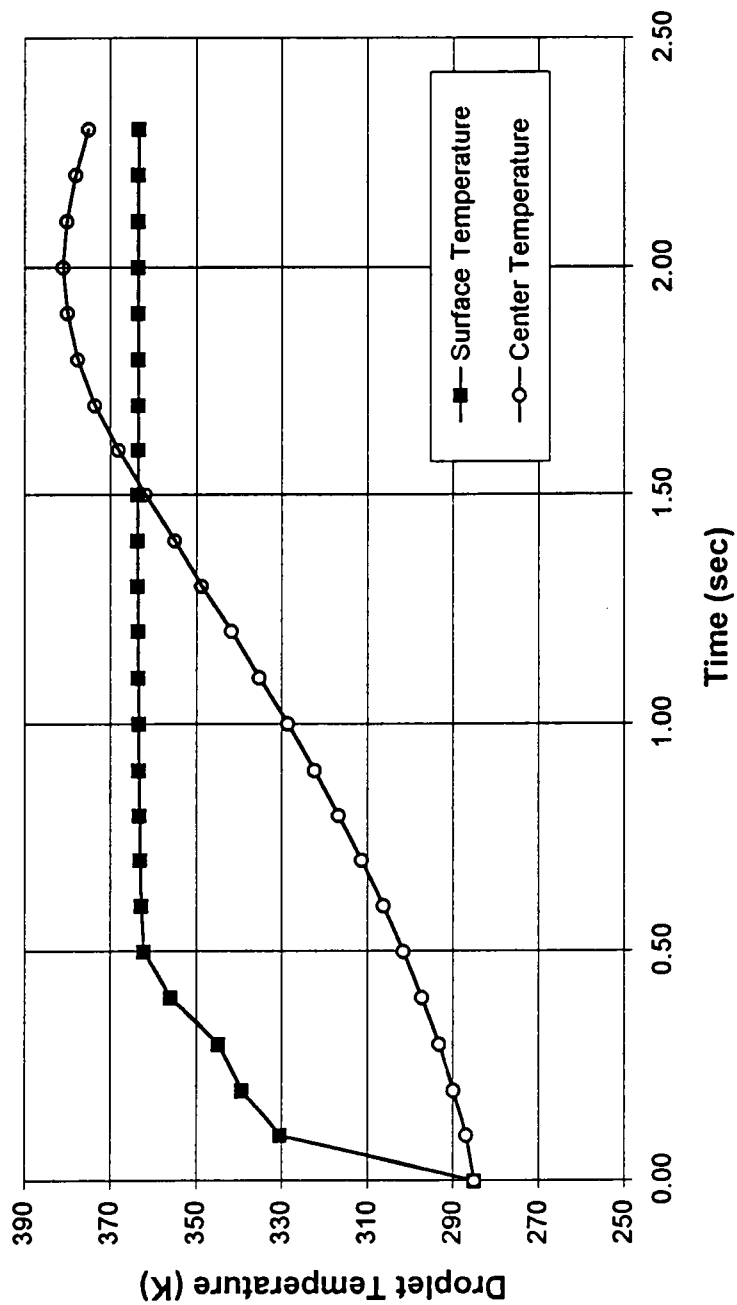


Figure 5.3. Model Results Using Iso-Octane Fuel: Droplet Center Temperature and Surface Temperature Variation with Time.

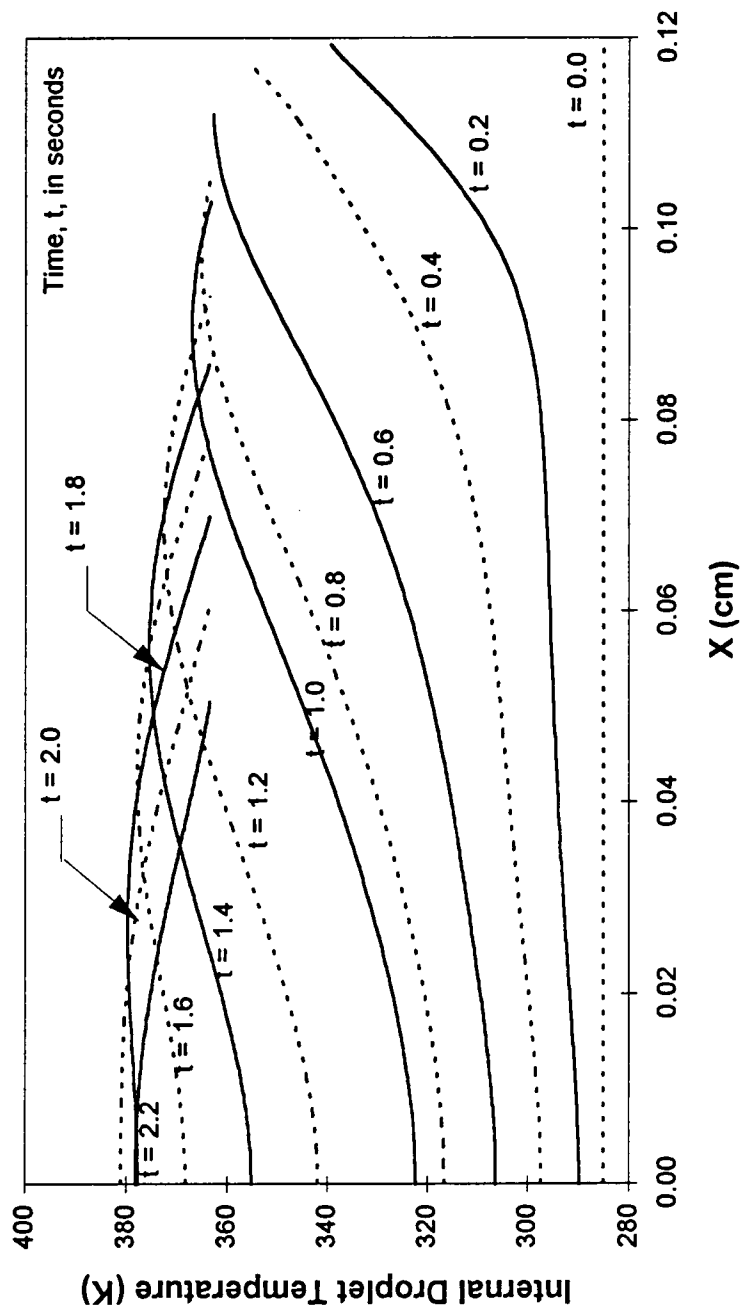


Figure 5.4. Model Results Using Iso-Octane Fuel: Internal Droplet Temperature Profiles.

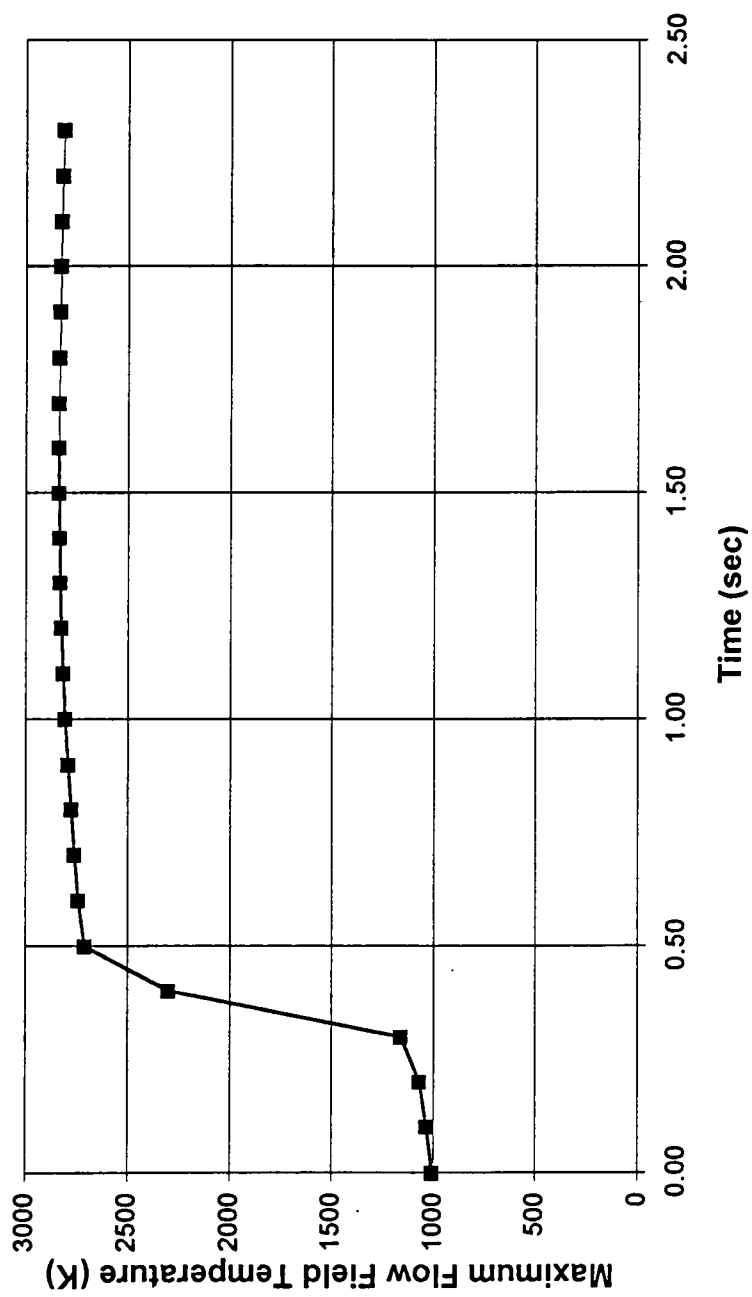


Figure 5.5. Model Results Using Iso-Octane Fuel: Maximum Gaseous Flow Field Temperature Variation with Time.

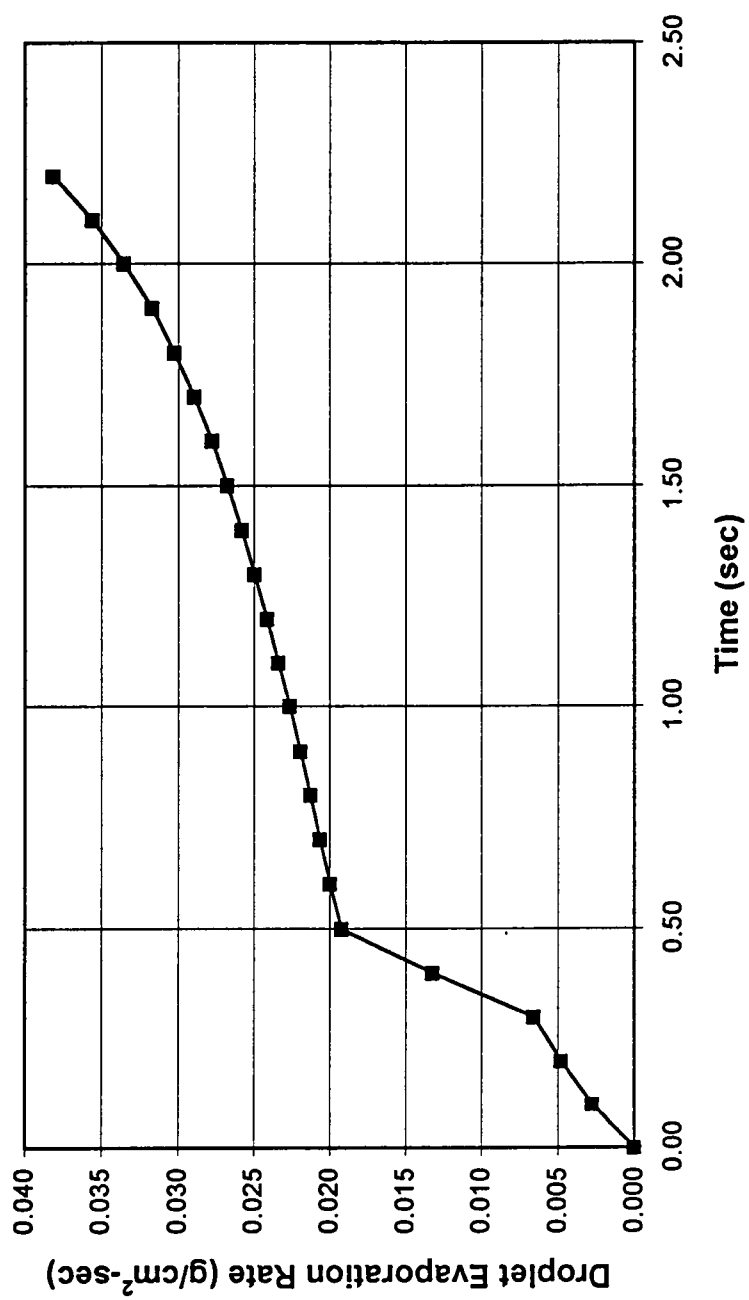


Figure 5.6. Model Results Using Iso-Octane Fuel: Droplet Evaporation Rate Variation with Time.

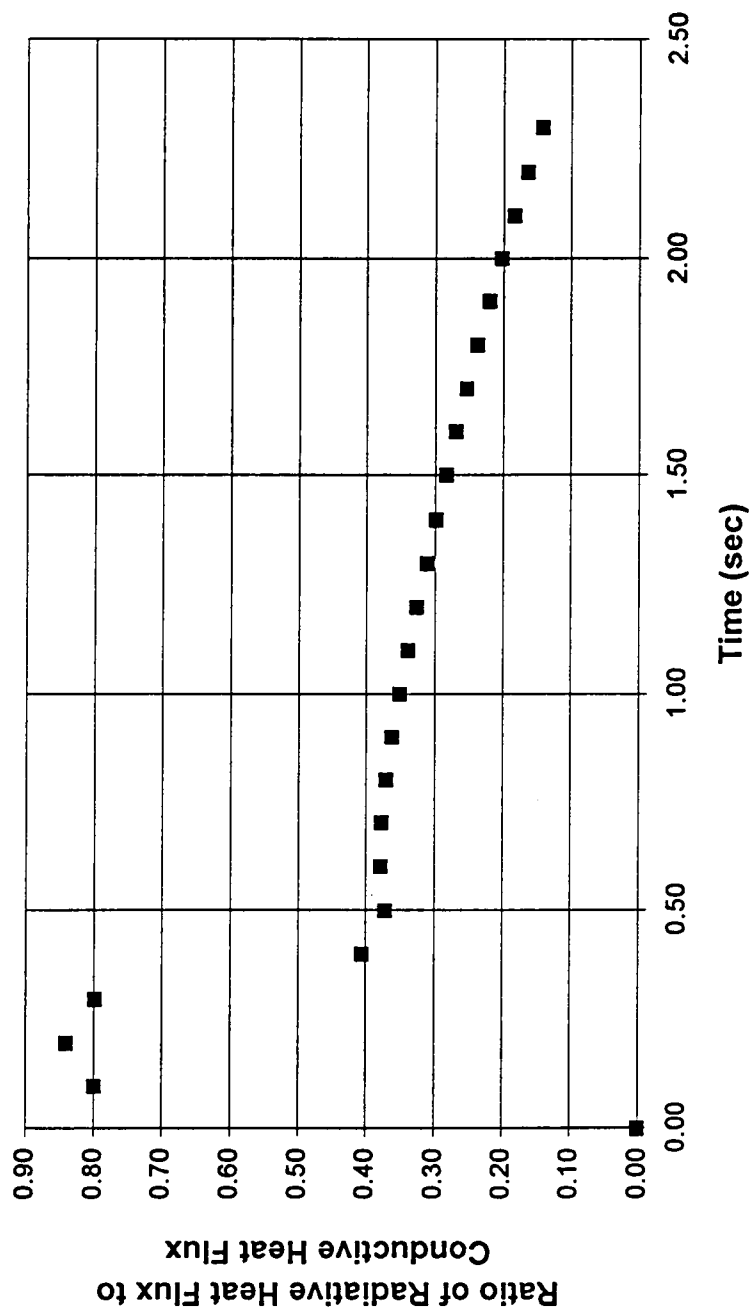


Figure 5.7. Model Results Using Iso-Octane Fuel: Ratio of Radiation Heat Flux to Conduction Heat Flux at the Droplet Surface.

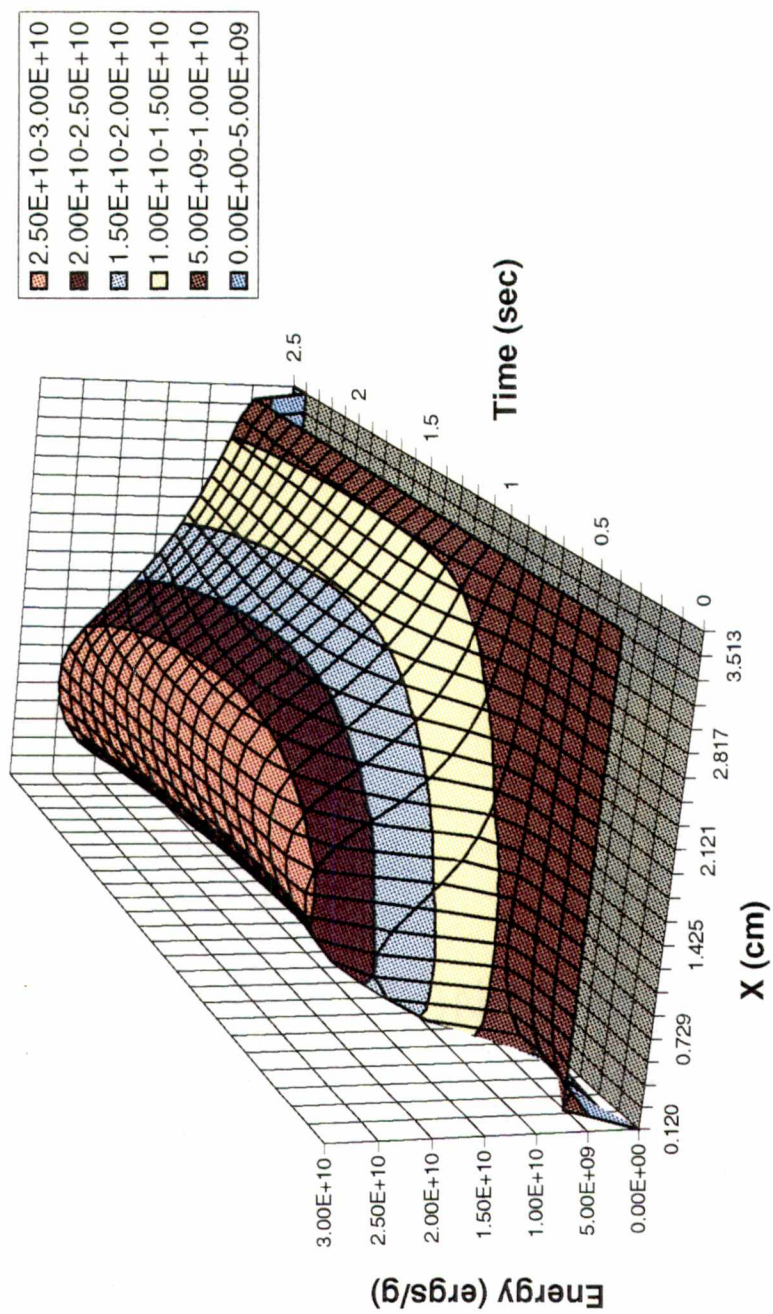


Figure 5.8. Model Results Using Iso-Octane Fuel: Gaseous Flow Field Energy Variation with Time and Space.

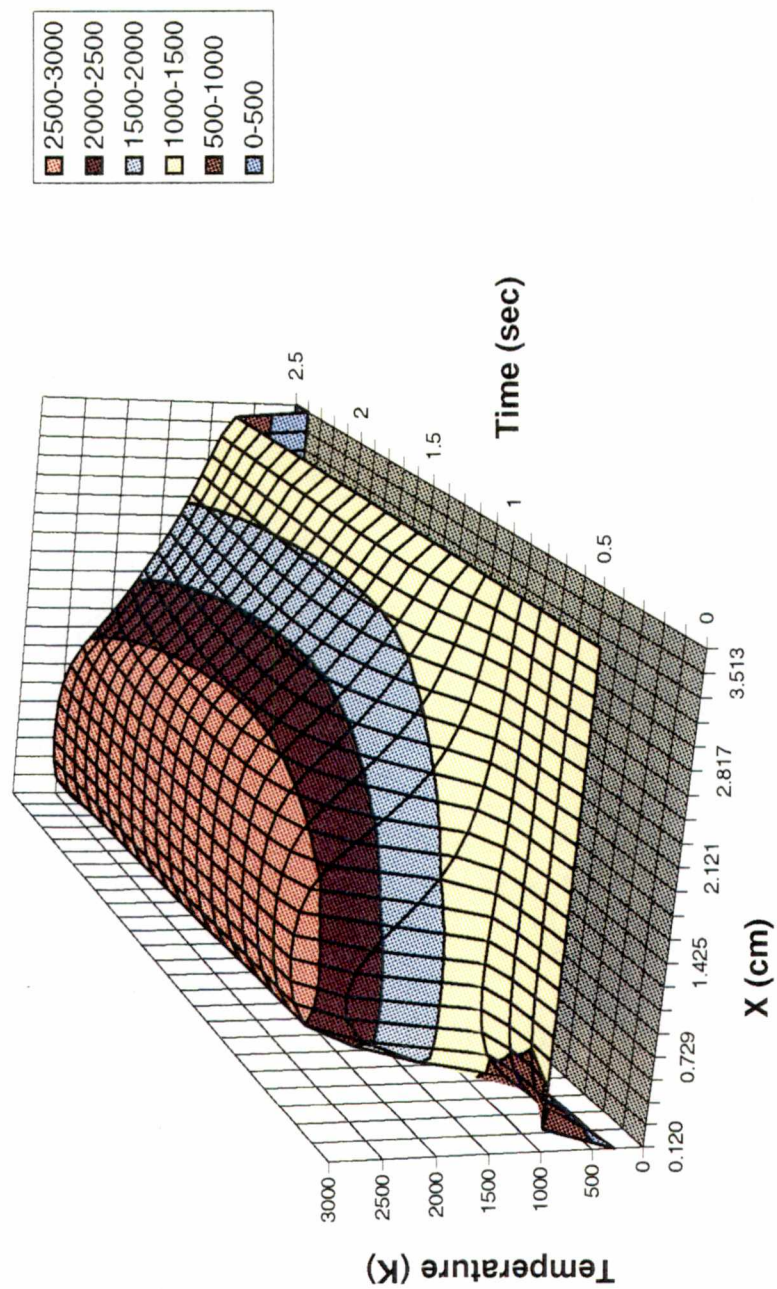


Figure 5.9. Model Results Using Iso-Octane Fuel: Gaseous Flow Field Static Temperature Variation with Time and Space.

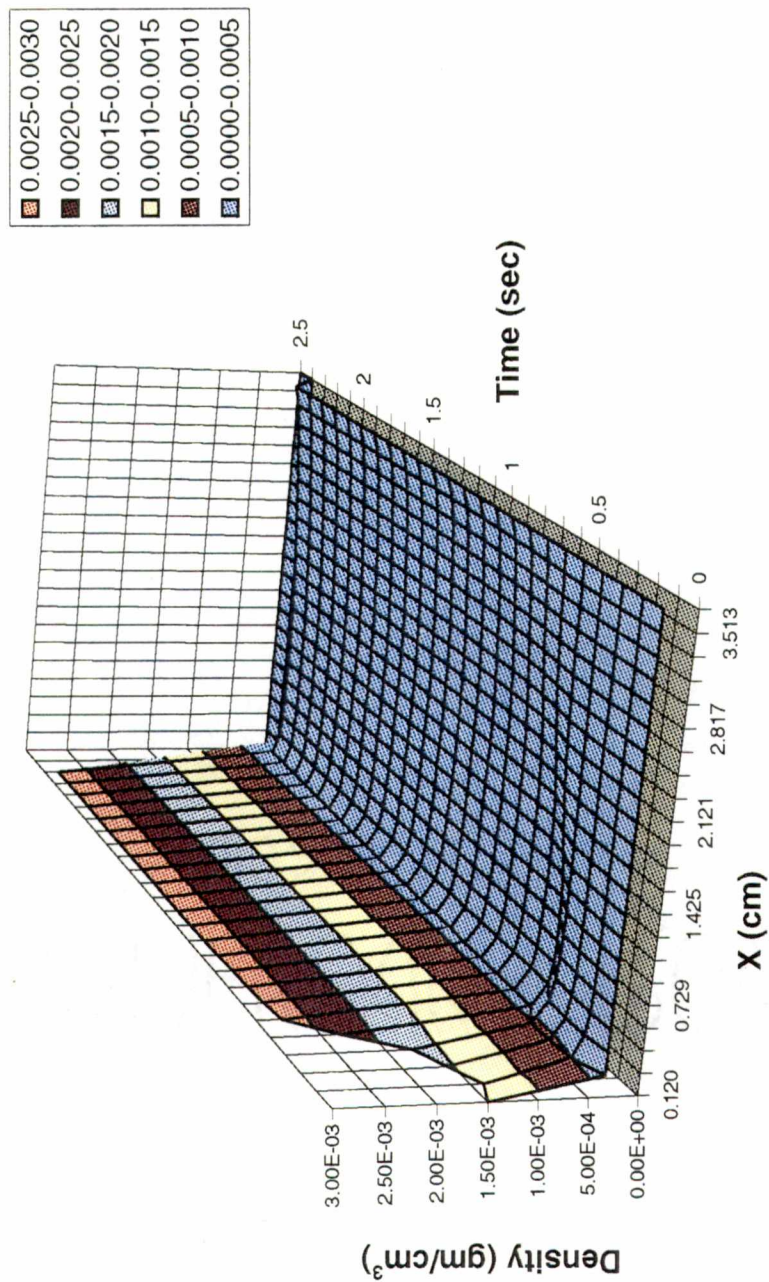


Figure 5.10. Model Results Using Iso-Octane Fuel: Gaseous Flow Field Density Variation with Time and Space.

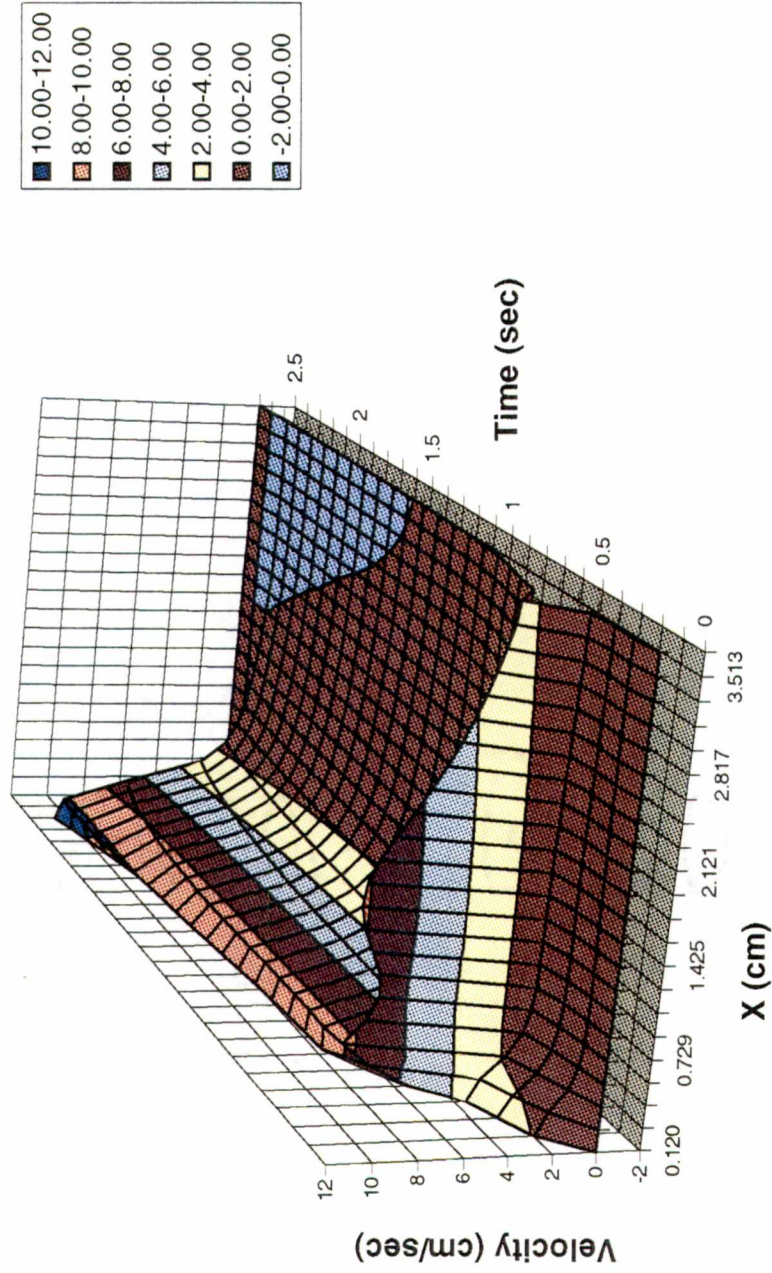


Figure 5.11. Model Results Using Iso-Octane Fuel: Gaseous Flow Field Bulk Velocity Variation with Time and Space.

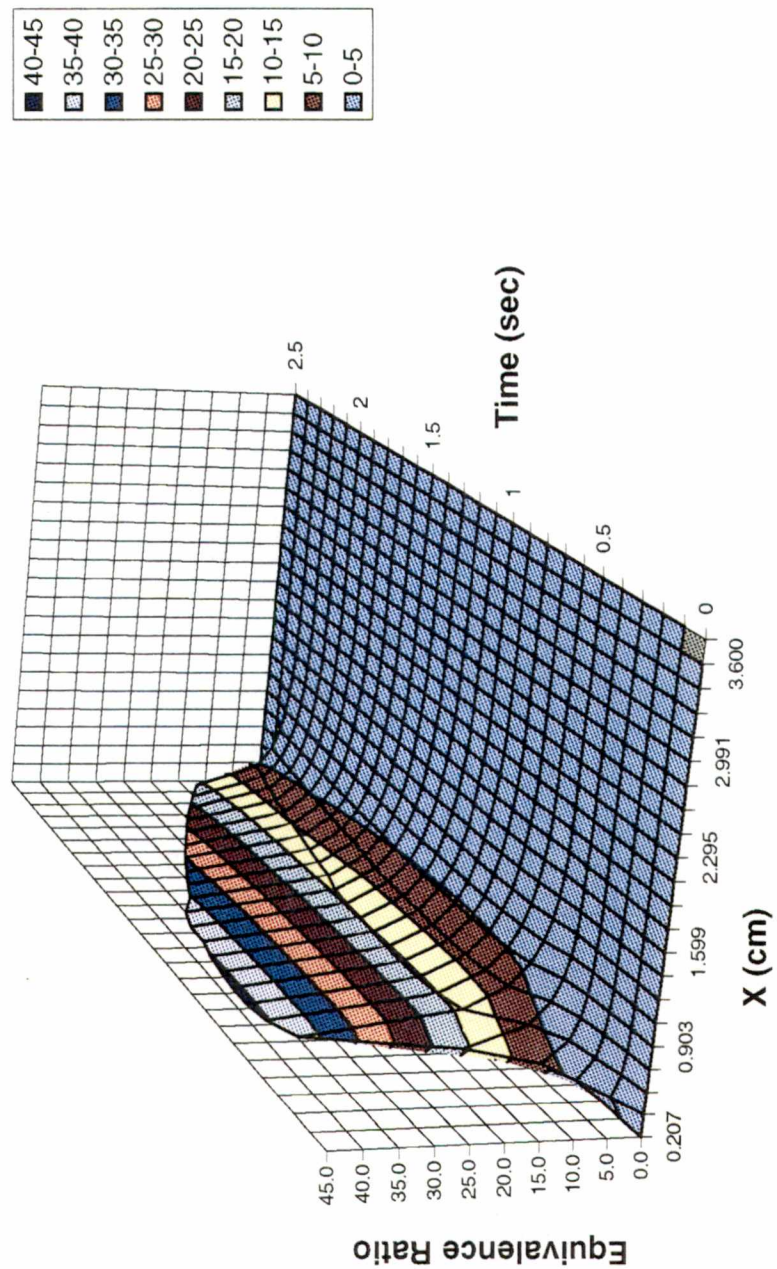


Figure 5.12. Model Results Using Iso-Octane Fuel: Gaseous Flow Field Equivalence Ratio Variation with Time and Space.

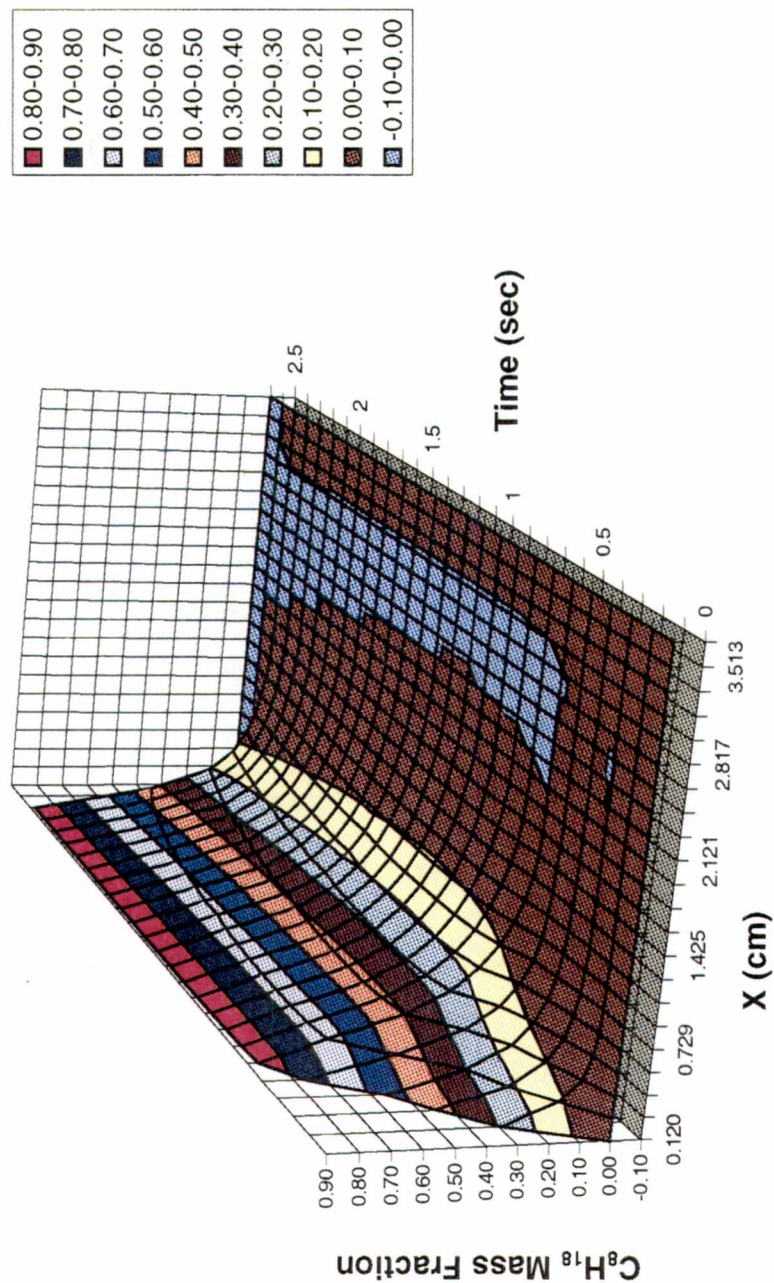


Figure 5.13. Model Results Using Iso-Octane Fuel: Gaseous Fuel Mass Fraction Variation with Time and Space.

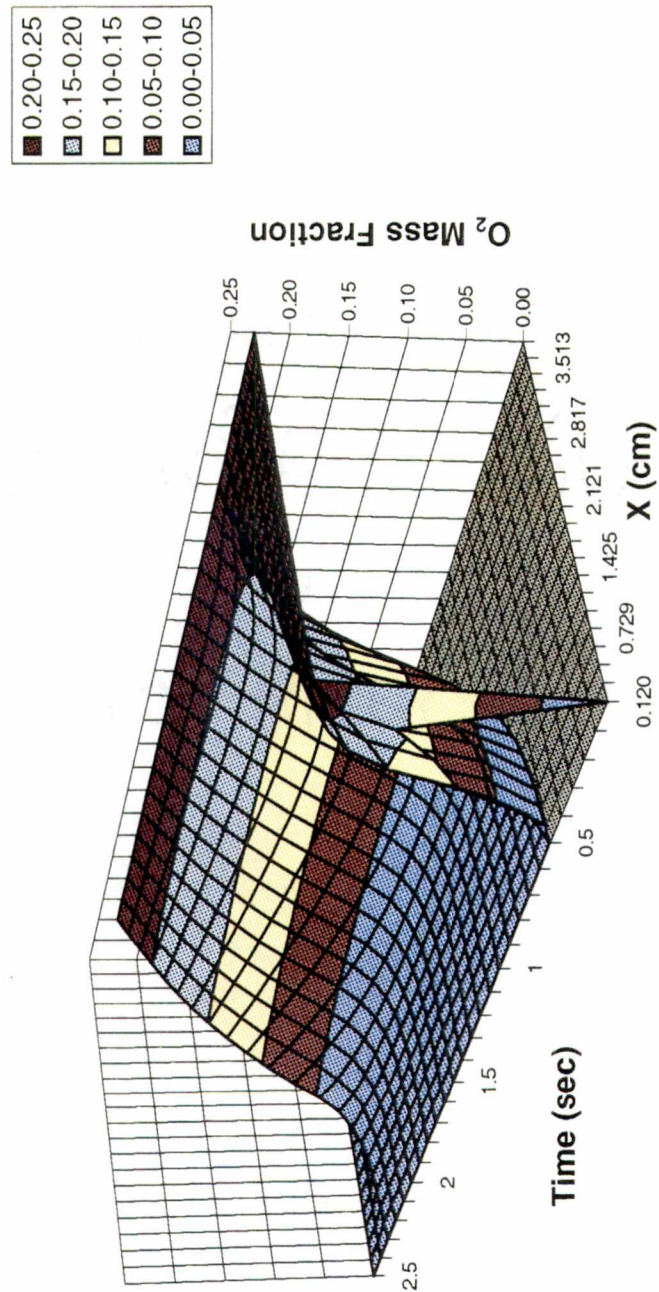


Figure 5.14. Model Results Using Iso-Octane Fuel: Oxygen Mass Fraction Variation with Time and Space.

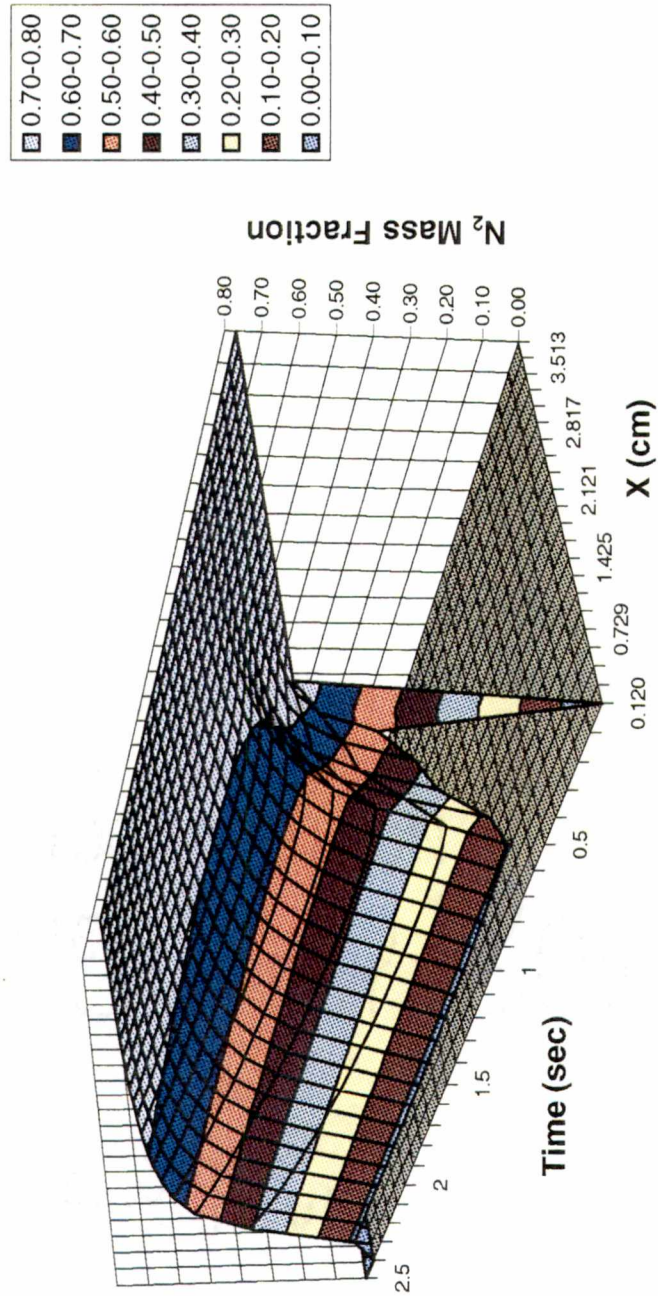


Figure 5.15. Model Results Using Iso-Octane Fuel: Nitrogen Mass Fraction Variation with Time and Space.

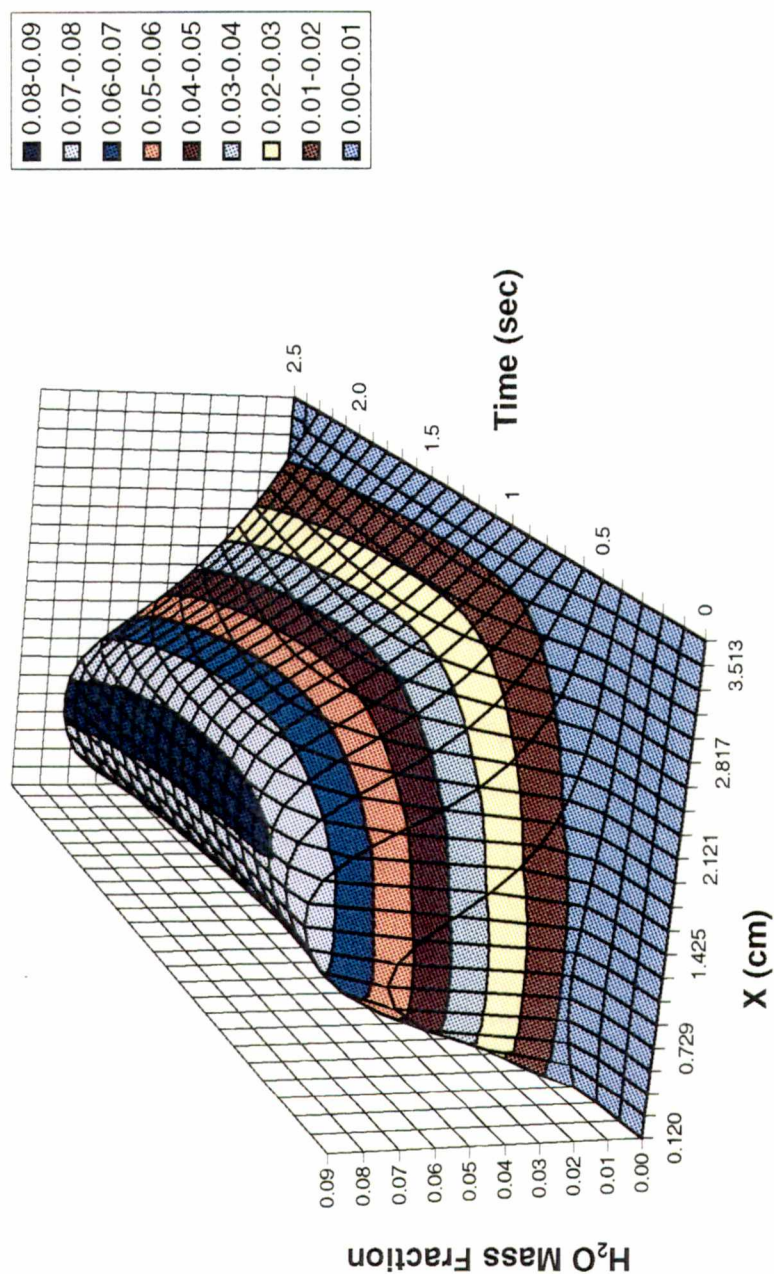


Figure 5.16. Model Results Using Iso-Octane Fuel: Water Vapor Mass Fraction Variation with Time and Space.

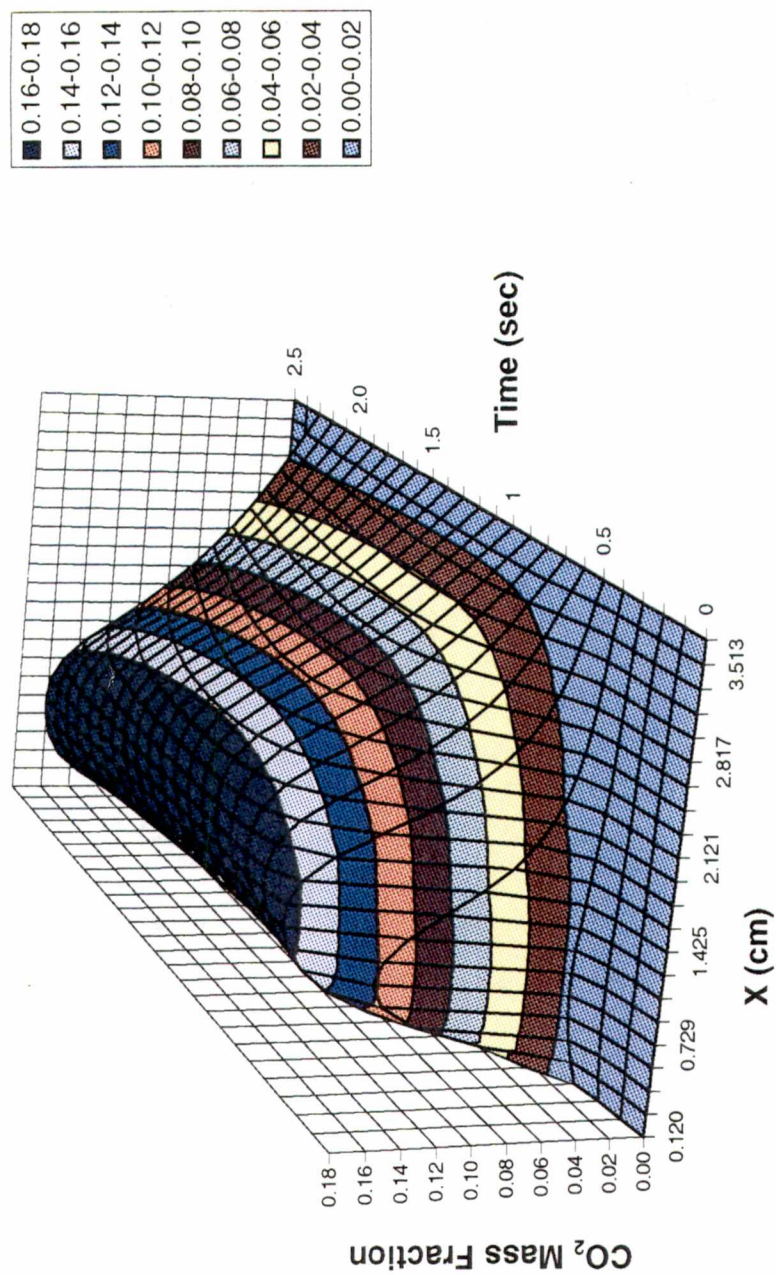


Figure 5.17. Model Results Using Iso-Octane Fuel: Carbon Dioxide Mass Fraction Variation with Time and Space.

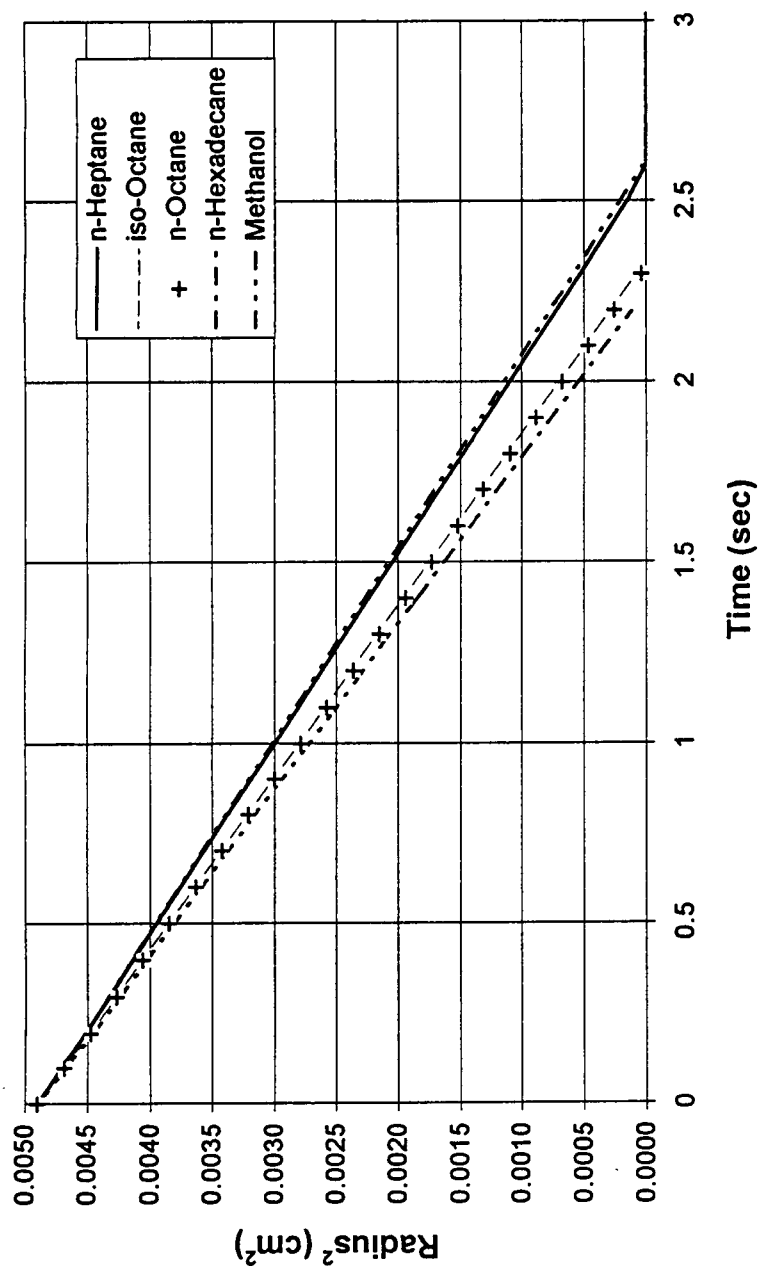


Figure 5.18. Theoretical Droplet Radius Variation with Time for Evaporating Hydrocarbon Fuels.

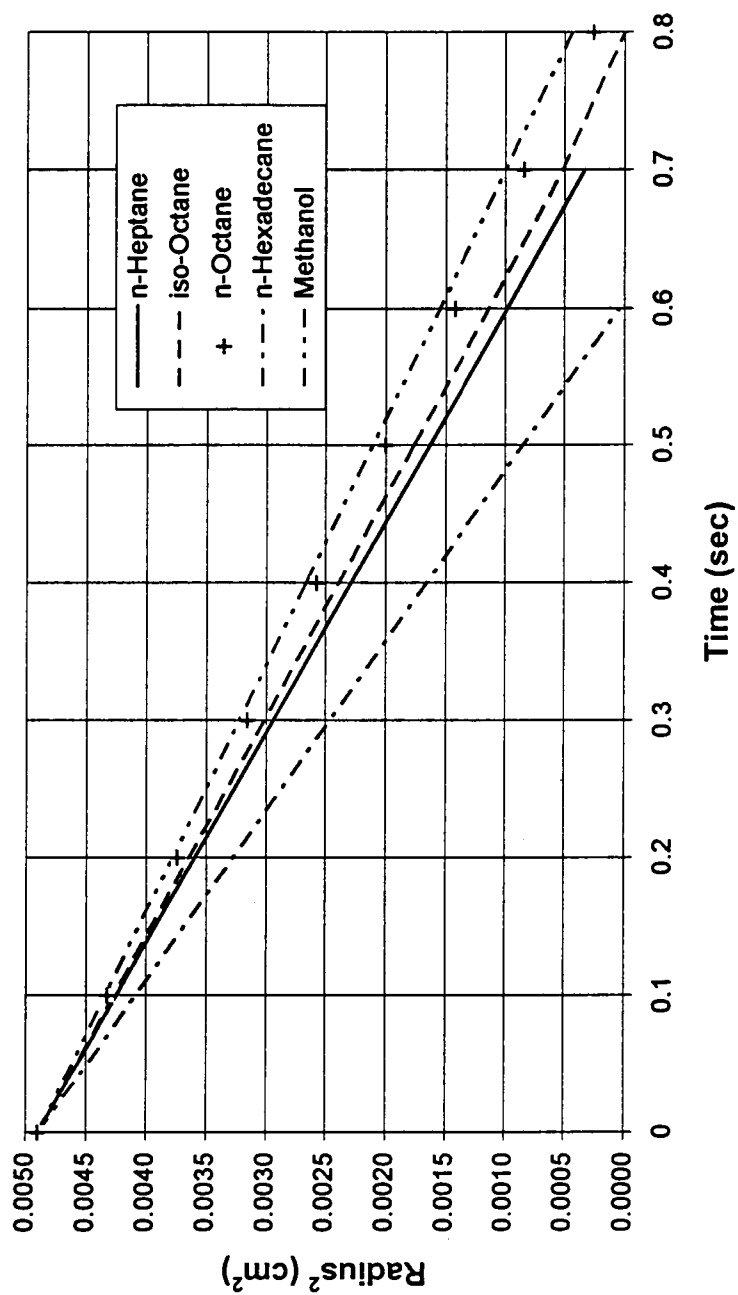


Figure 5.19. Theoretical Droplet Radius Variation with Time for Burning Hydrocarbon Fuels.

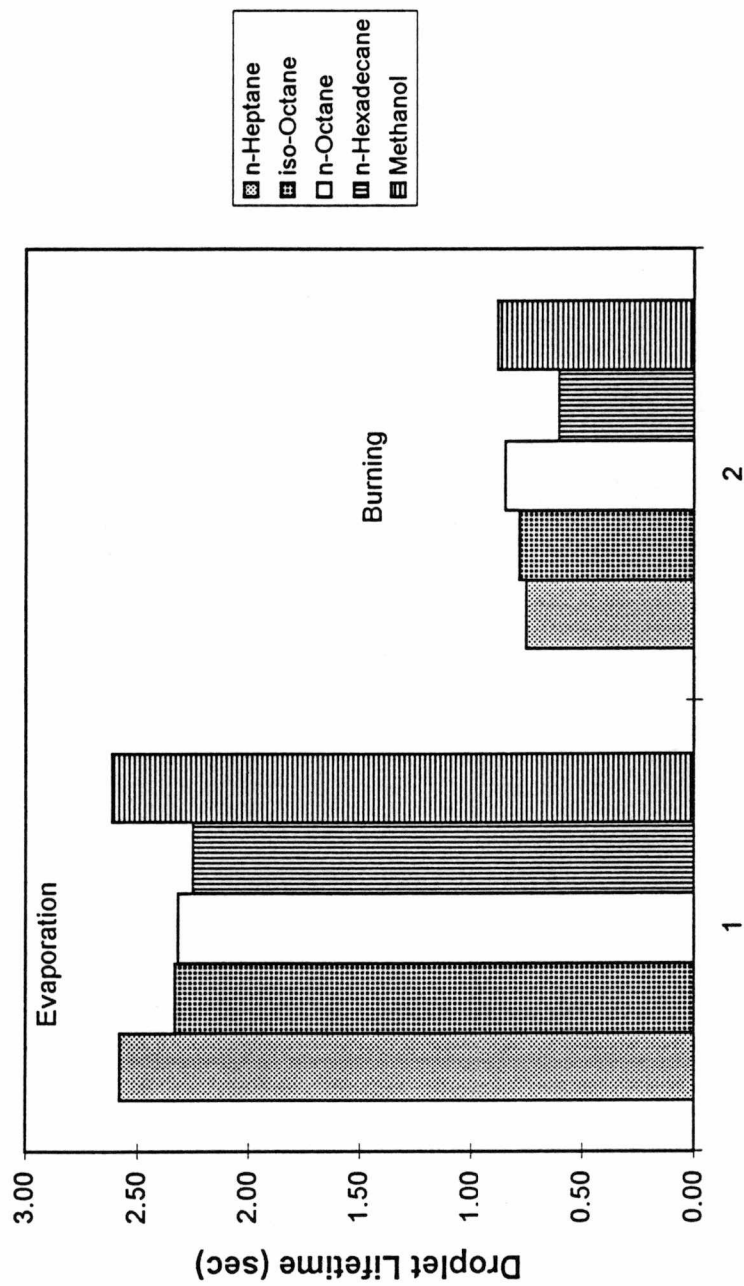


Figure 5.20. Theoretical Droplet Lifetimes for Evaporating and Burning Hydrocarbon Fuels.

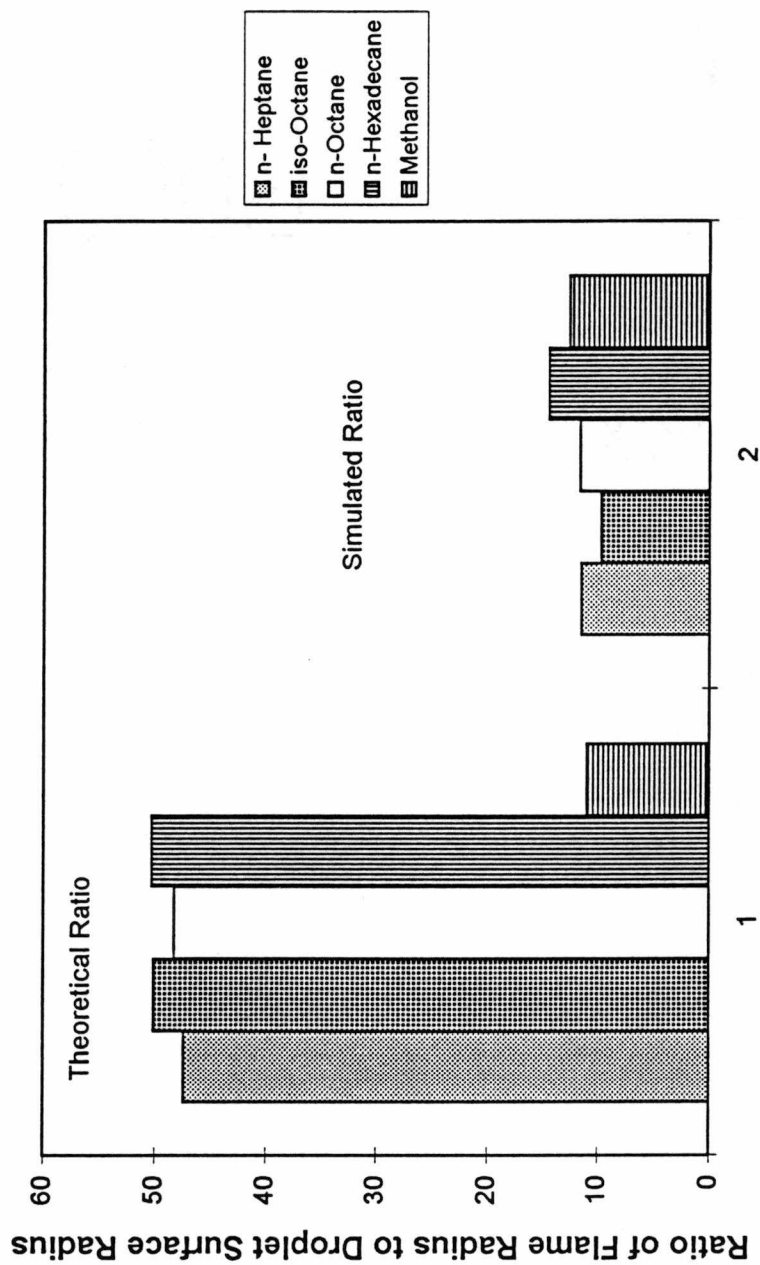


Figure 5.21. Comparison Between the Theoretical and Simulated Flame Standoff Distance for Selected Hydrocarbon Fuels.

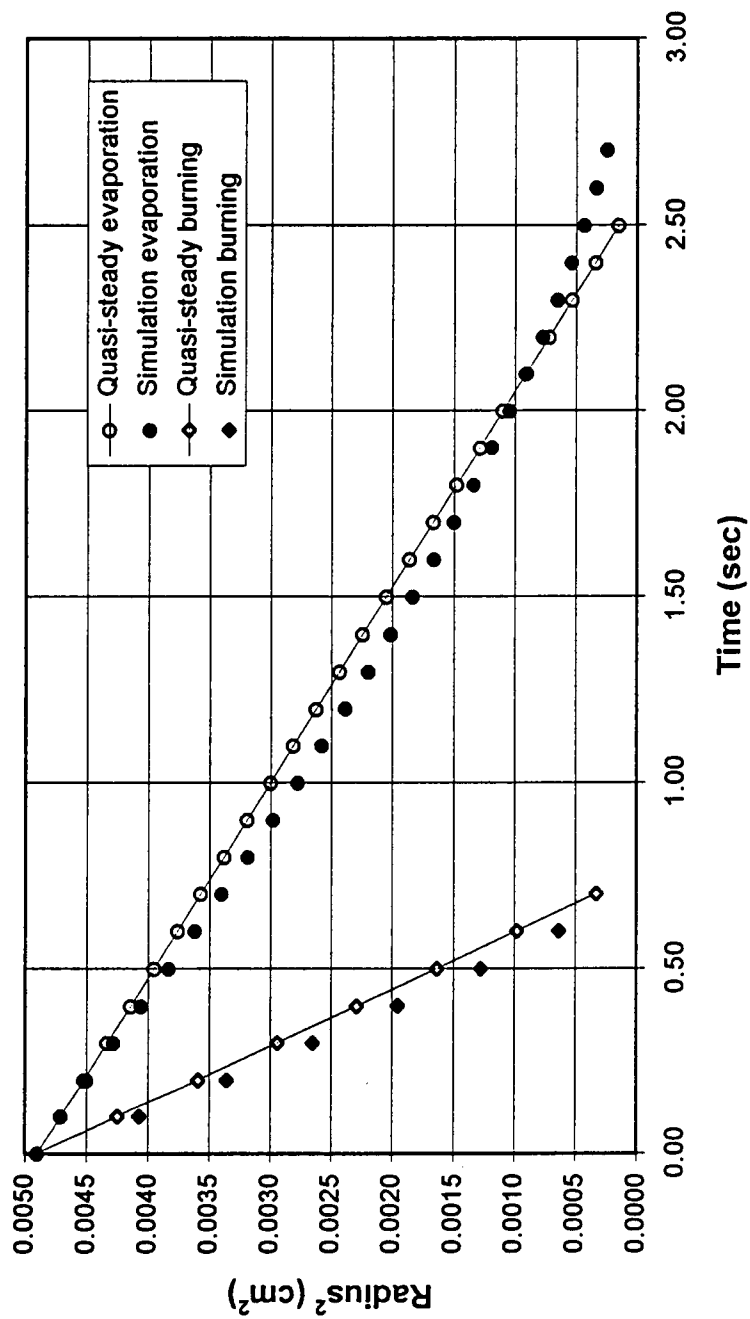


Figure 5.22. Comparison of Model Predicted and Theoretical Droplet Radius Variation with Time for n-Heptane Fuel in 950 K Ambient Air.

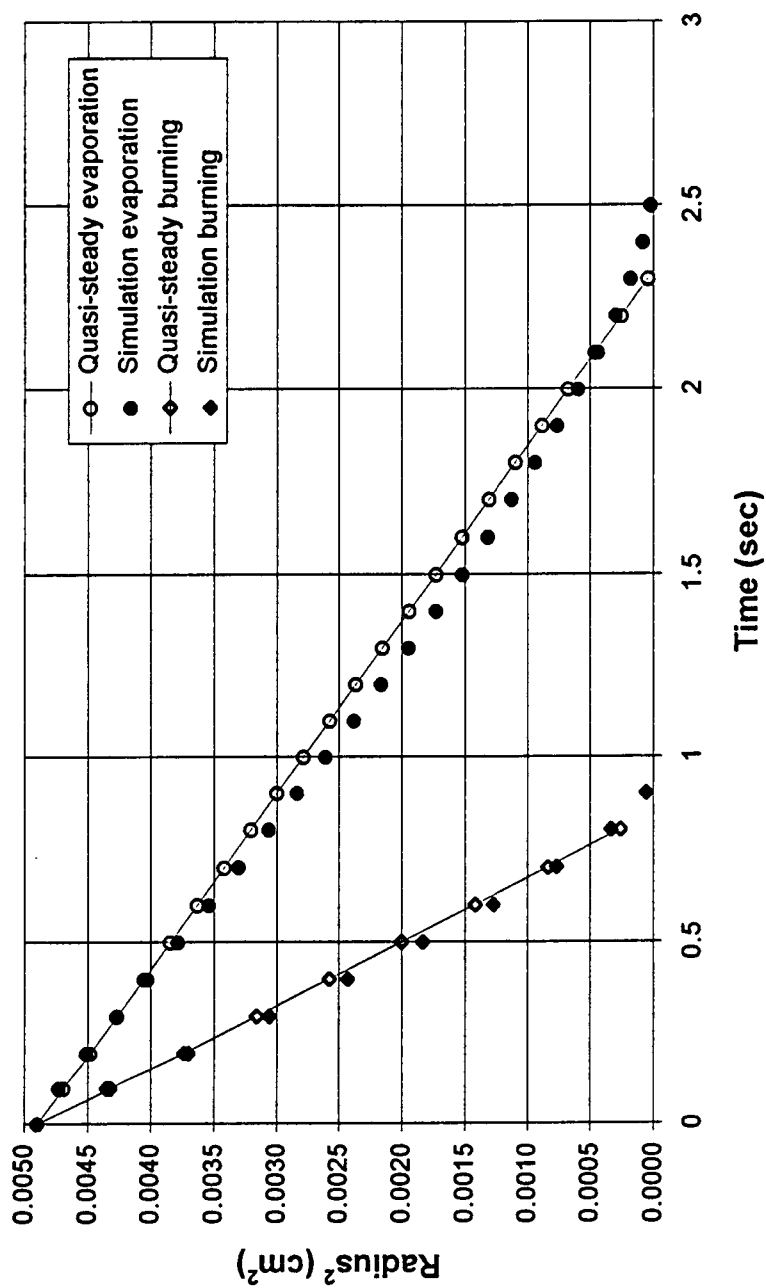


Figure 5.23. Comparison of Model Predicted and Theoretical Droplet Radius Variation with Time for n-Octane Fuel in 950 K Ambient Air.

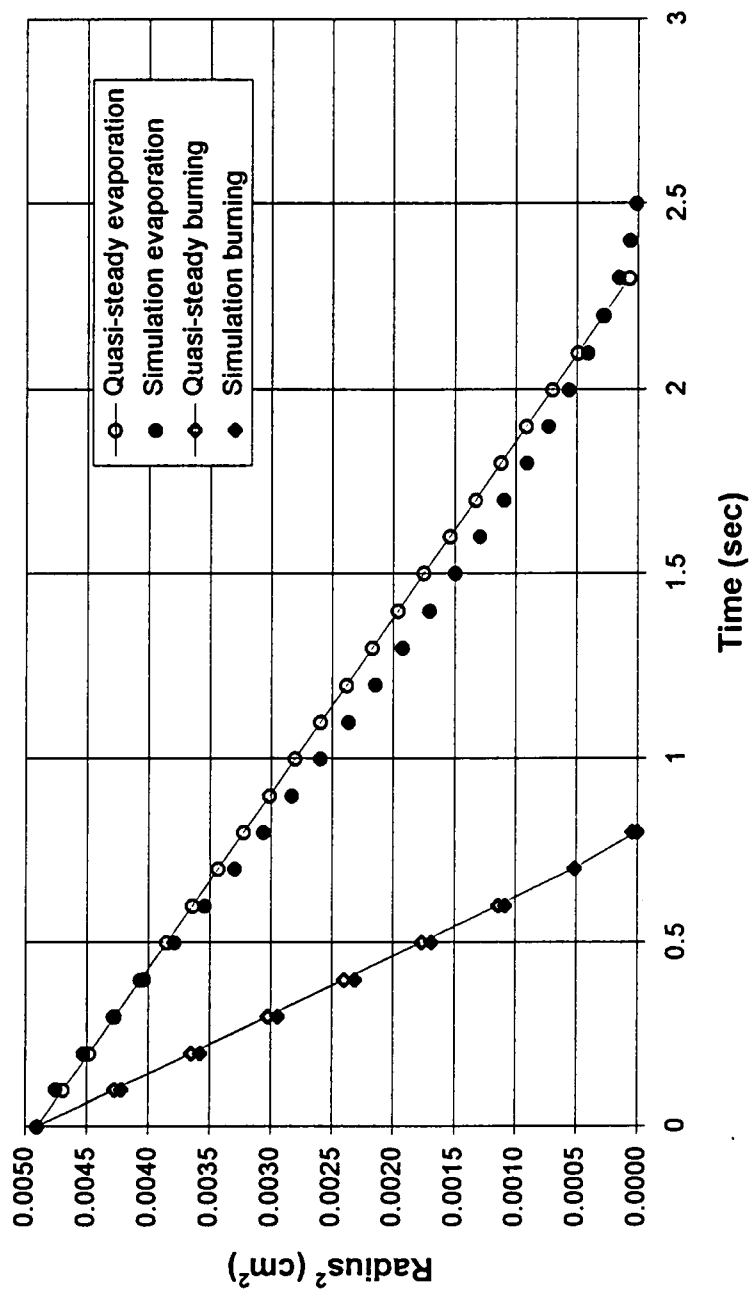


Figure 5.24. Comparison of Model Predicted and Theoretical Droplet Radius Variation with Time for iso-Octane Fuel in 950 K Ambient Air.

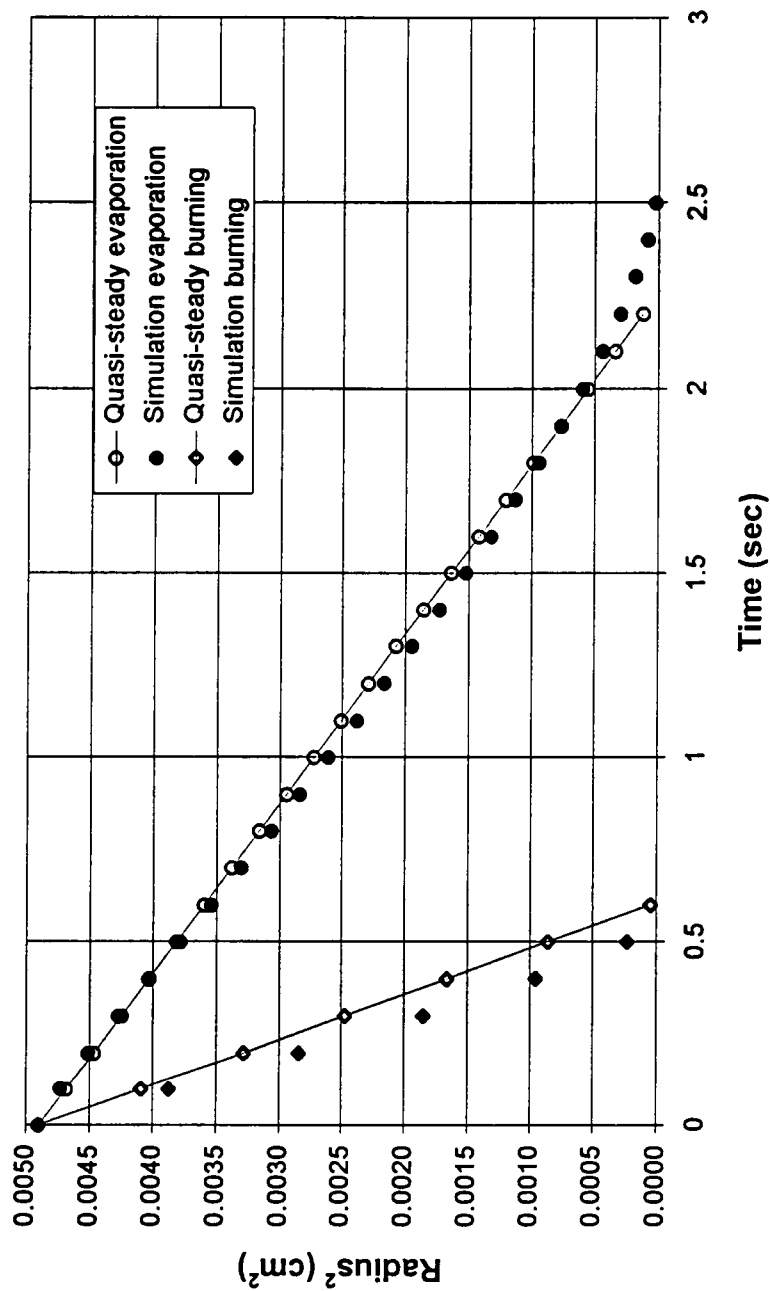


Figure 5.25. Comparison of Model Predicted and Theoretical Droplet Radius Variation with Time for n-Hexadecane Fuel in 950 K Ambient Air.

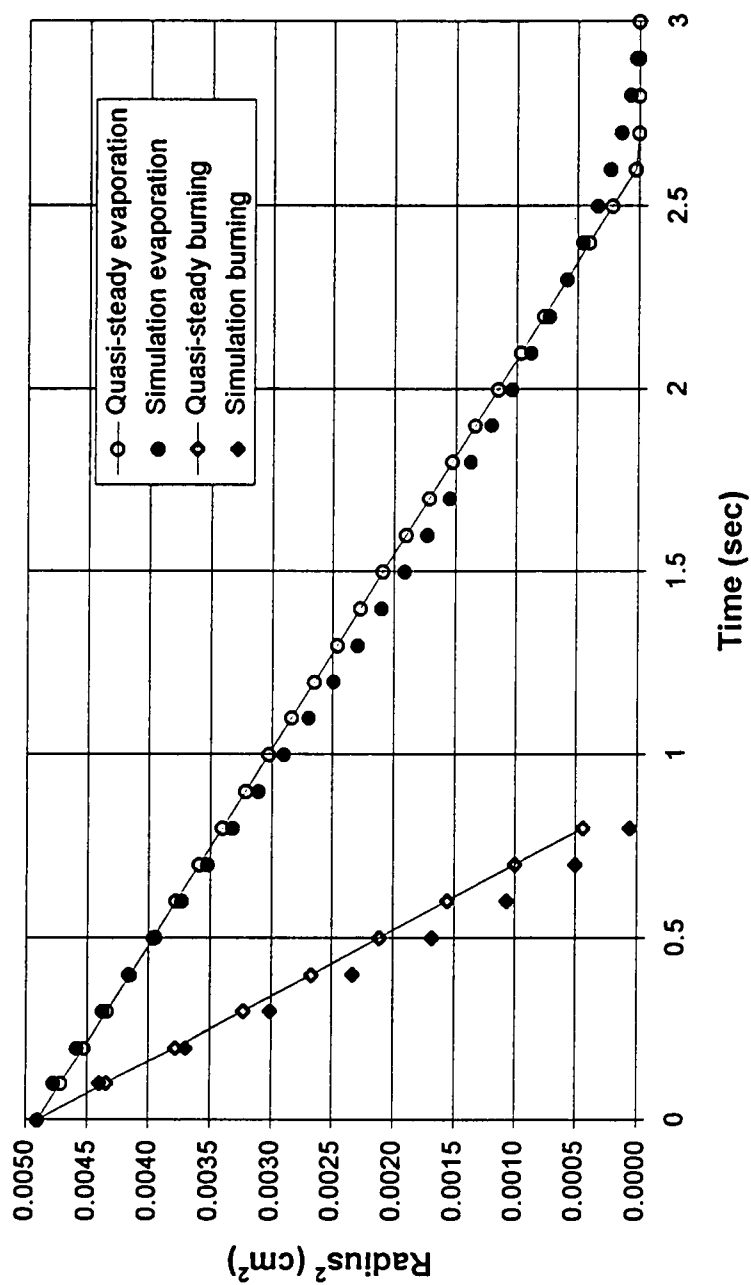


Figure 5.26. Comparison of Model Predicted and Theoretical Droplet Radius Variation with Time for Methanol Fuel in 950 K Ambient Air.

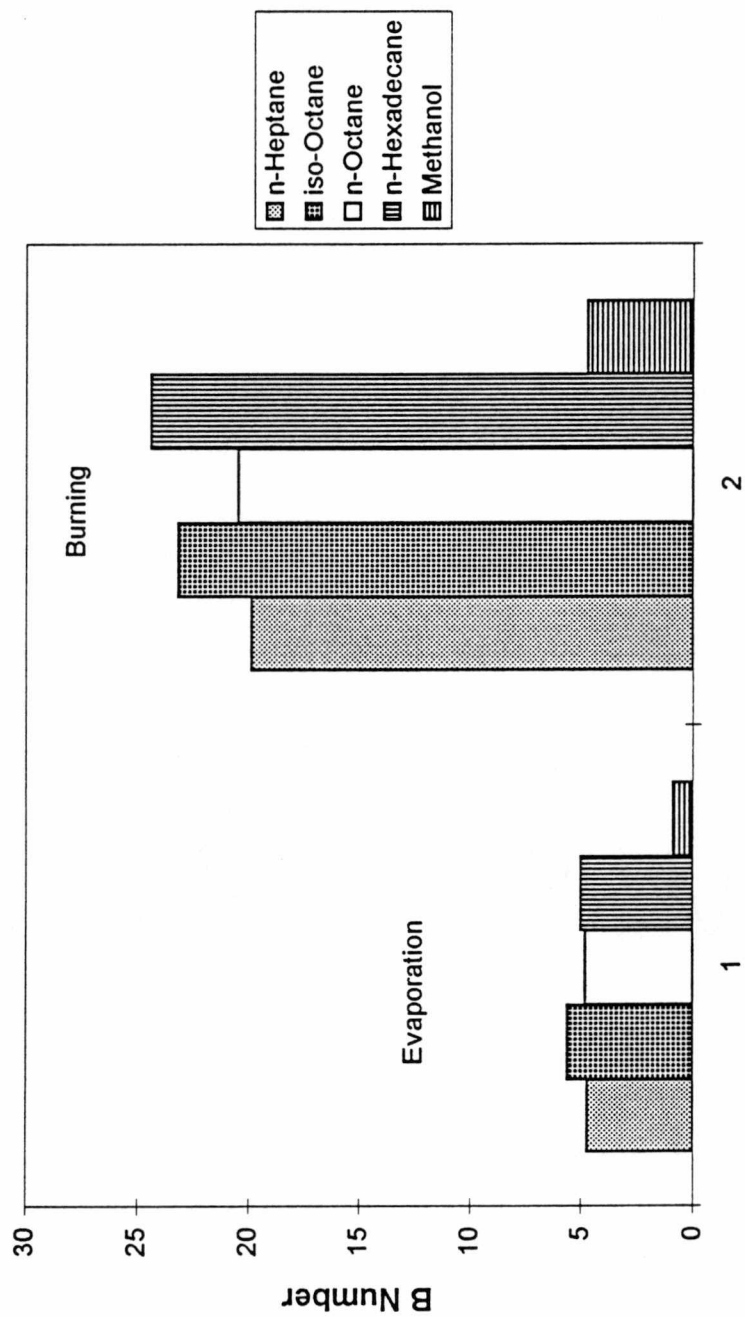


Figure 5.27. Theoretical B Numbers for Evaporation and Burning of Selected Hydrocarbon Fuels.

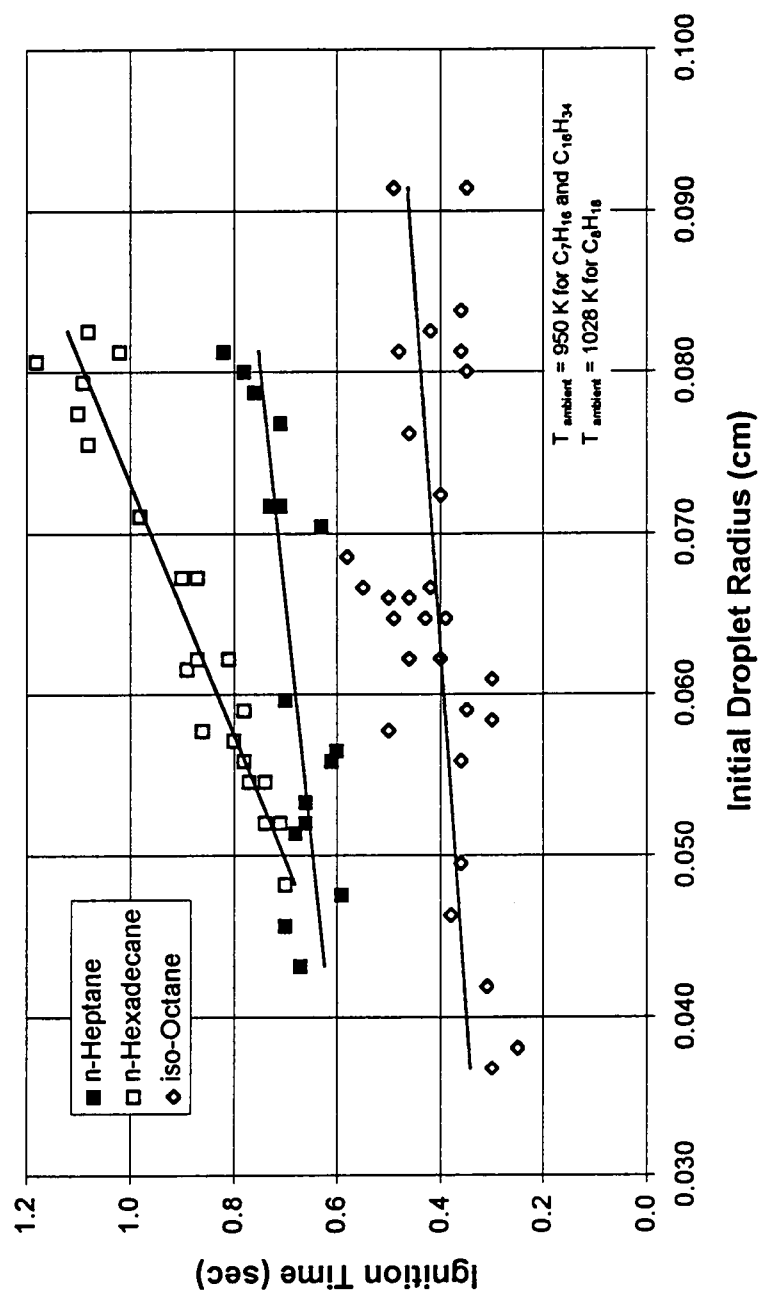


Figure 5.28. Experimental Ignition Delay as a Function of Initial Droplet Radius As Measured by Faeth.

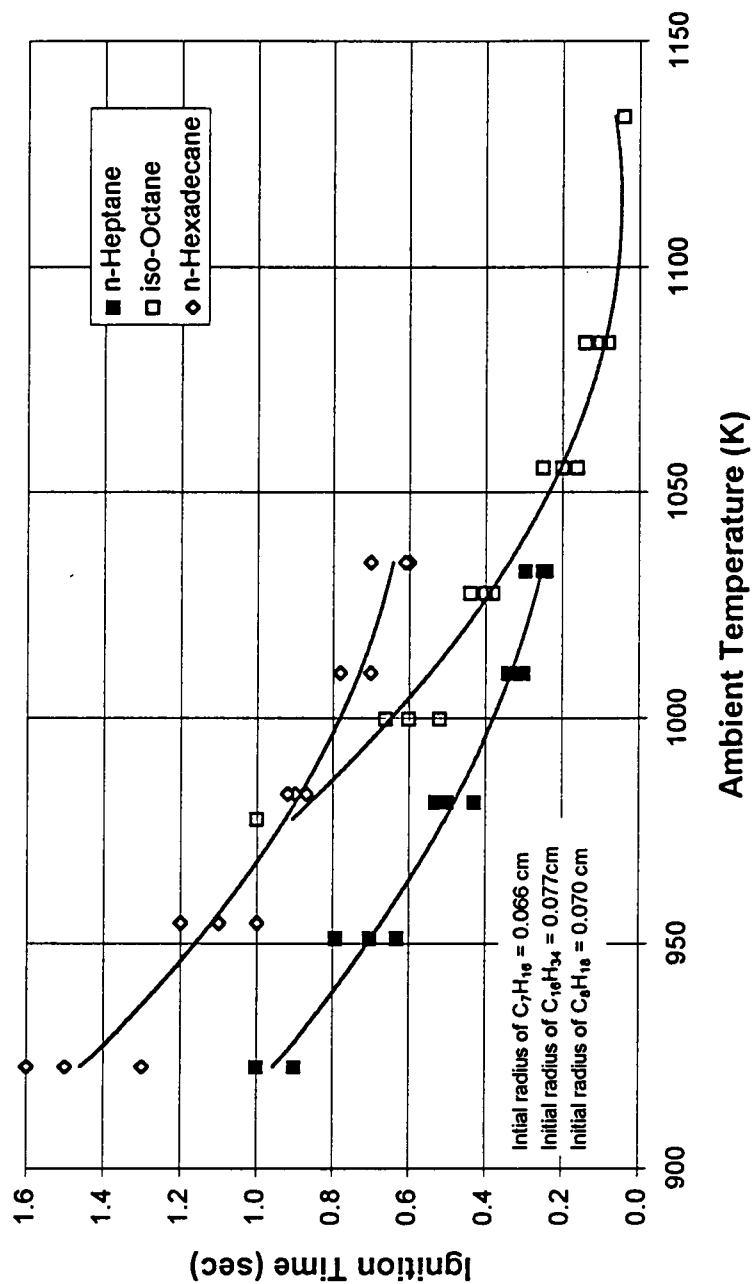


Figure 5.29. Experimental Ignition Delay as a Function of Initial Ambient Temperature As Measured by Faeth.

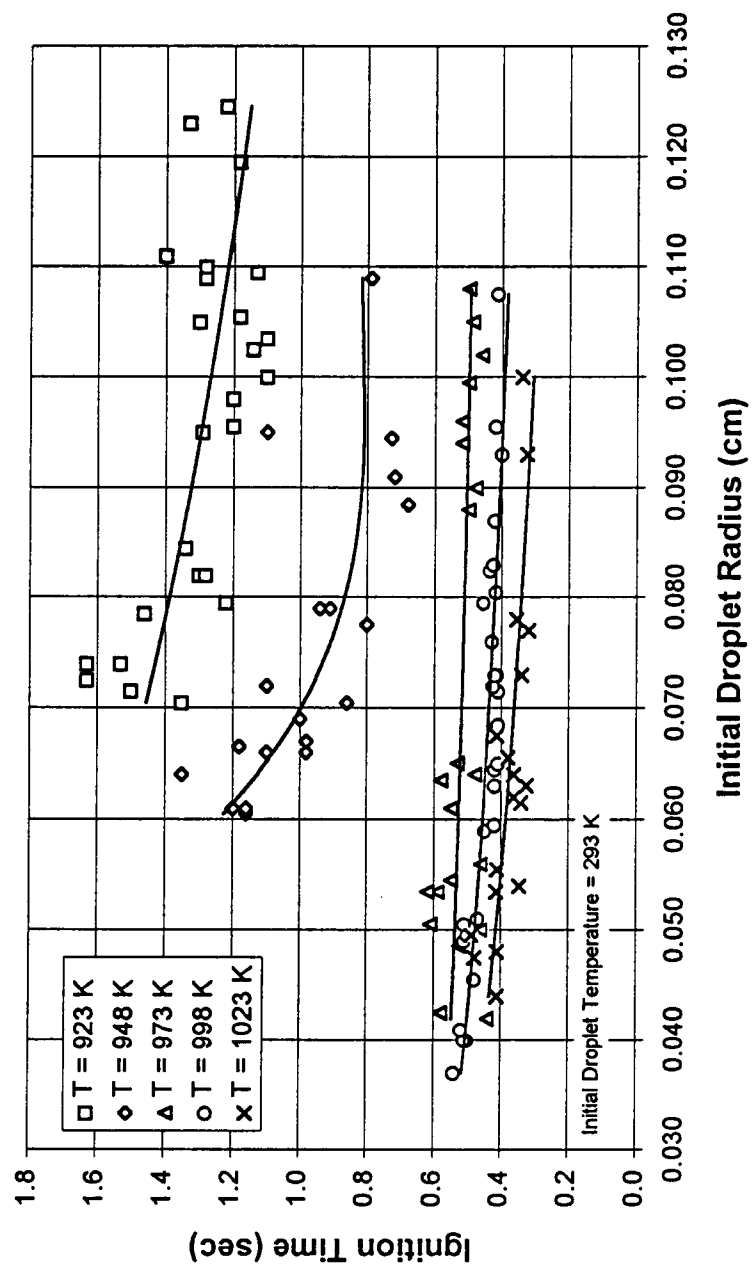


Figure 5.30. Experimental Ignition Delay for n-Heptane as a Function of Initial Droplet Radius and Initial Ambient Temperature as Measured by Saitoh.

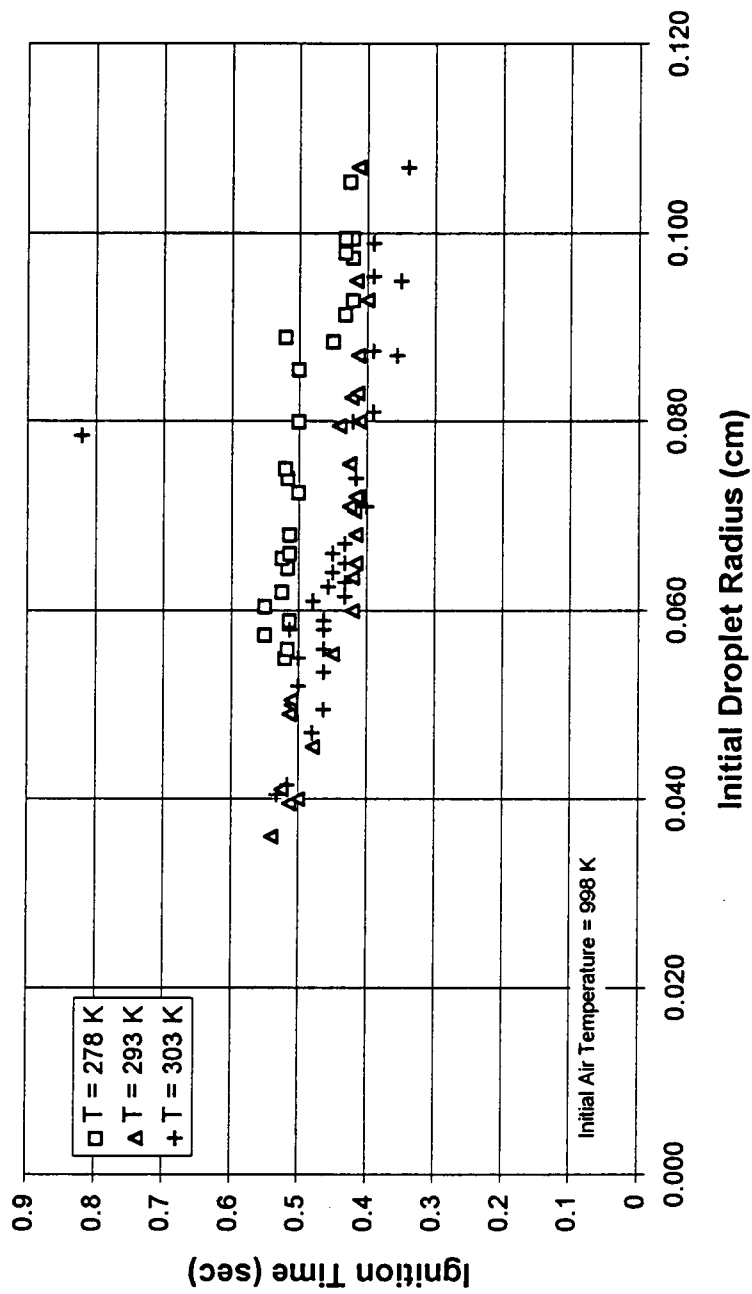


Figure 5.31. Experimental Ignition Delay for n-Heptane as a Function of Initial Droplet Temperature as Measured by Saitoh.

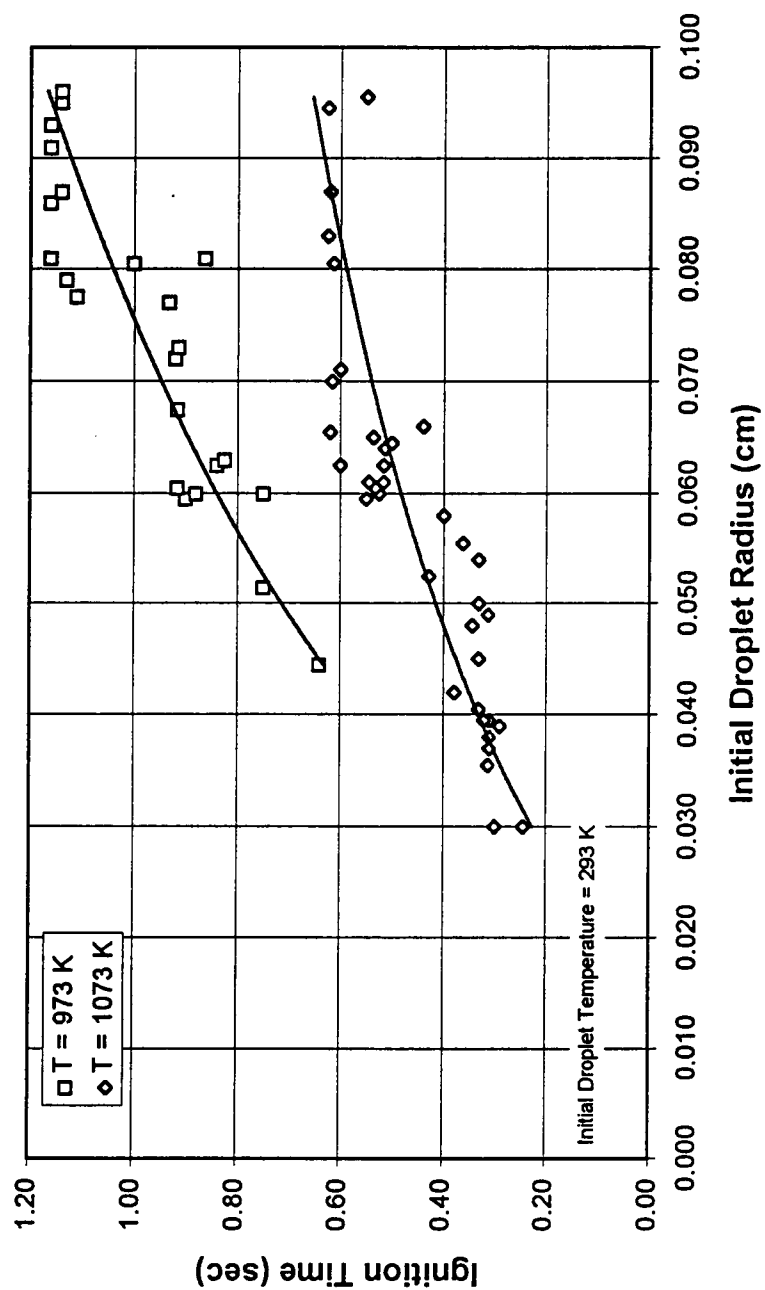


Figure 5.32. Experimental Ignition Delay for n-Hexadecane as a Function of Initial Droplet Radius and Initial Ambient Temperature As Measured by Saitoh.

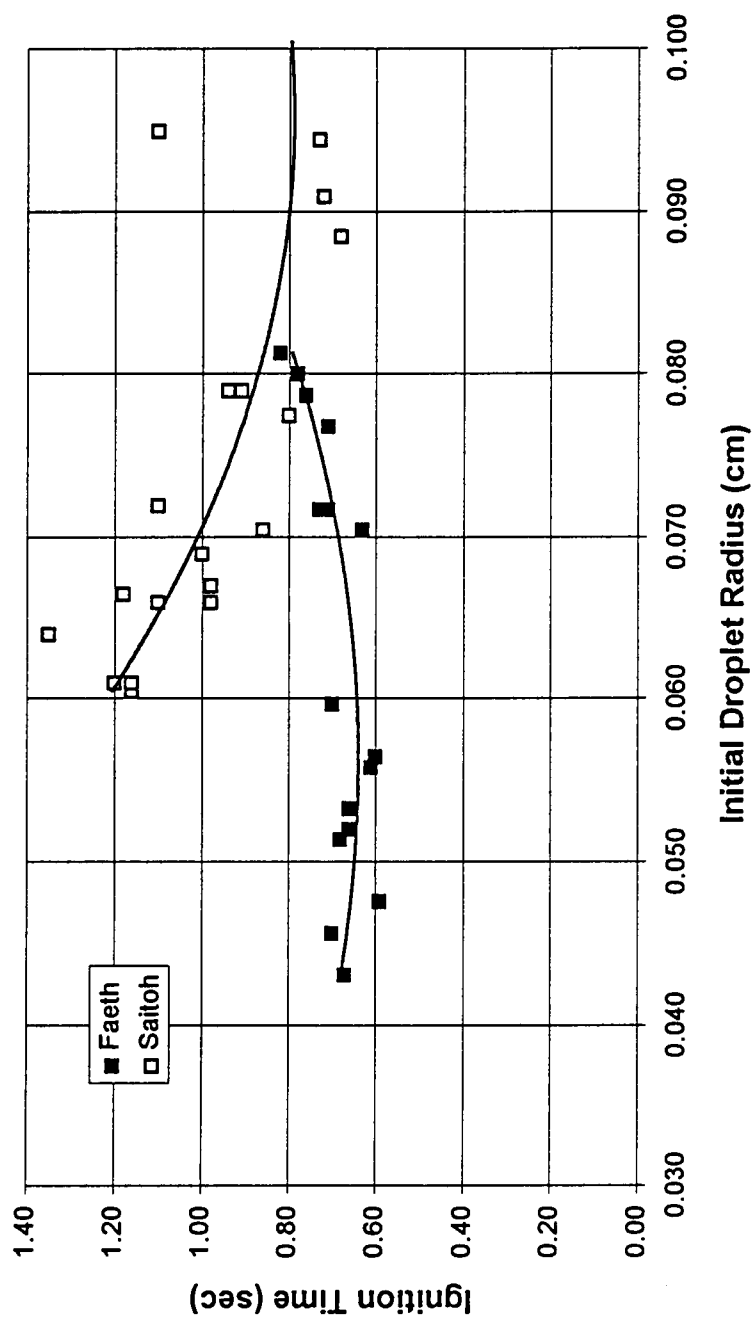


Figure 5.33. Comparison of n-Heptane Ignition Data As Measured by Faeth and Saitoh.

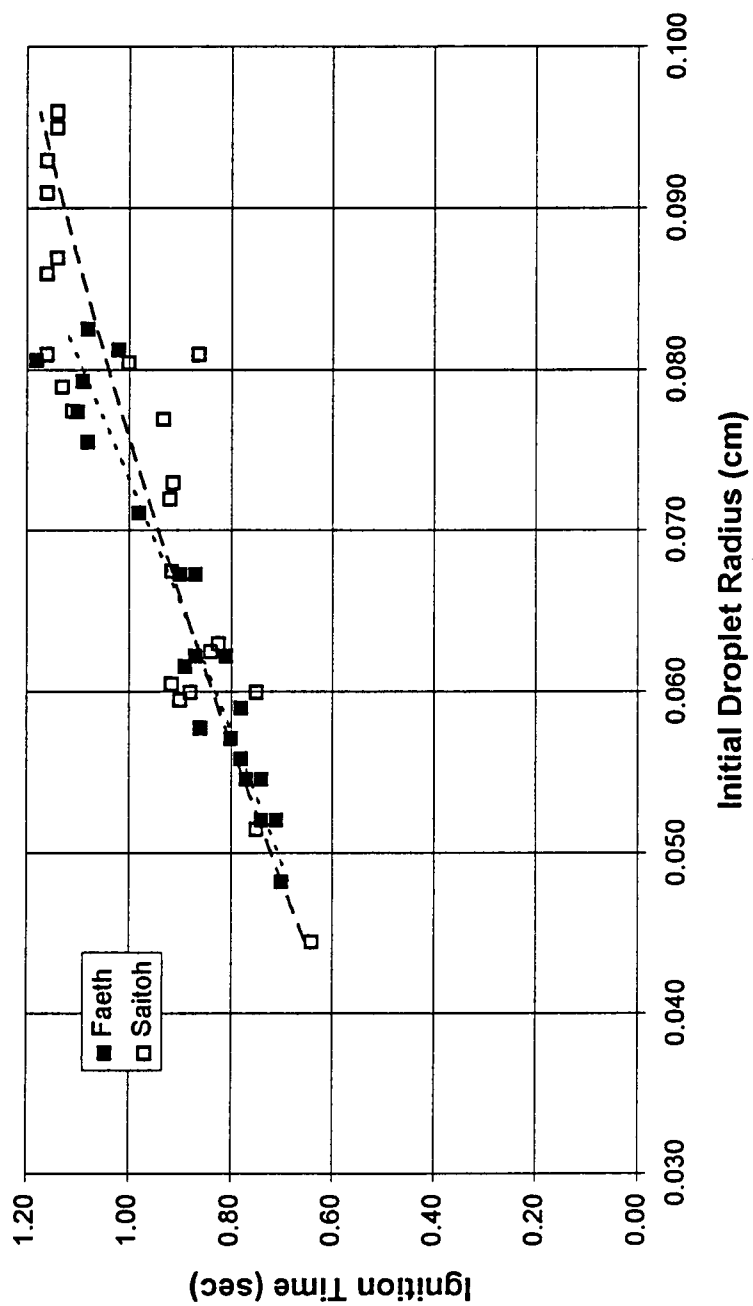


Figure 5.34. Comparison of n-Hexadecane Ignition Data As Measured by Faeth and Saitoh.

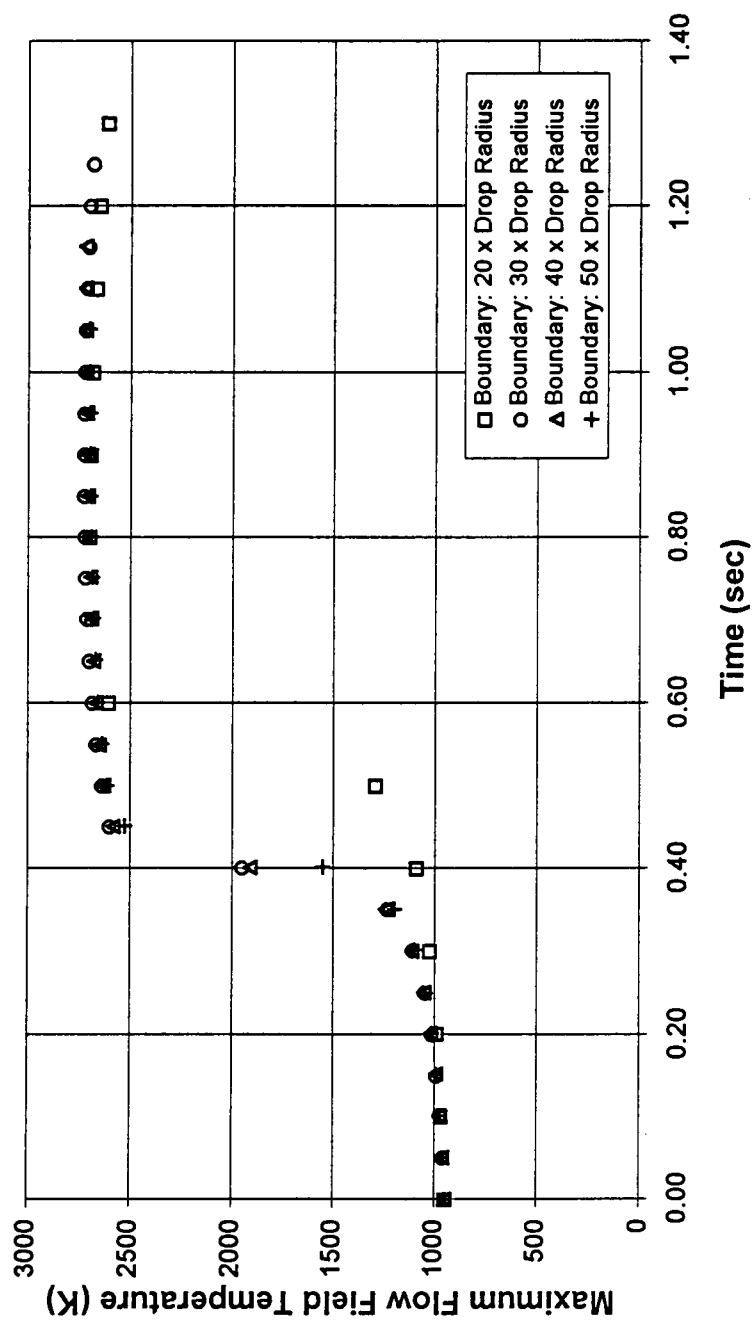


Figure 5.35. Effects of the Numerical Boundary Location on n-Heptane Ignition Delay Assuming a 20-noded Grid.

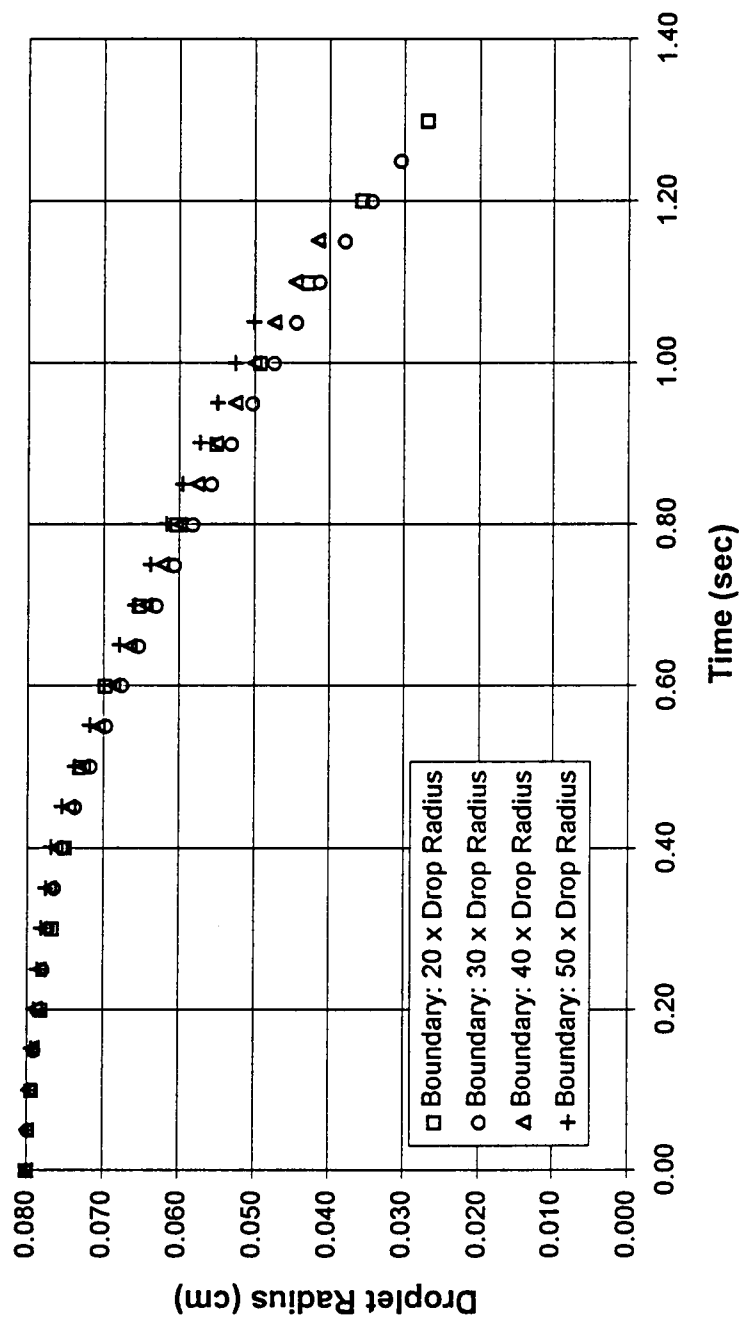


Figure 5.36. Effects of the Numerical Boundary Location on n-Heptane Droplet Surface Regression Assuming a 20-noded Grid.

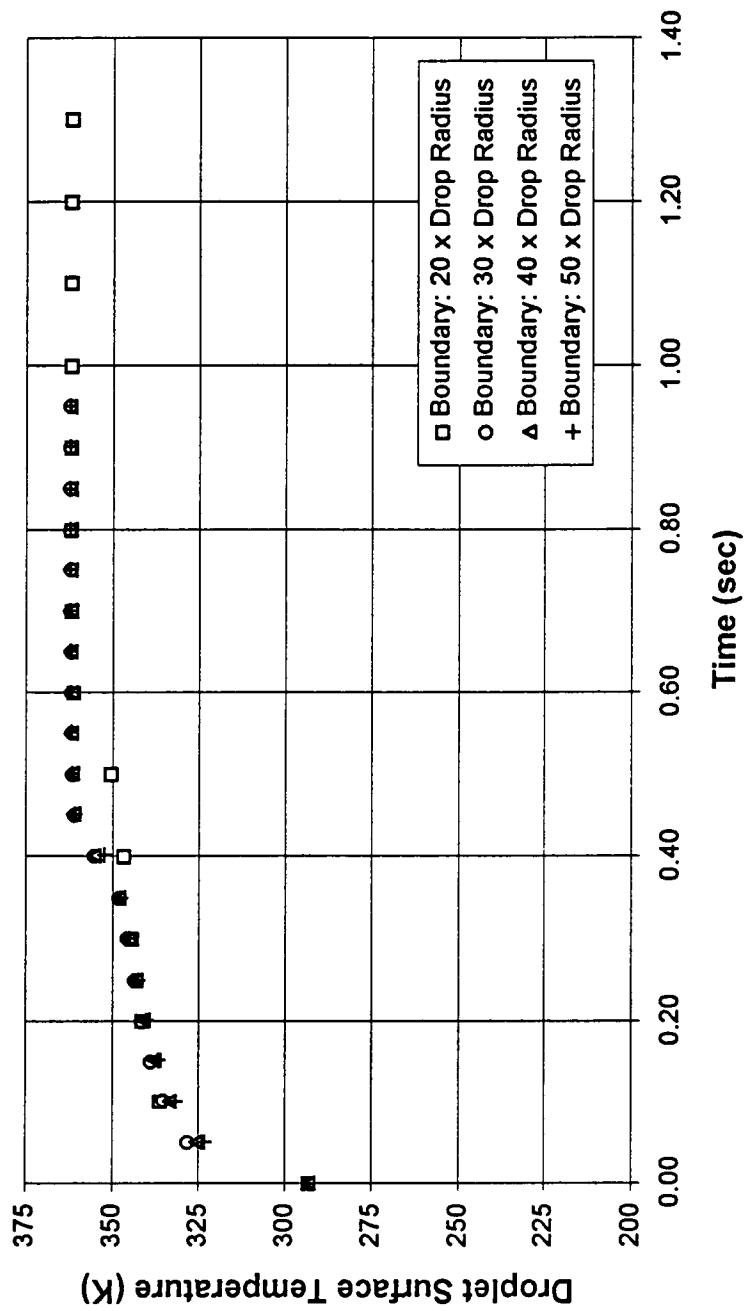


Figure 5.37. Effects of the Numerical Boundary Location on n-Heptane Droplet Surface Temperature Assuming a 20-noded Grid.

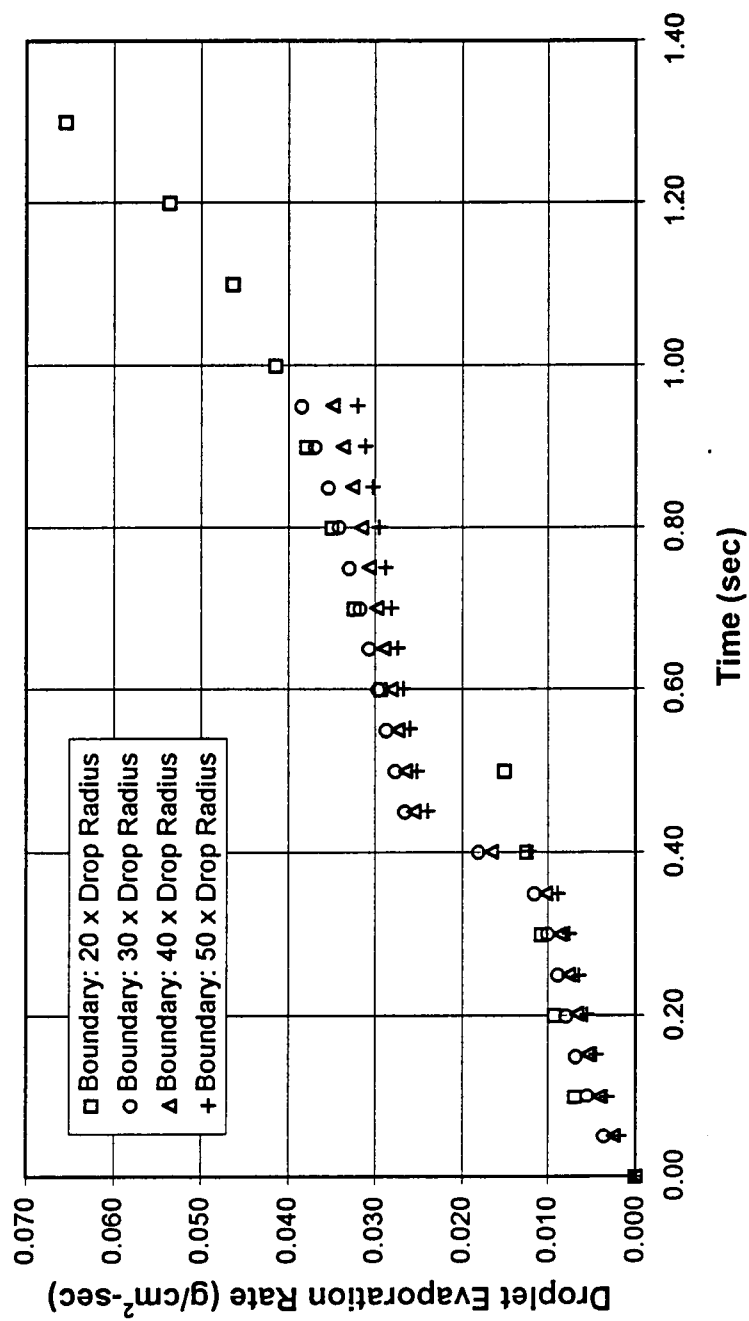


Figure 5.38. Effects of the Numerical Boundary Location on n-Heptane Droplet Evaporation Rate Assuming a 20-noded Grid.

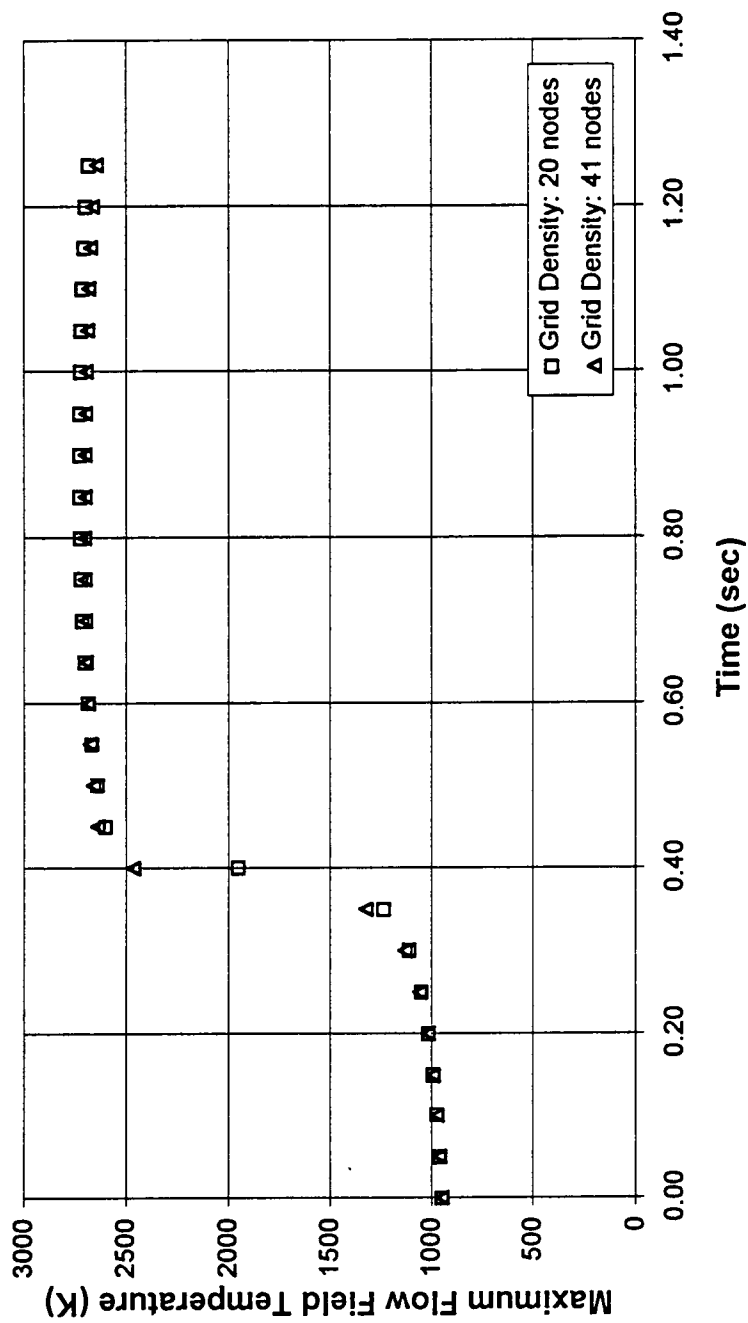


Figure 5.39. Effects of Numerical Grid Density on n-Heptane Ignition Delay Assuming a Numerical Boundary Located at Thirty Times the Initial Droplet Radius.

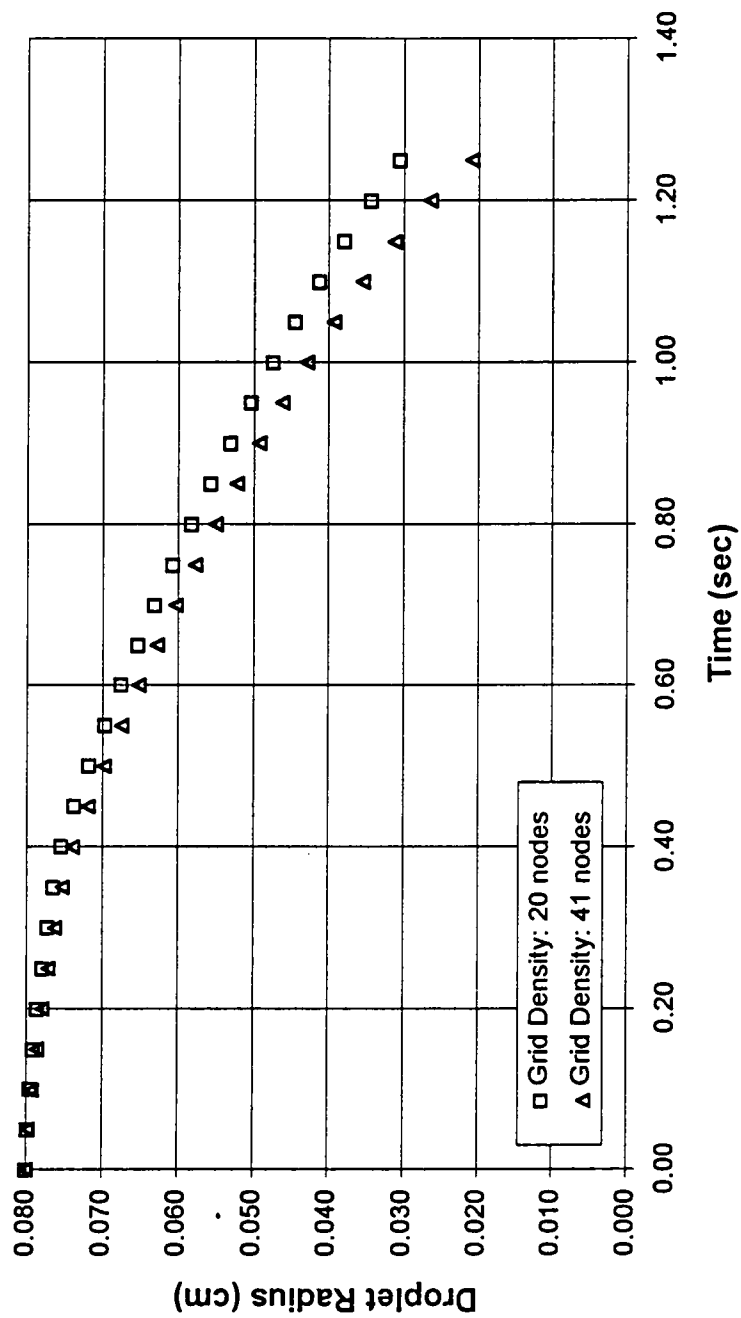


Figure 5.40. Effects of Numerical Grid Density on n-Heptane Droplet Surface Regression Assuming a Numerical Boundary Located at Thirty Times the Initial Droplet Radius.

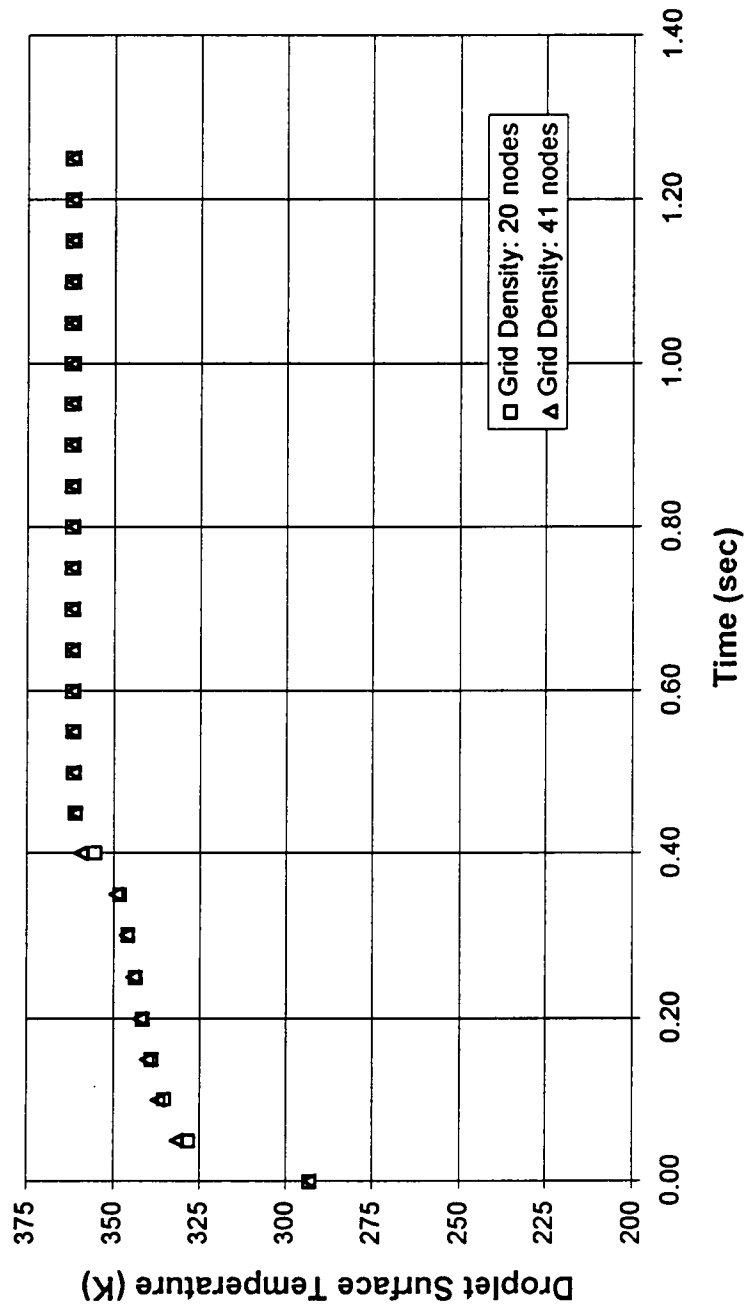


Figure 5.41. Effects of Numerical Grid Density on n-Heptane Droplet Surface Temperature Assuming a Numerical Boundary Located at Thirty Times the Initial Droplet Radius.

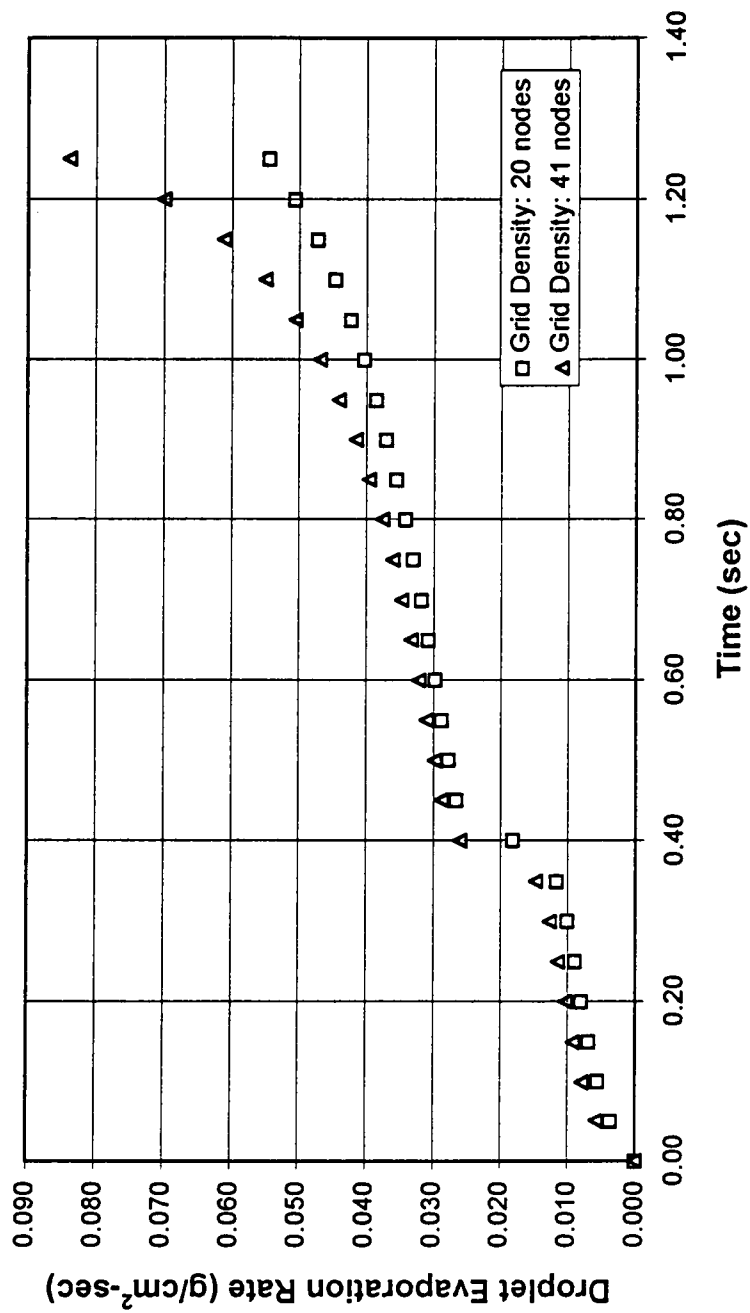


Figure 5.42. Effects of Numerical Grid Density on n-Heptane Droplet Evaporation Rate Assuming a Numerical Boundary Located at Thirty Times the Initial Droplet Radius.

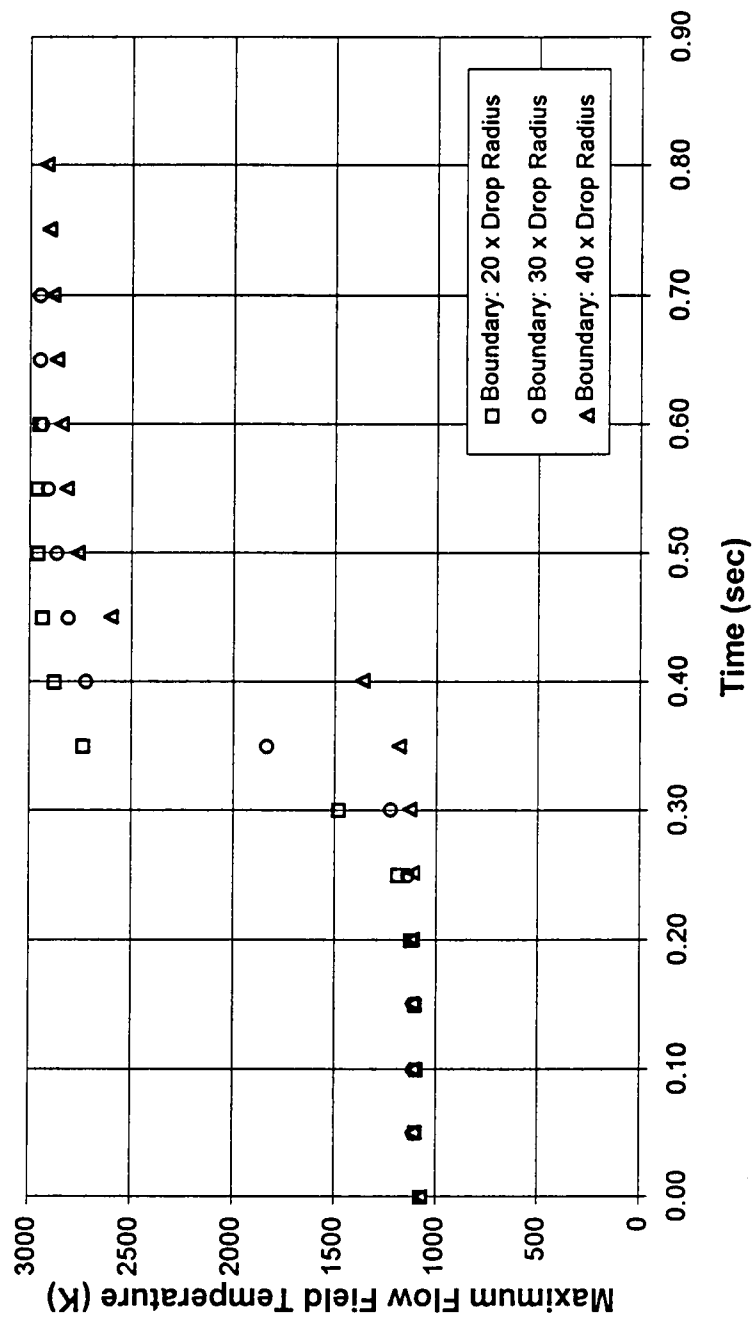


Figure 5.43. Effects of the Numerical Boundary Location on n-Hexadecane Ignition Delay Assuming a 20-noded Grid.

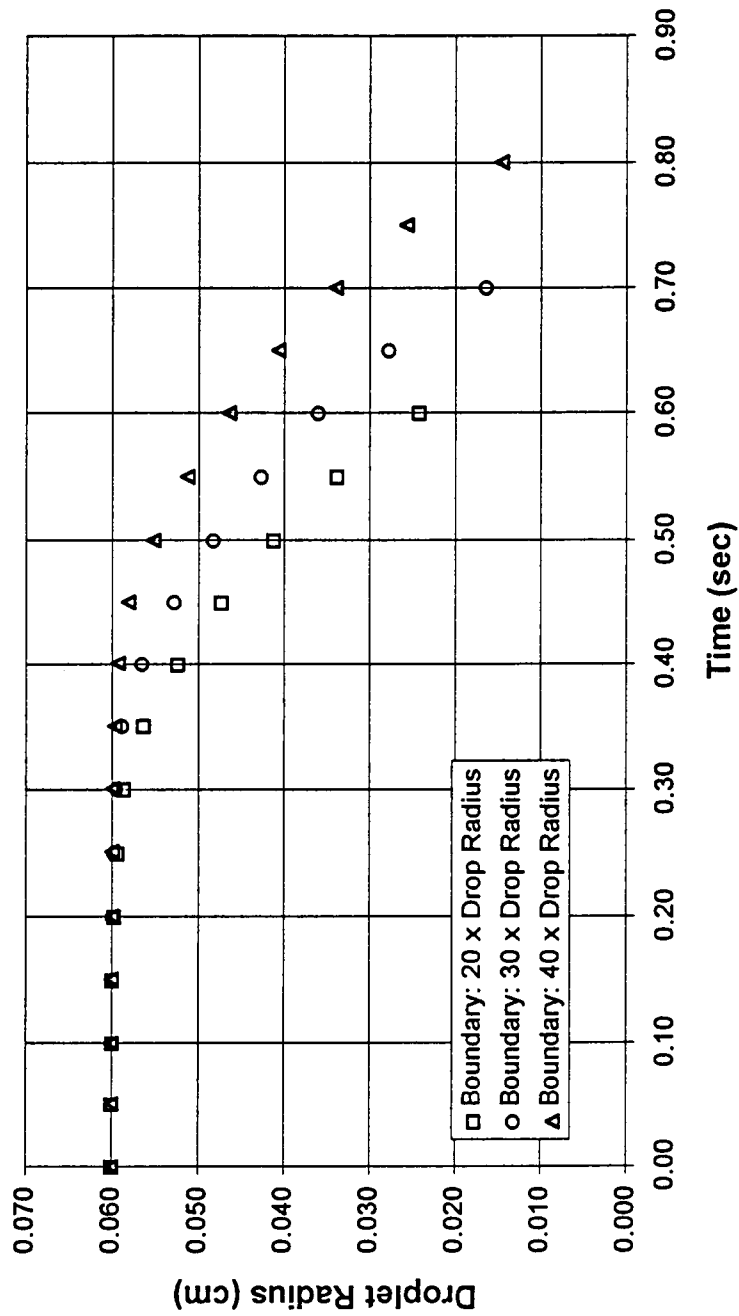


Figure 5.44. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Surface Regression Assuming a 20-noded Grid.

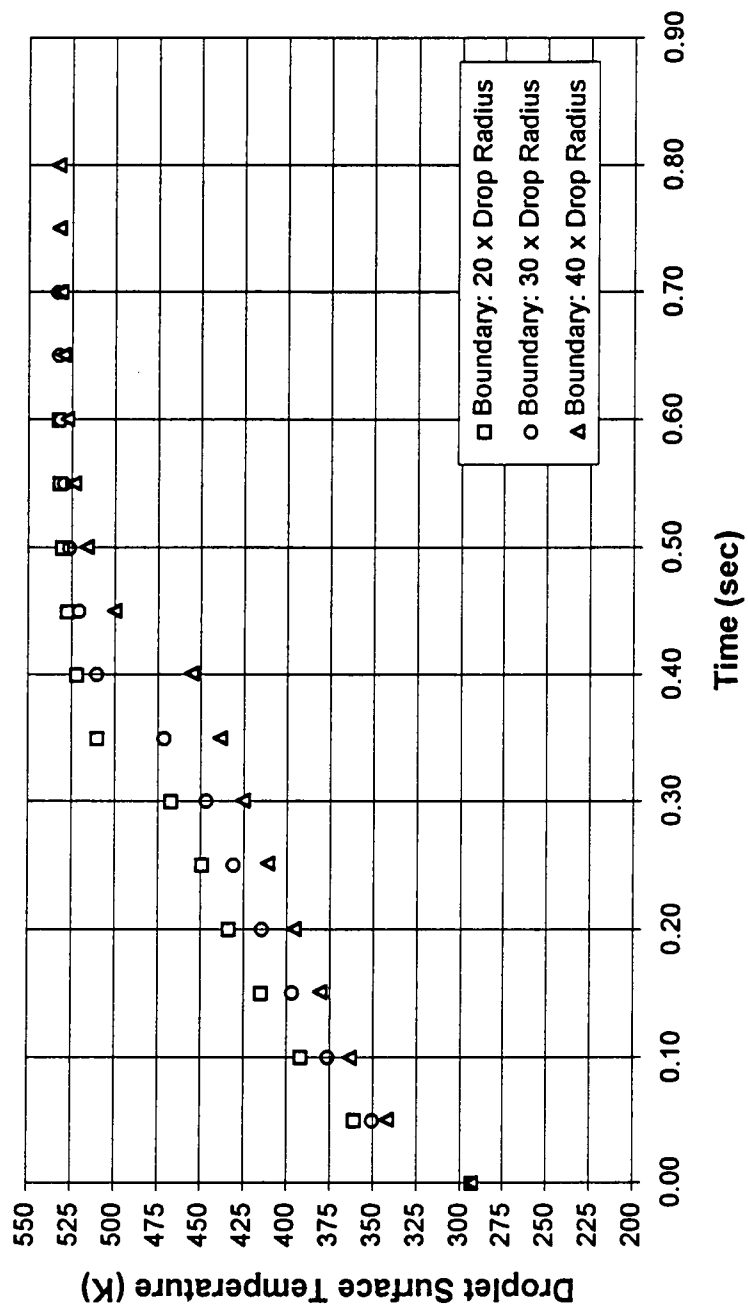


Figure 5.45. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Surface Temperature Assuming a 20-noded Grid.

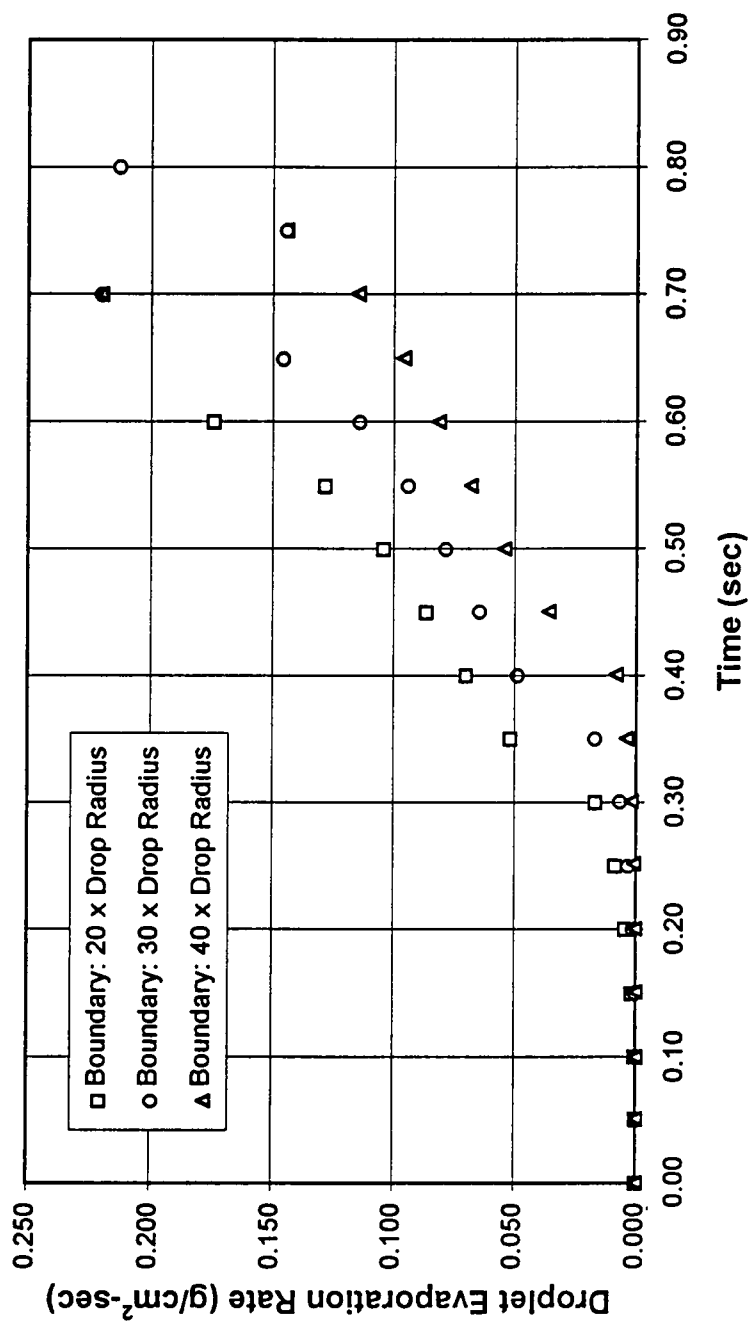


Figure 5.46. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Evaporation Rate Assuming a 20-noded Grid.

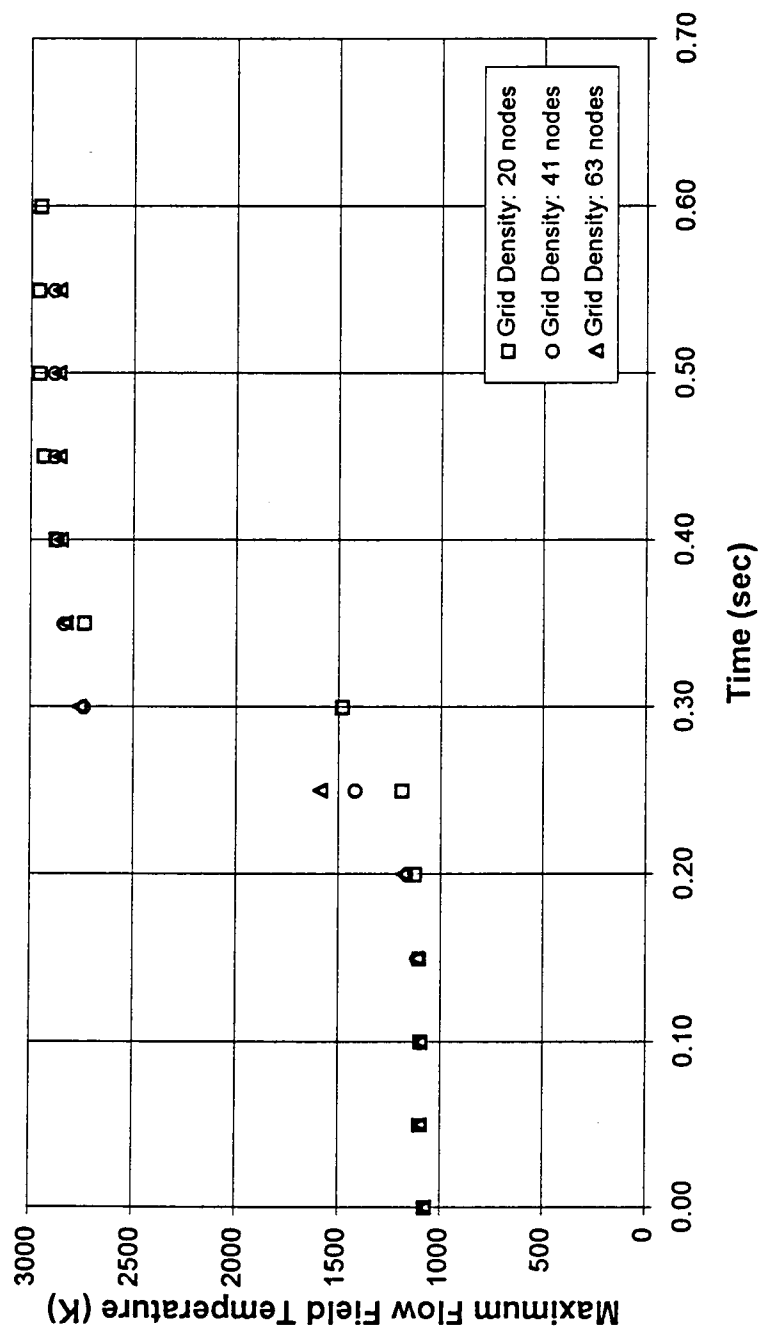


Figure 5.47. Effects of Numerical Grid Density on n-Hexadecane Ignition Delay Assuming a Numerical Boundary Located at Twenty Times the Initial Droplet Radius.

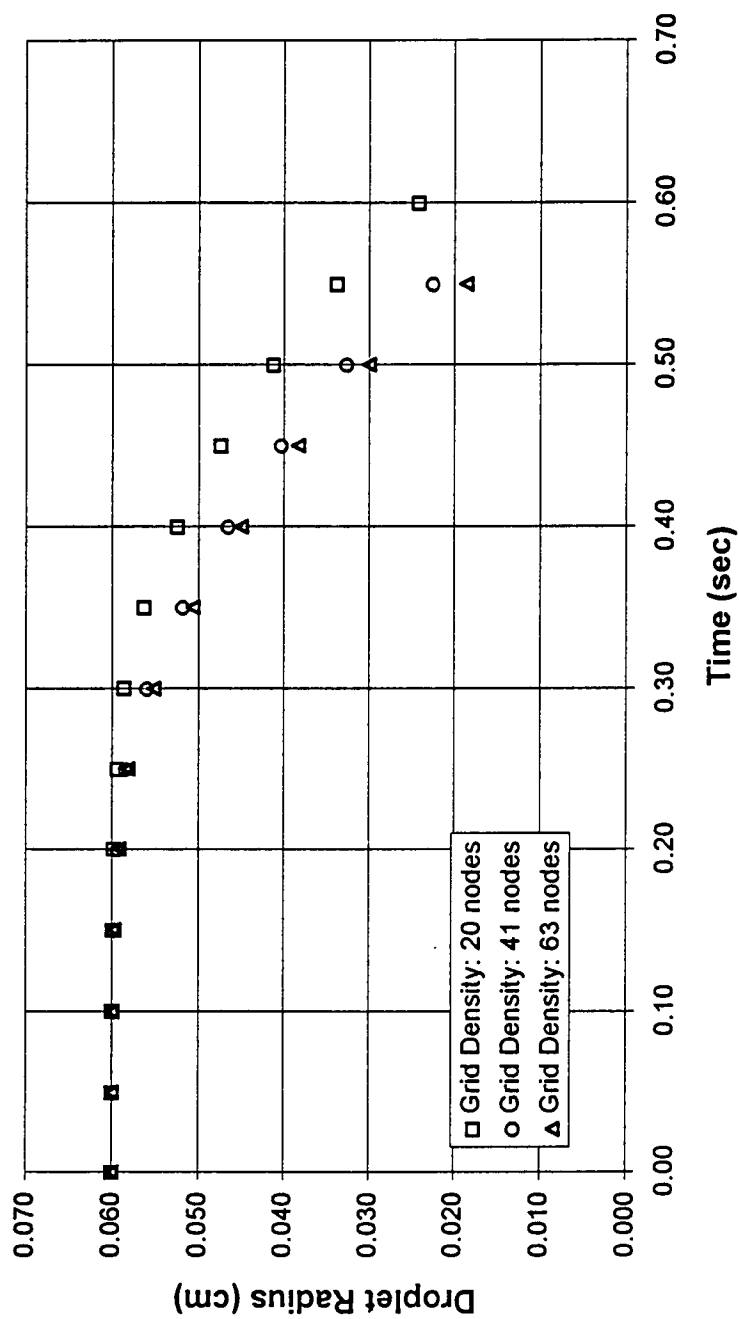


Figure 5.48. Effects of Numerical Grid Density on n-Hexadecane Droplet Surface Regression Assuming a Numerical Boundary Located at Twenty Times the Initial Droplet Radius.

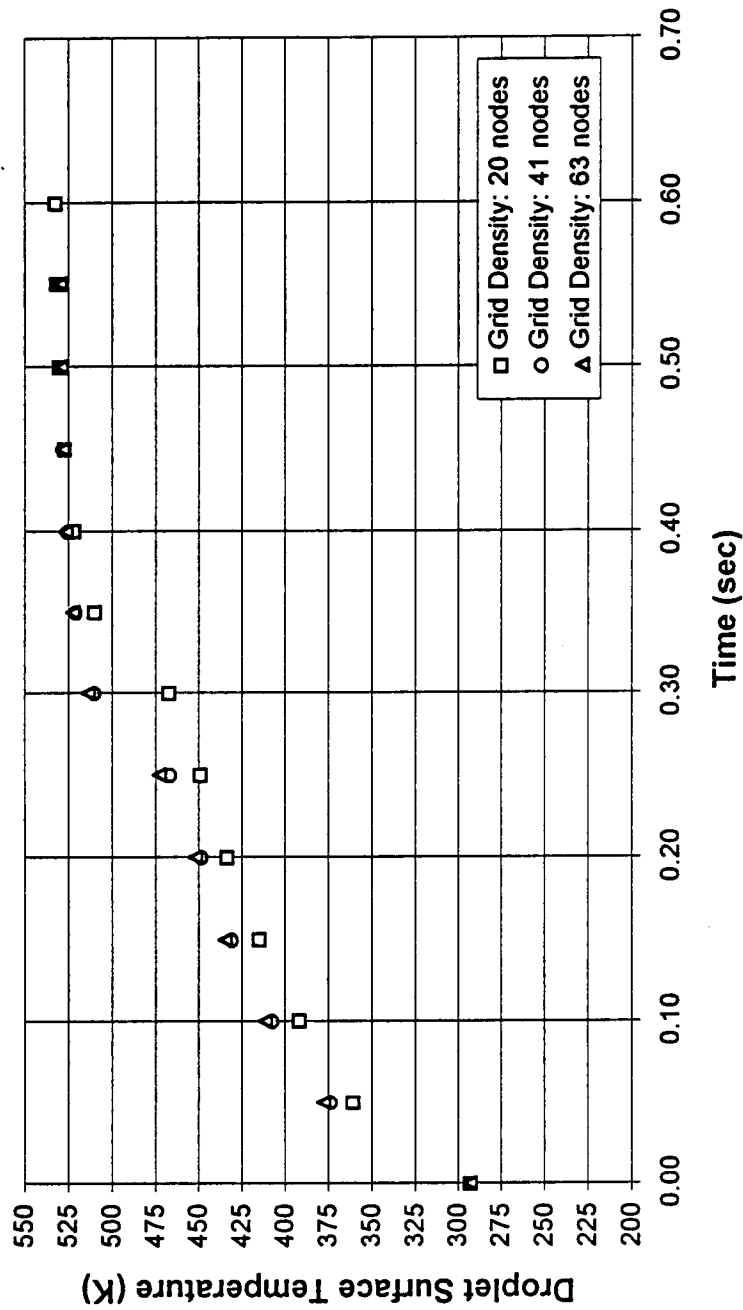


Figure 5.49. Effects of Numerical Grid Density on n-Hexadecane Droplet Surface Temperature Assuming a Numerical Boundary Located at Twenty Times the Initial Droplet Radius.

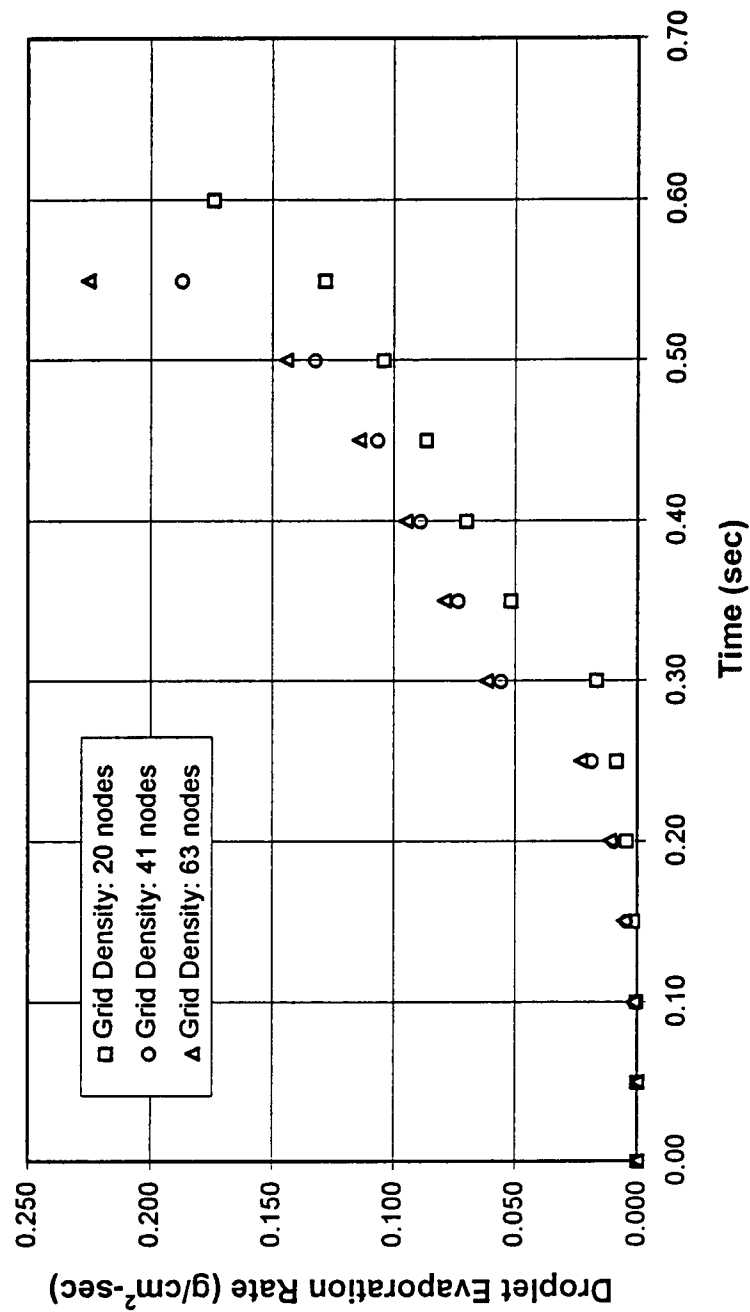


Figure 5.50. Effects of Numerical Grid Density on n-Hexadecane Droplet Evaporation Rate Assuming a Numerical Boundary Located at Twenty Times the Initial Droplet Radius.

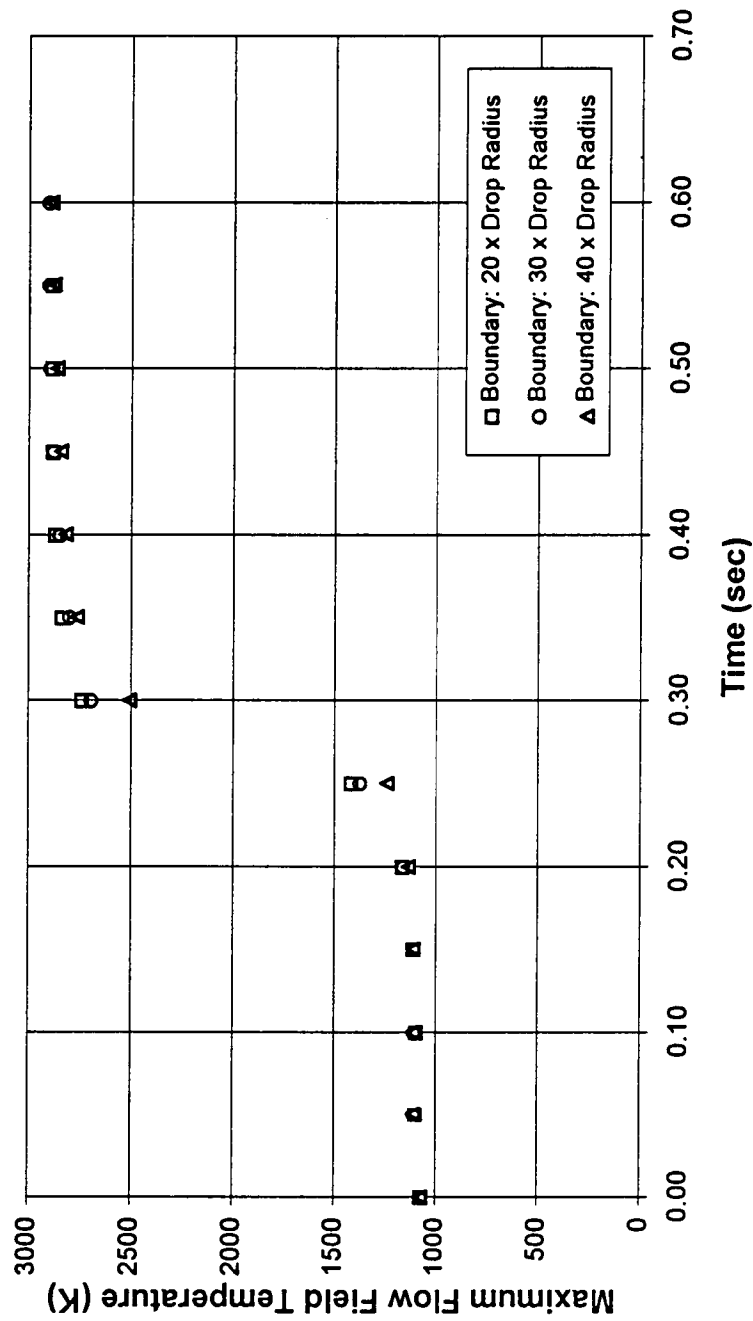


Figure 5.51. Effects of the Numerical Boundary Location on n-Hexadecane Ignition Delay Assuming a 41-noded Grid.

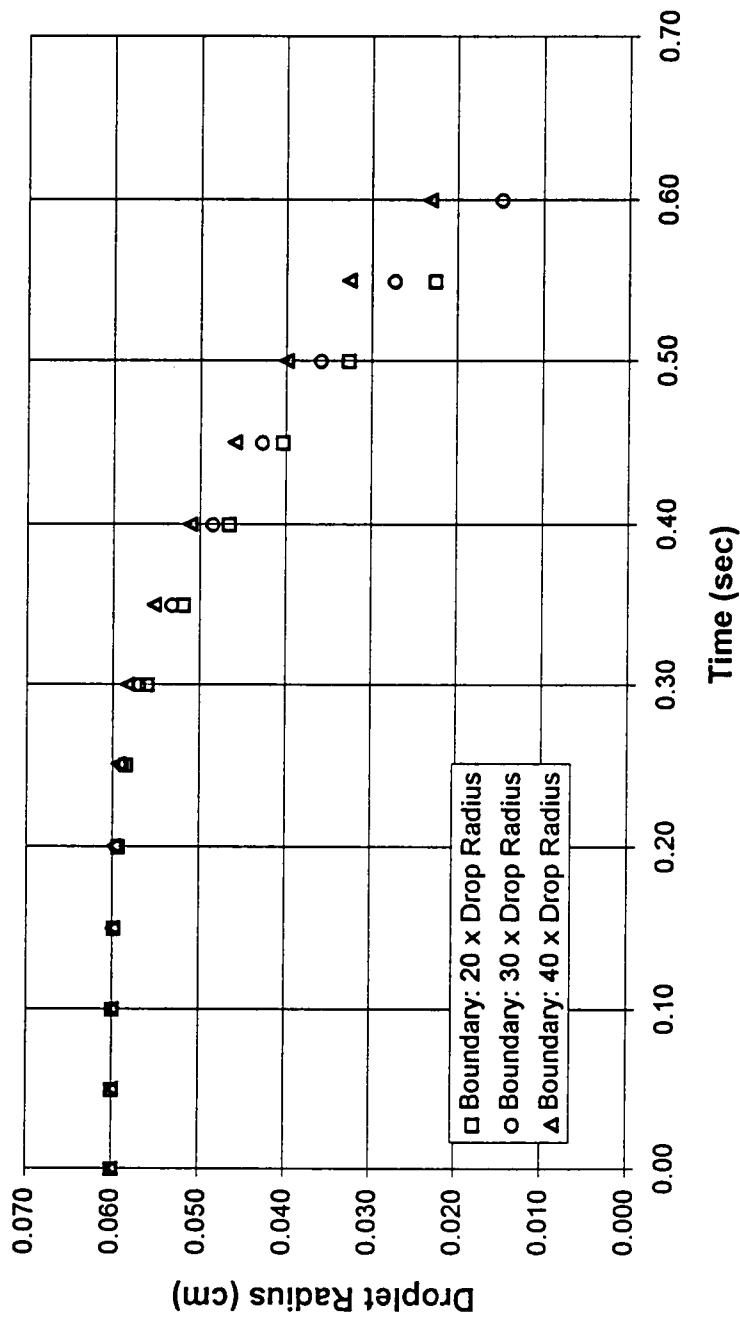


Figure 5.52. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Surface Regression Assuming a 41-noded Grid.

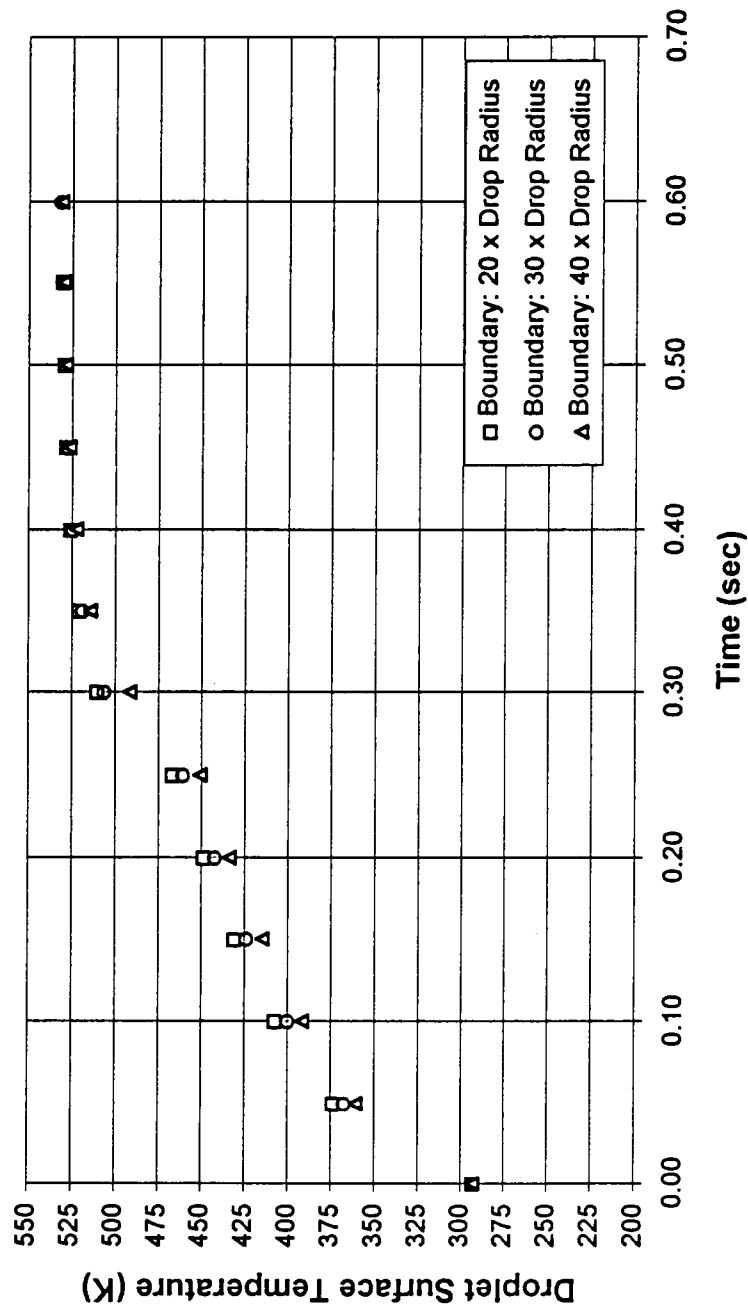


Figure 5.53. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Surface Temperature Assuming a 41-noded Grid.

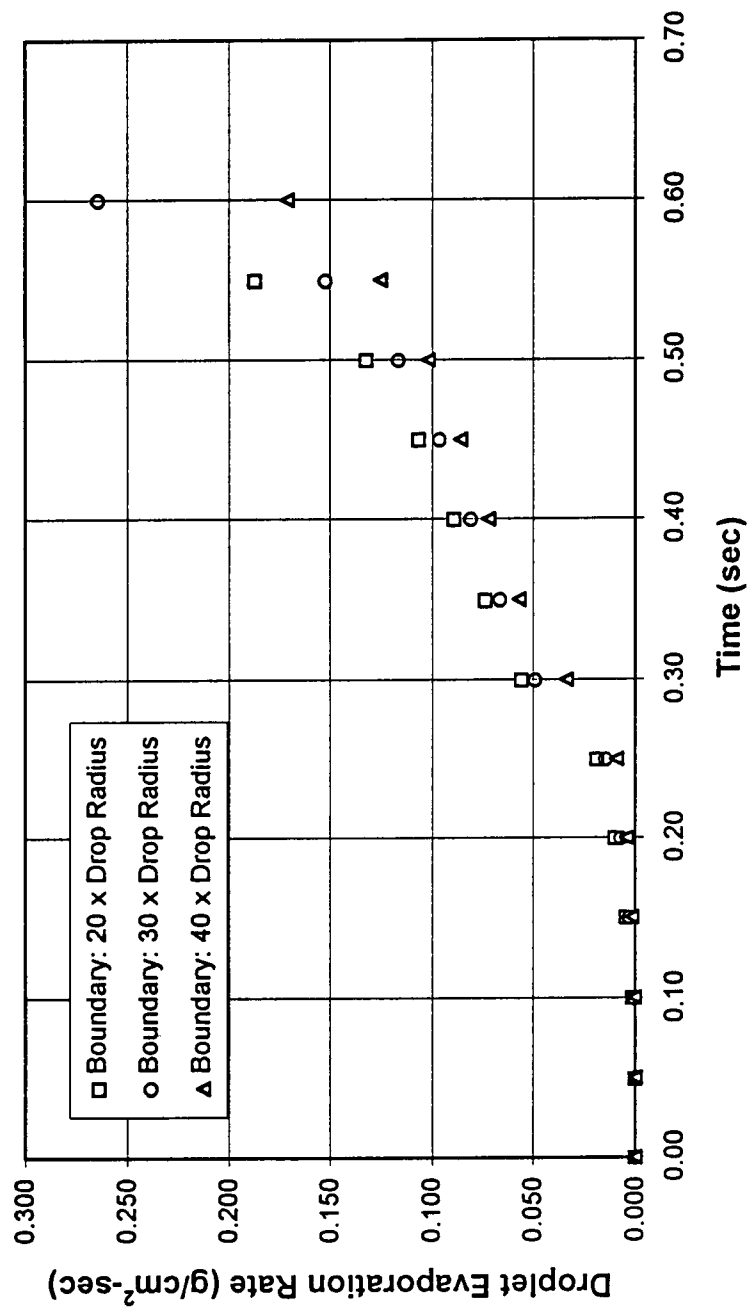


Figure 5.54. Effects of the Numerical Boundary Location on n-Hexadecane Droplet Evaporation Rate Assuming a 41-noded Grid.

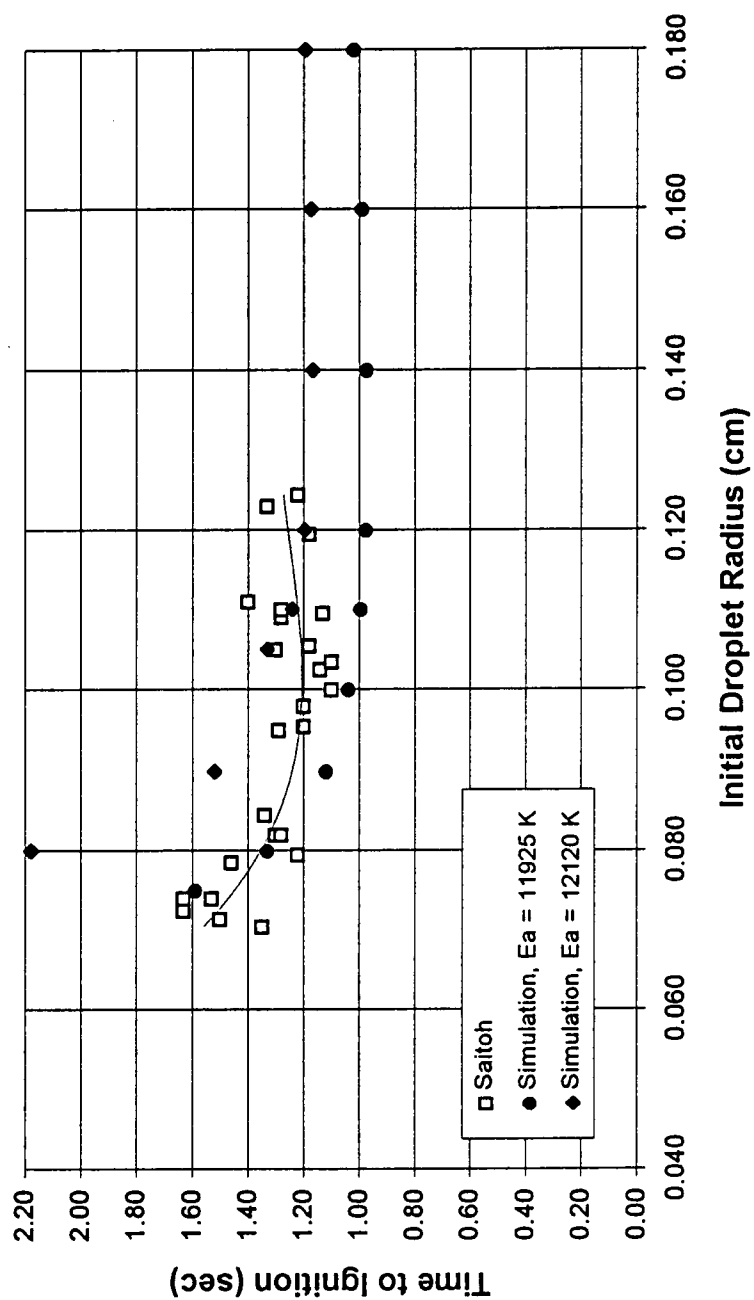


Figure 5.55. Comparison of Computed and Measured Ignition Delay as a Function of Initial Droplet Radius for n-Heptane in Air at 923 K.

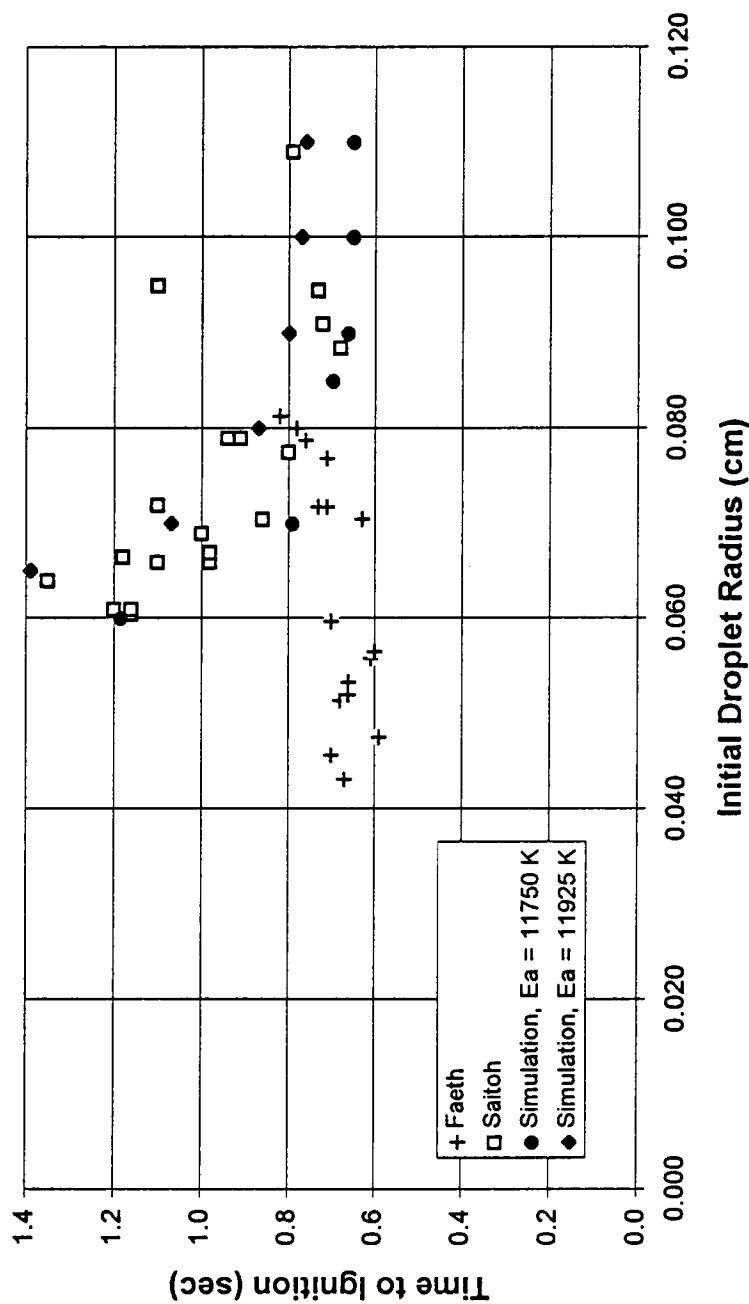


Figure 5.56. Comparison of Computed and Measured Ignition Delay as a Function of Initial Droplet Radius for n-Heptane in Air at 948 K.

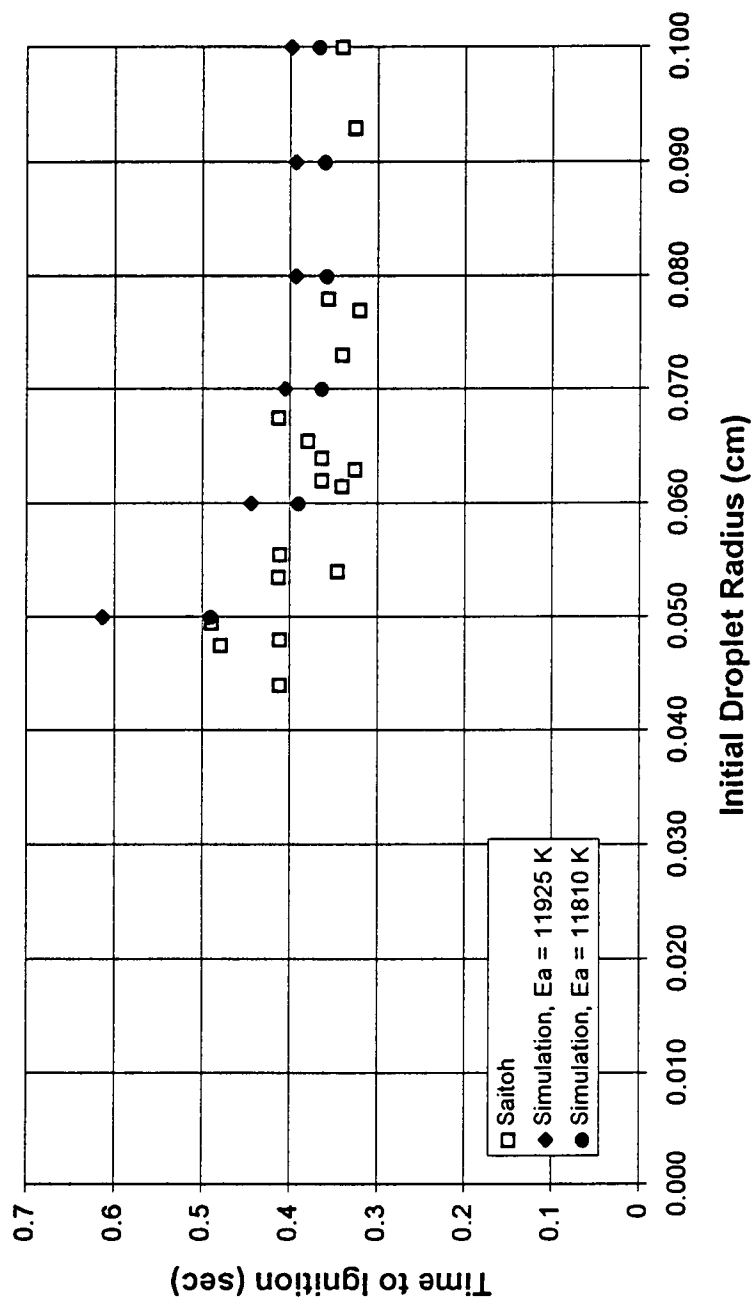


Figure 5.57. Comparison of Computed and Measured Ignition Delay as a Function of Initial Droplet Radius for n-Heptane in Air at 1023 K.

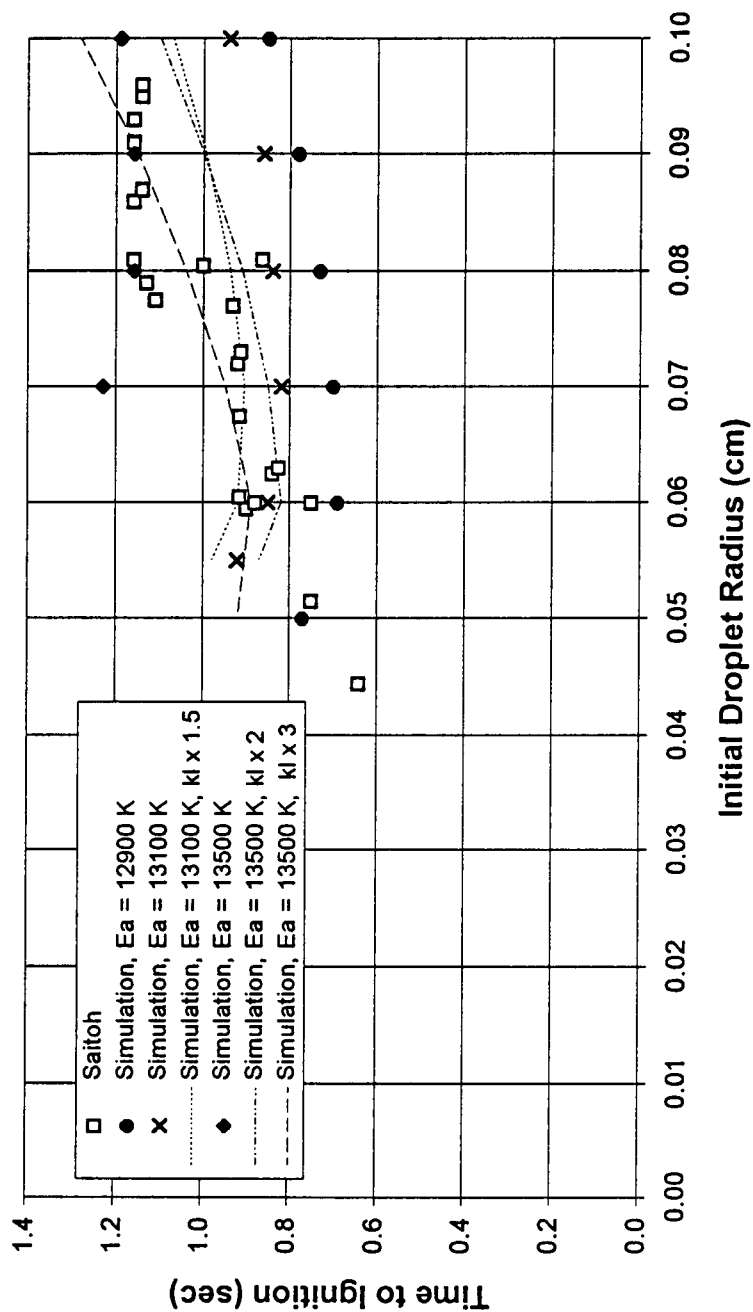


Figure 5.58. Comparison of Computed and Measured Ignition Delay as a Function of Initial Droplet Radius for n-Hexadecane in Air at 973 K.

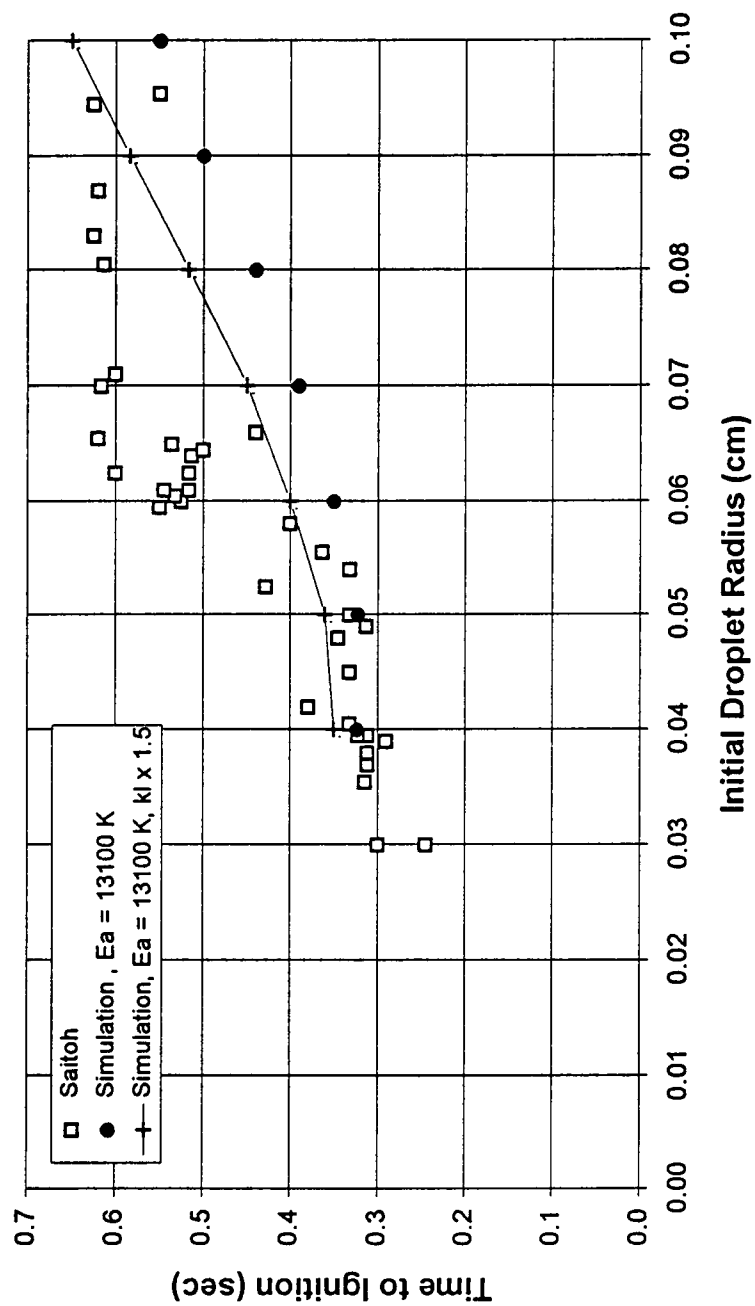


Figure 5.59. Comparison of Computed and Measured Ignition Delay as a Function of Initial Droplet Radius for n-Hexadecane in Air at 1073 K.

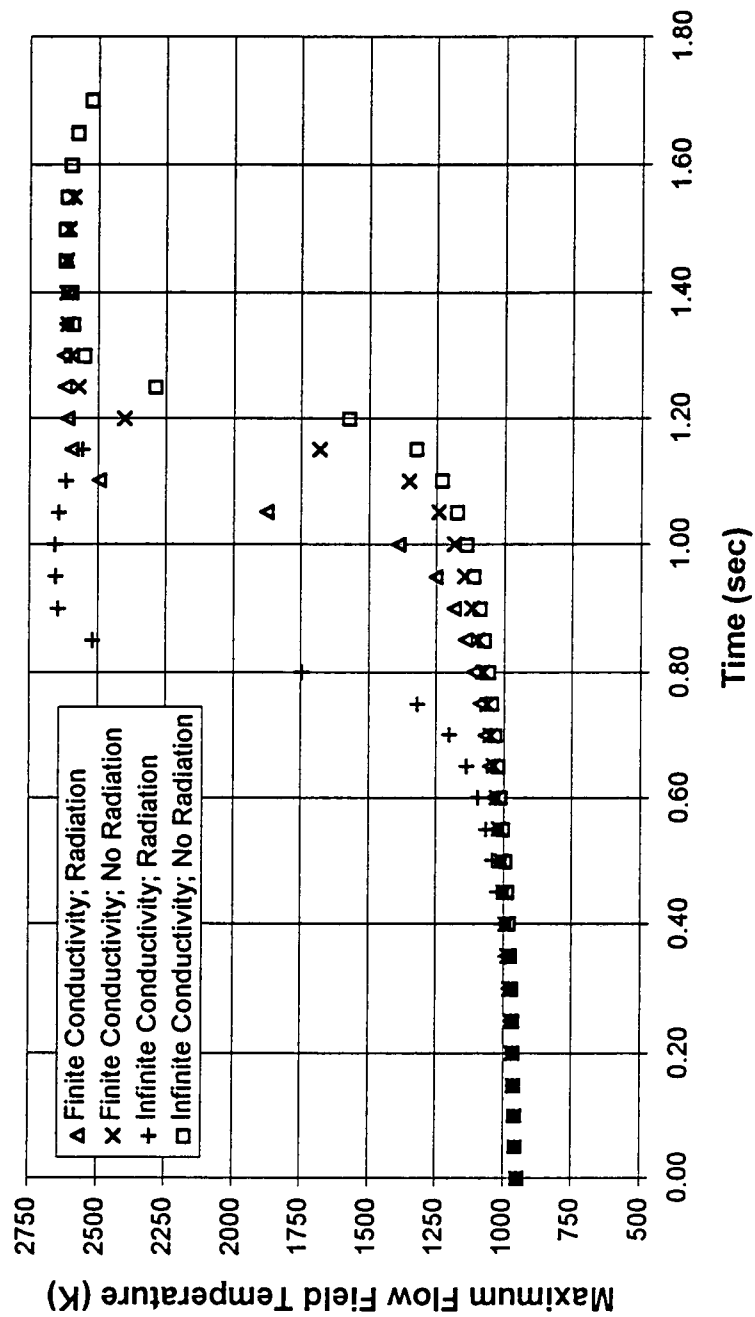


Figure 5.60. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

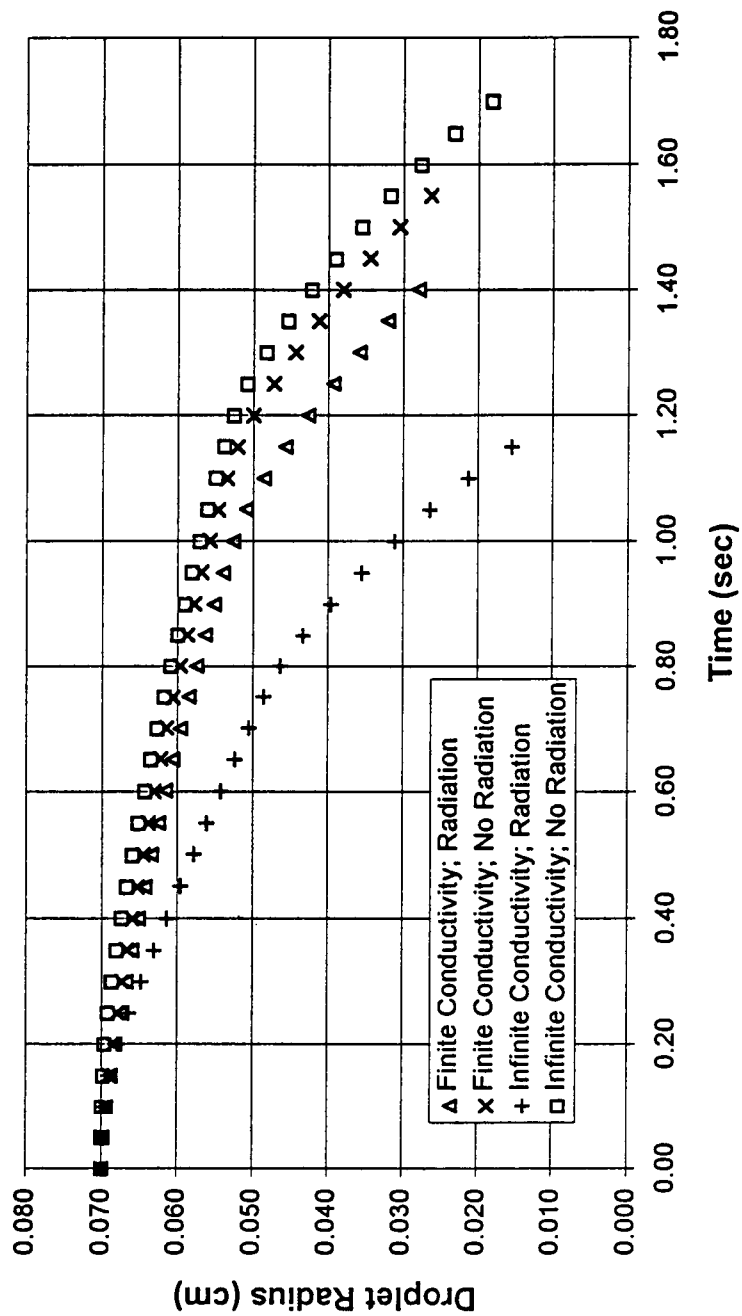


Figure 5.61. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

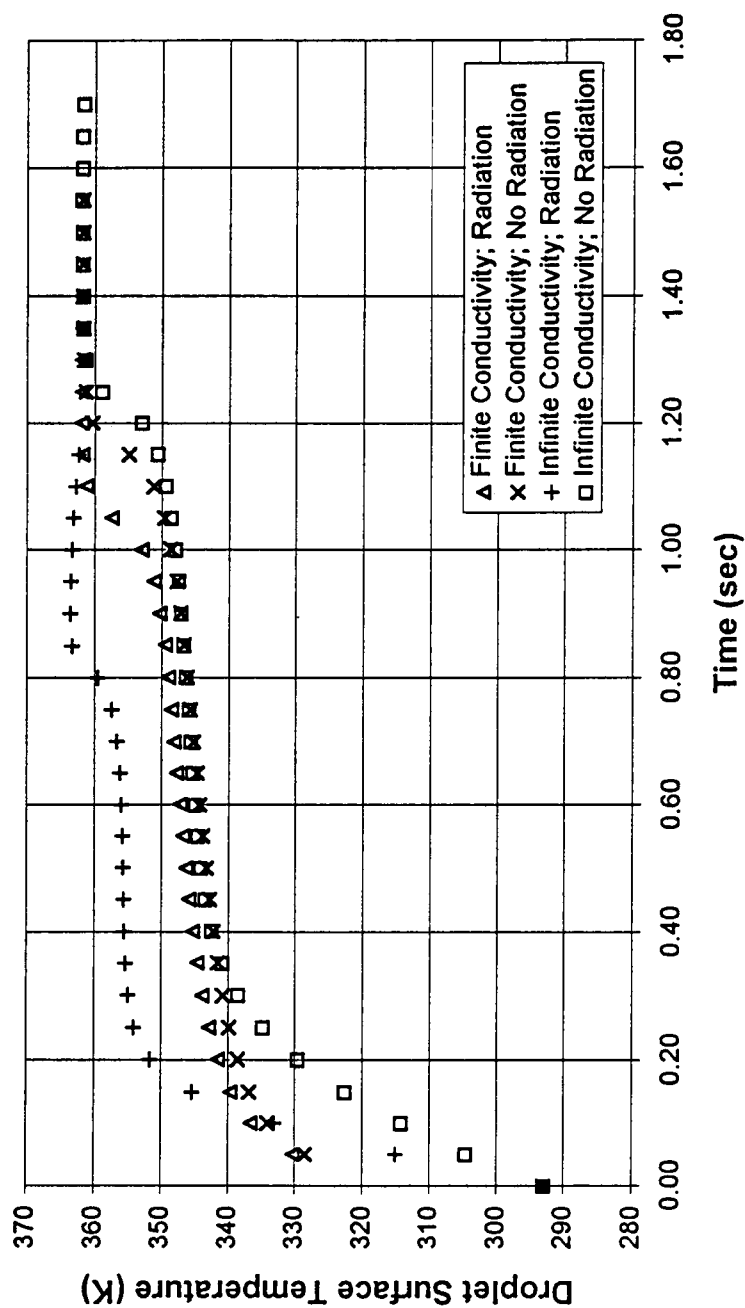


Figure 5.62. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

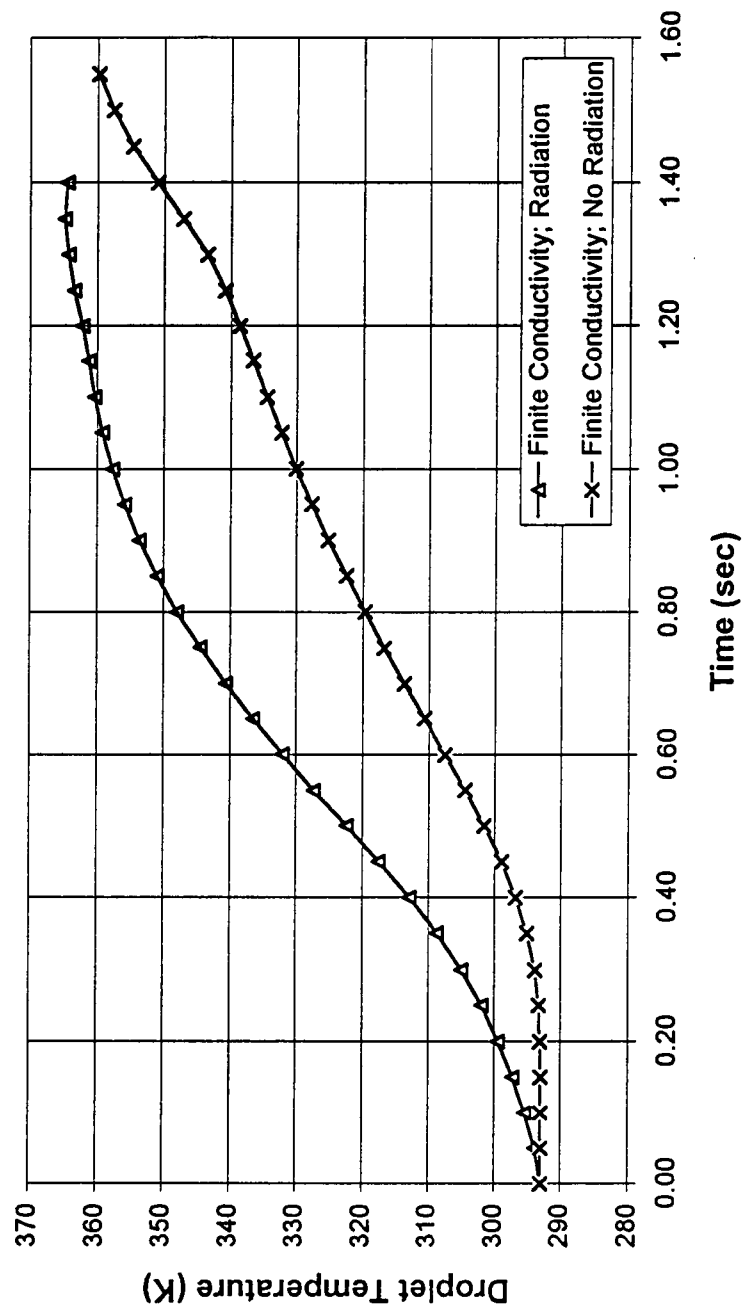


Figure 5.63. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

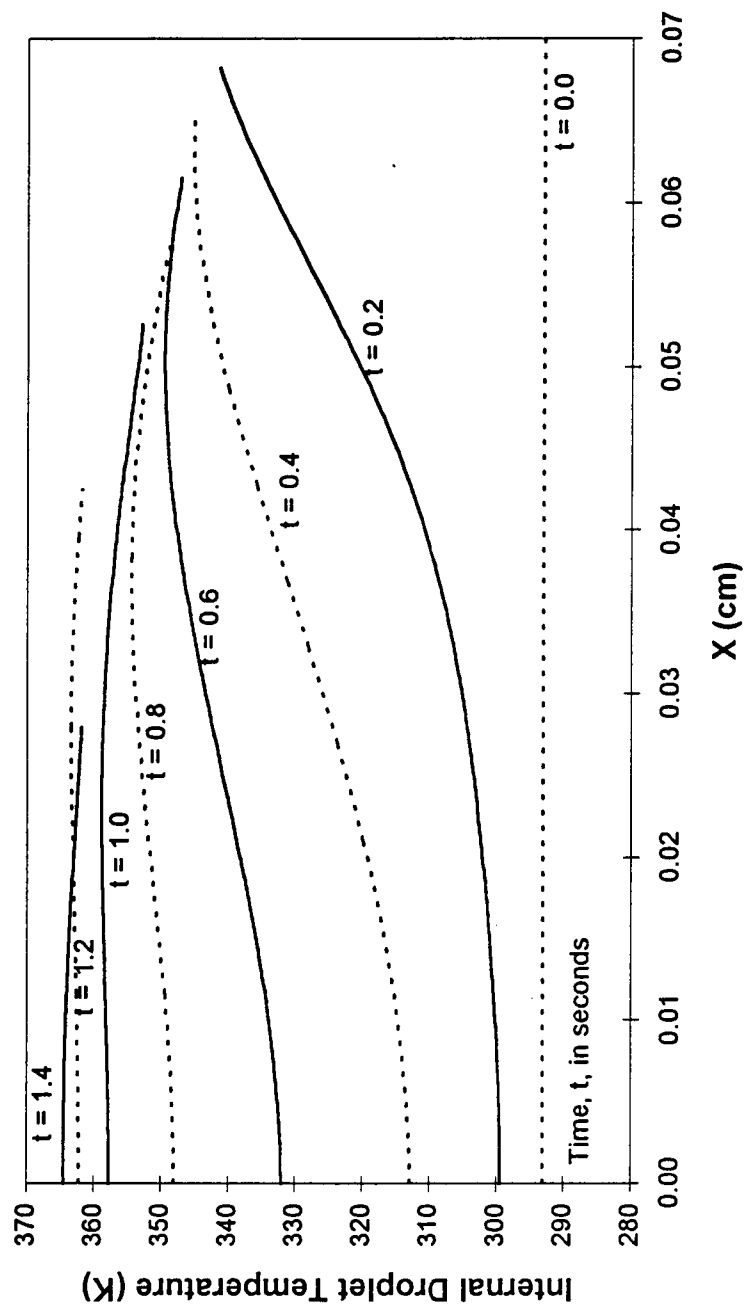


Figure 5.64. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K with Incident Radiation.

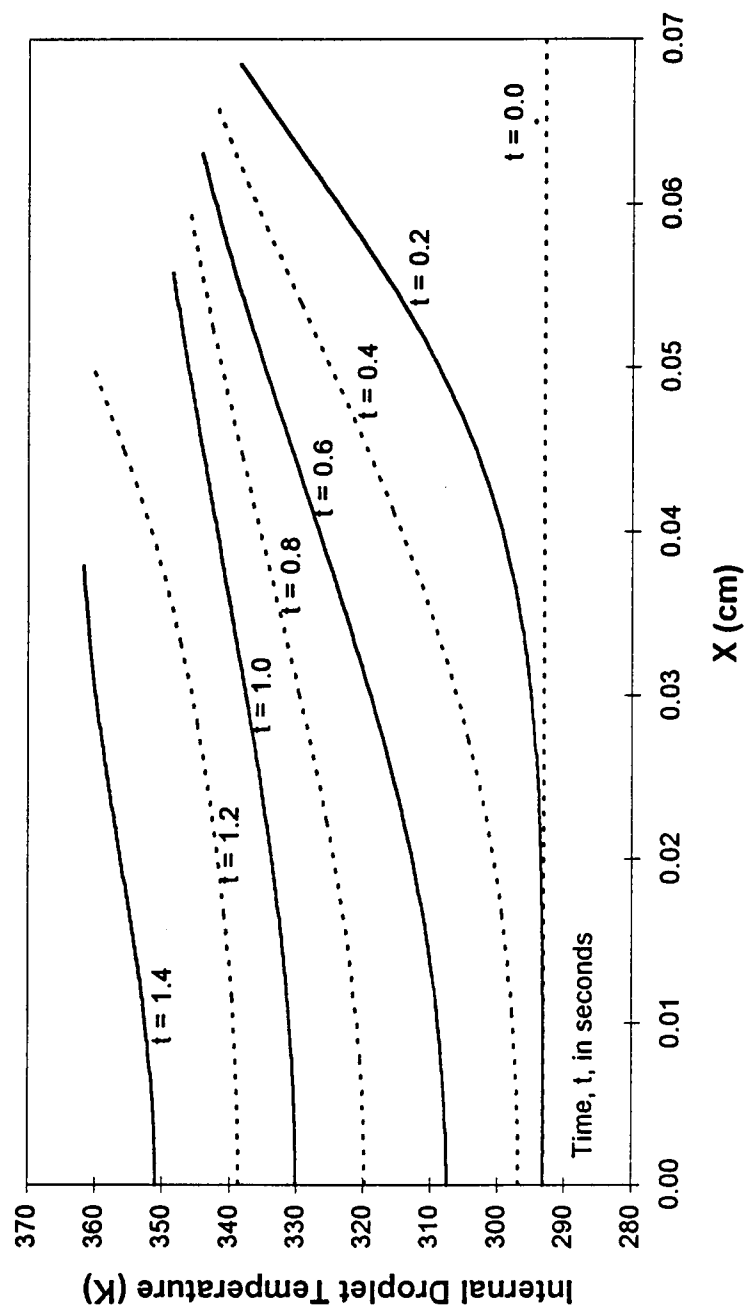


Figure 5.65. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K without Incident Radiation.

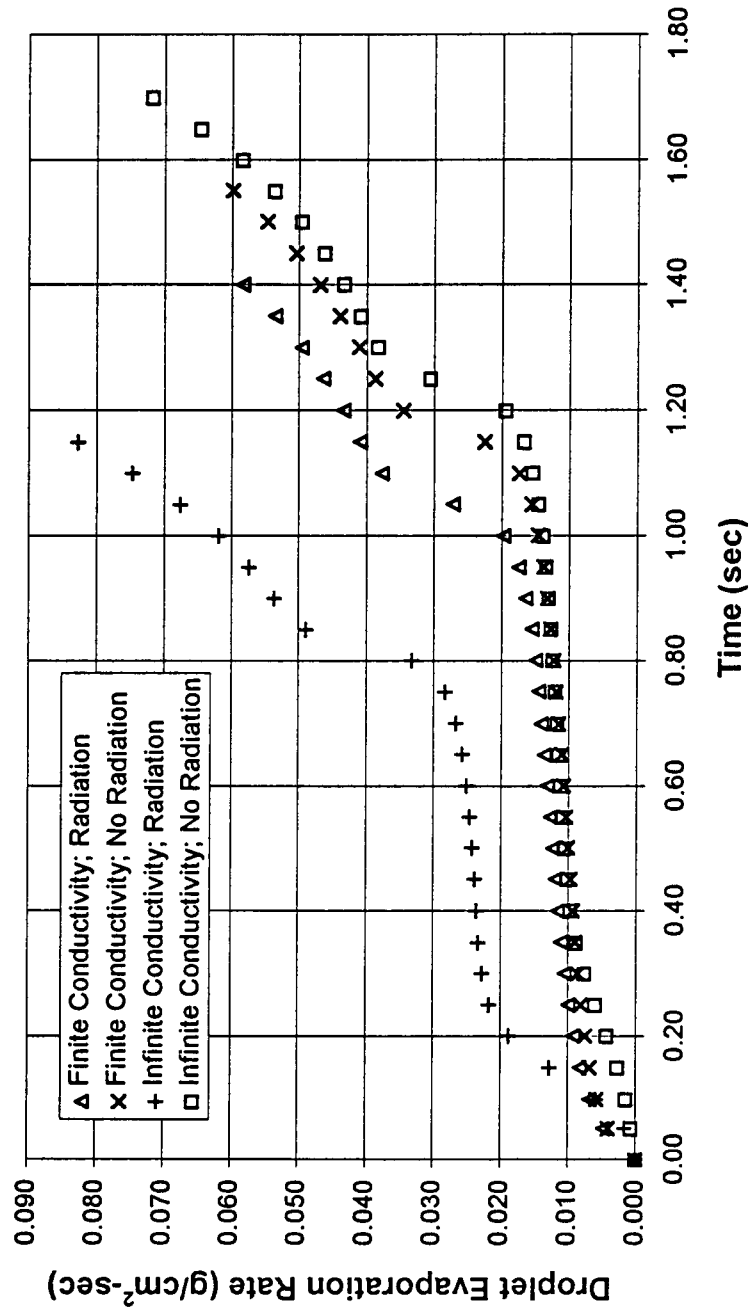


Figure 5.66. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

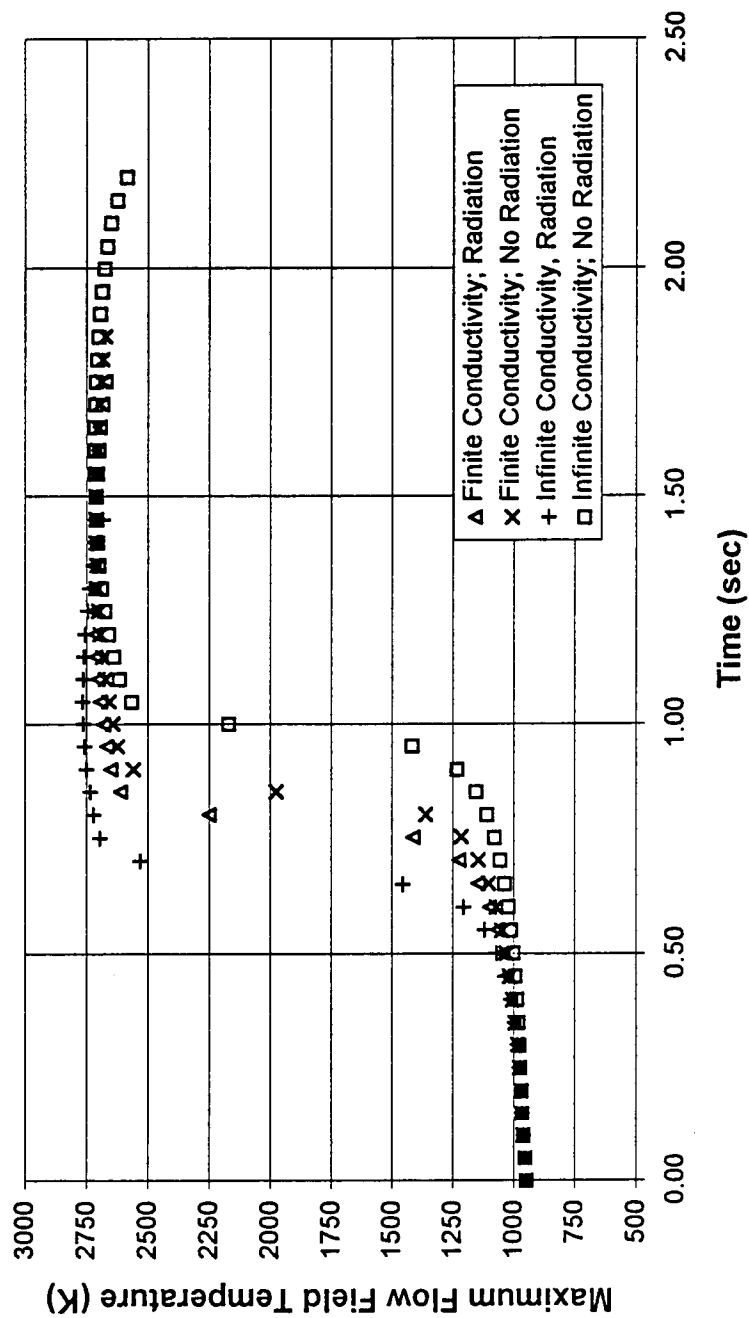


Figure 5.67. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

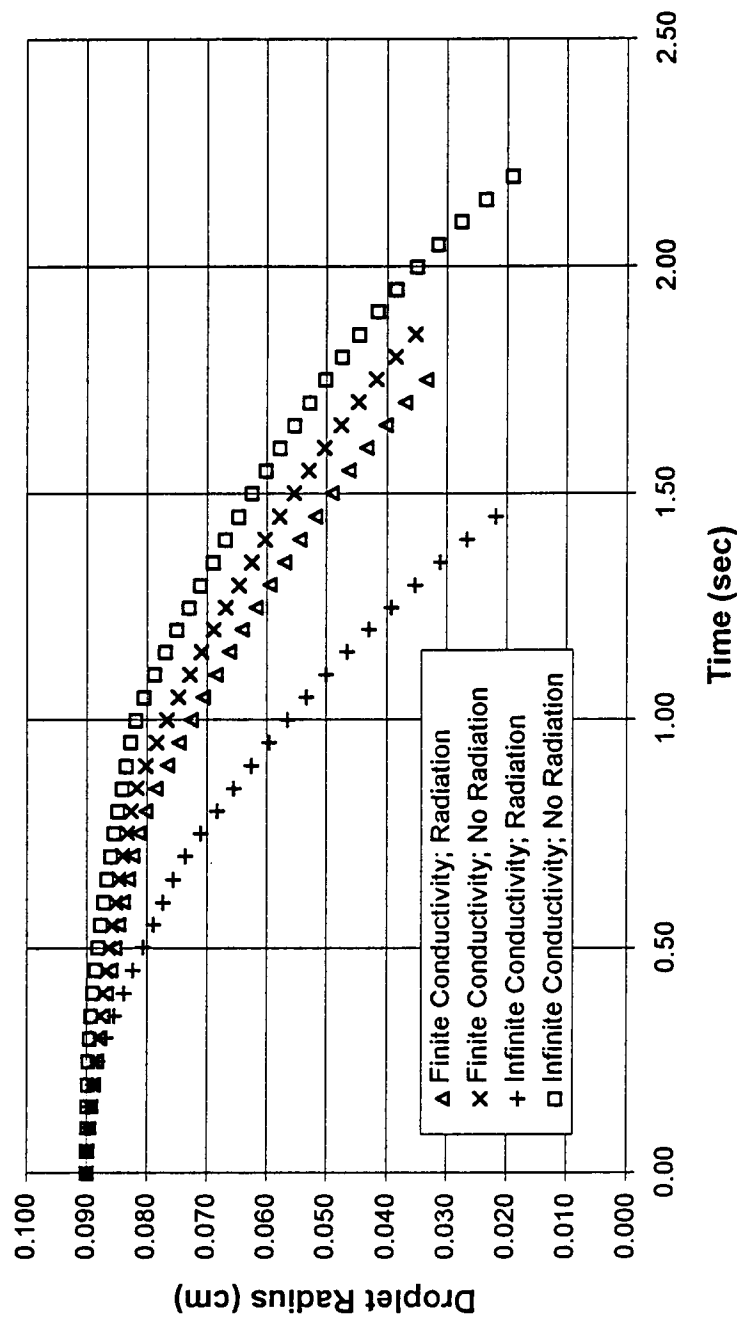


Figure 5.68. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

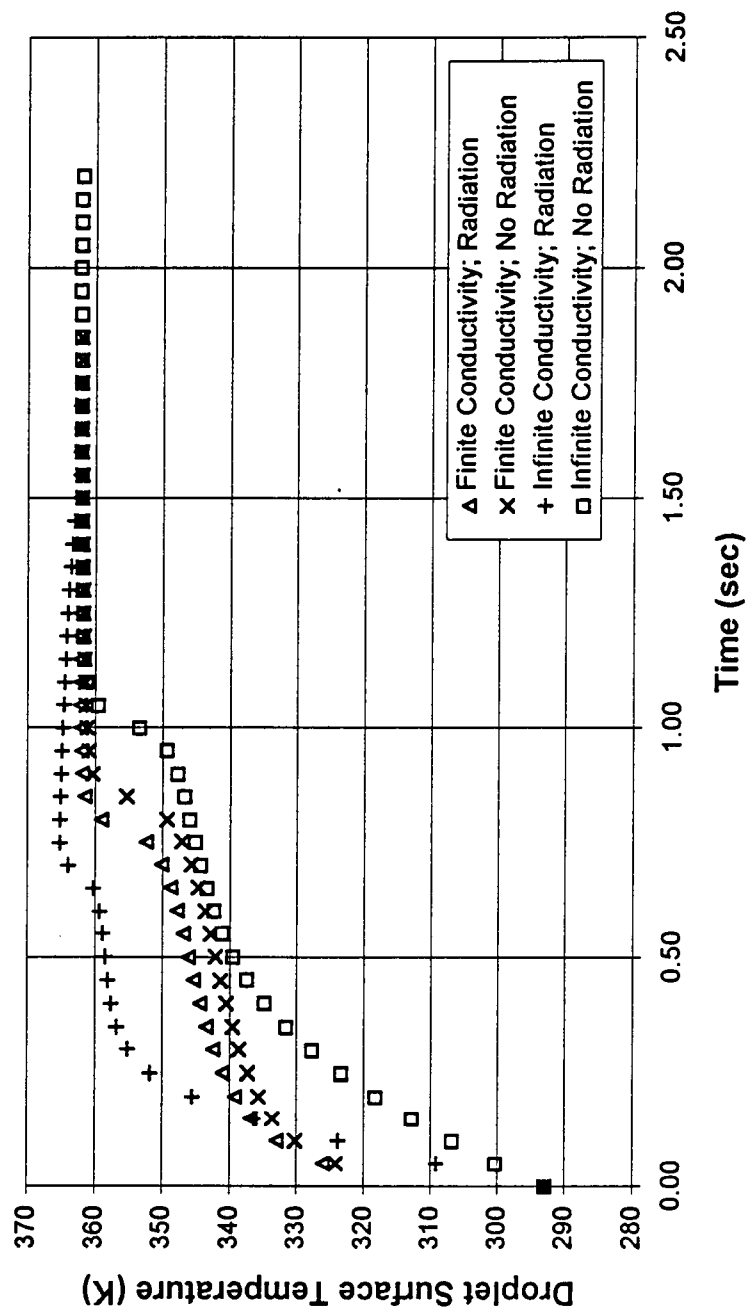


Figure 5.69. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

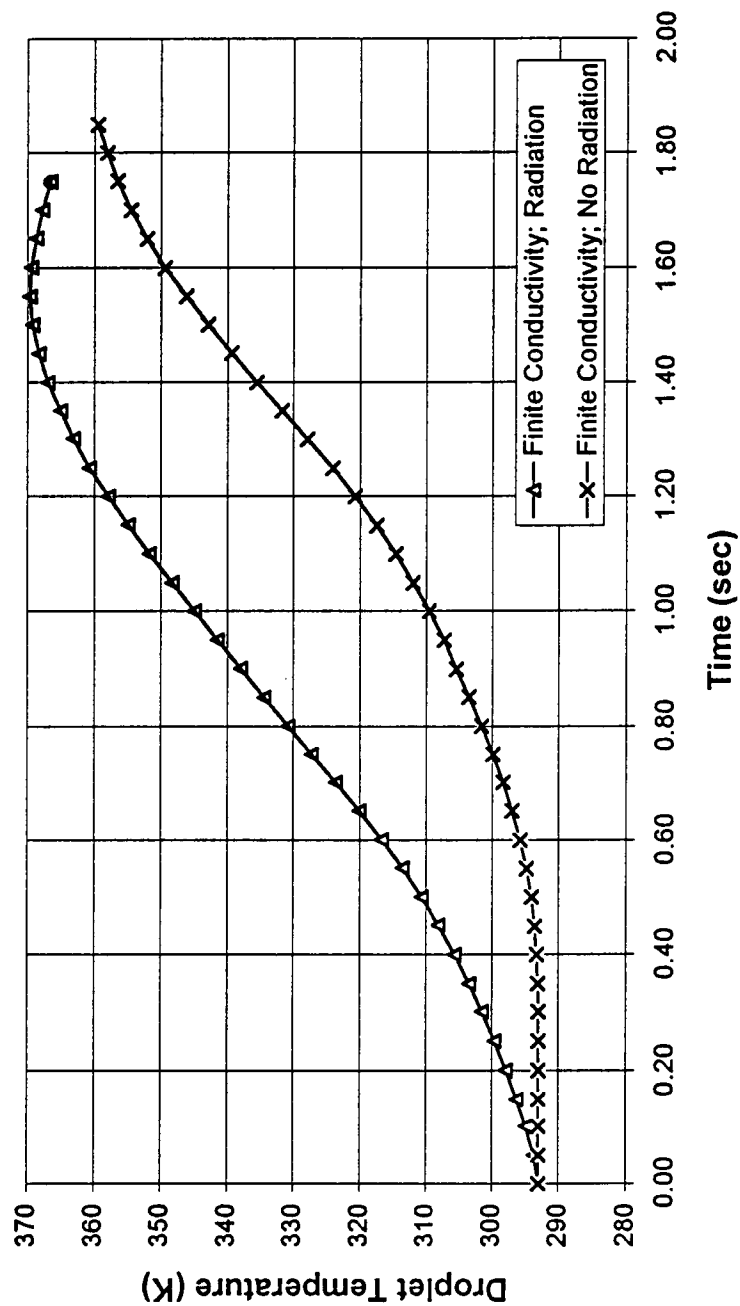


Figure 5.70. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

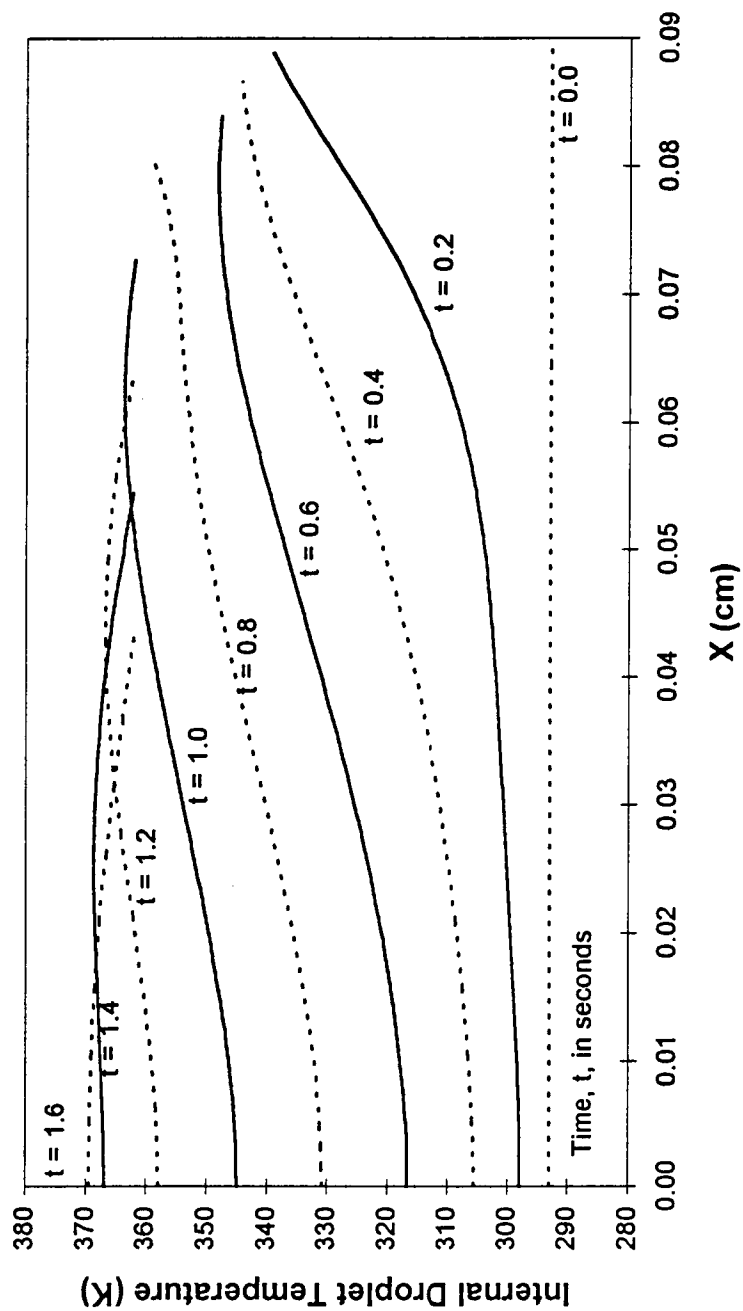


Figure 5.71. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K with Incident Radiation.

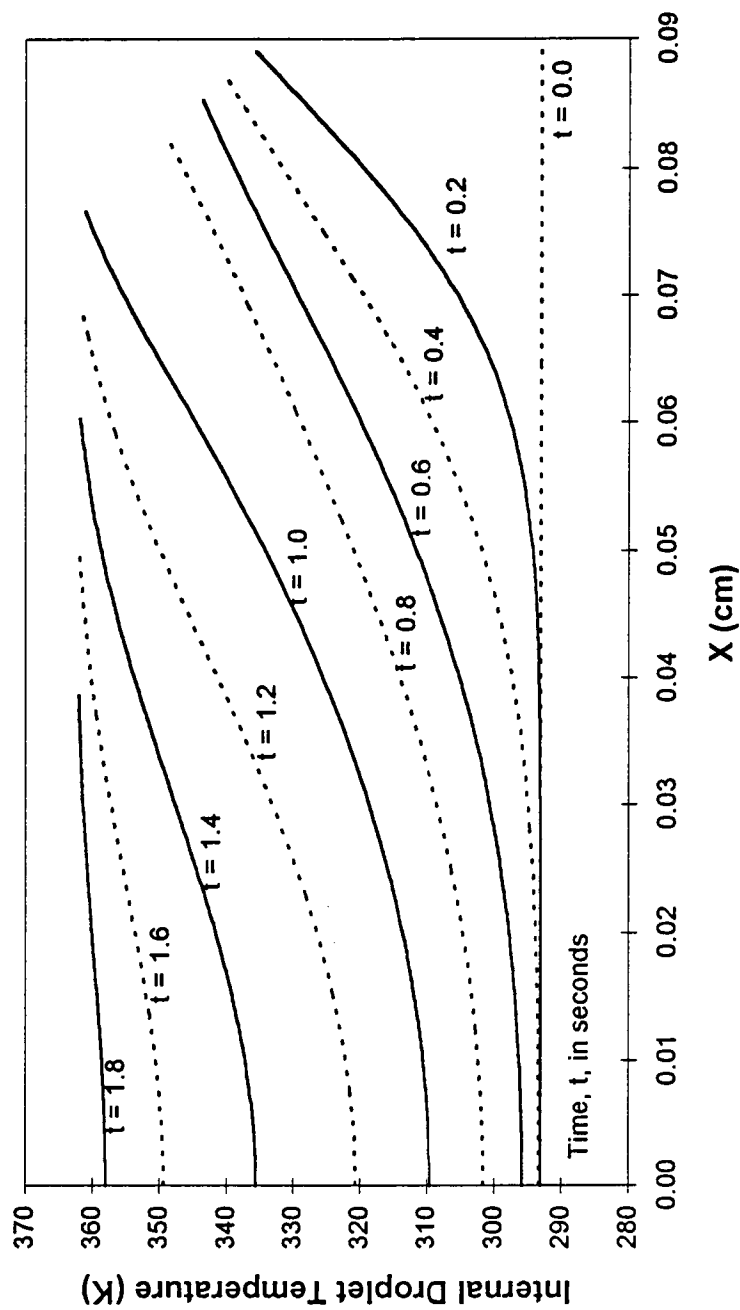


Figure 5.72. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K without Incident Radiation.

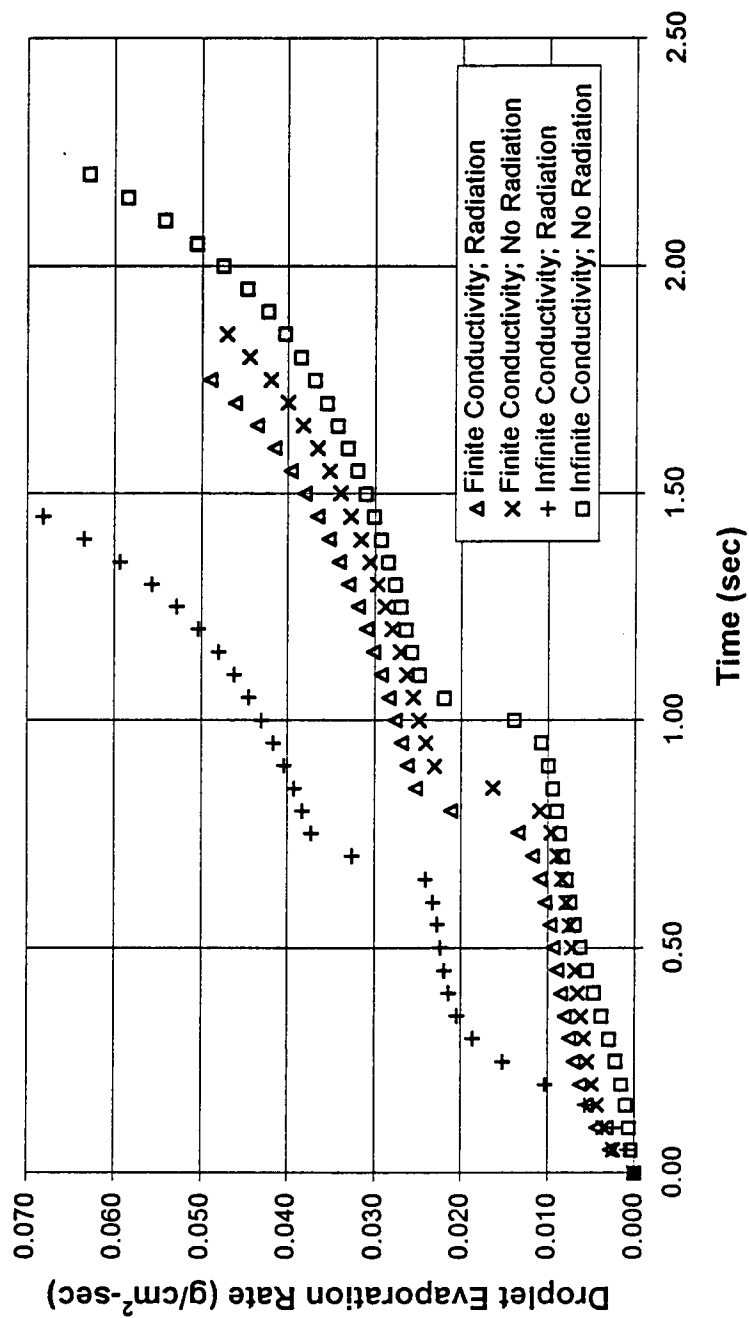


Figure 5.73. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

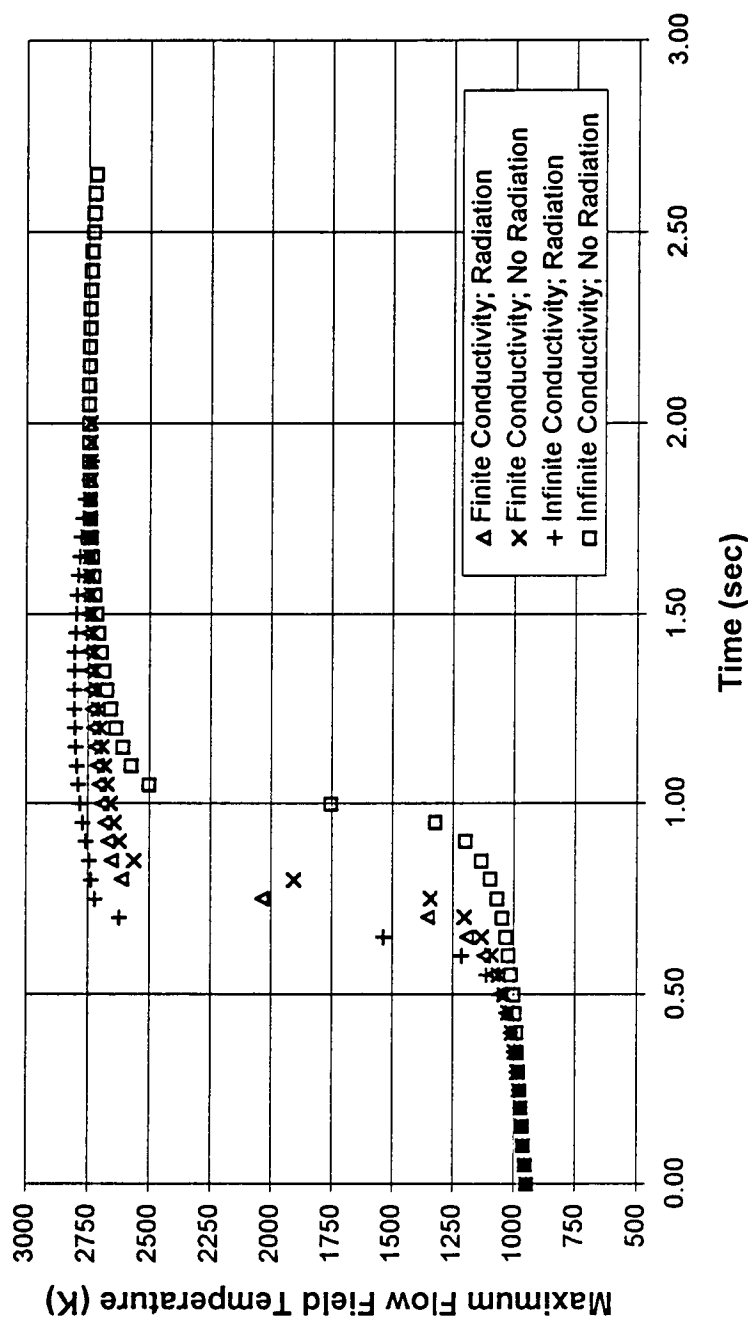


Figure 5.74. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

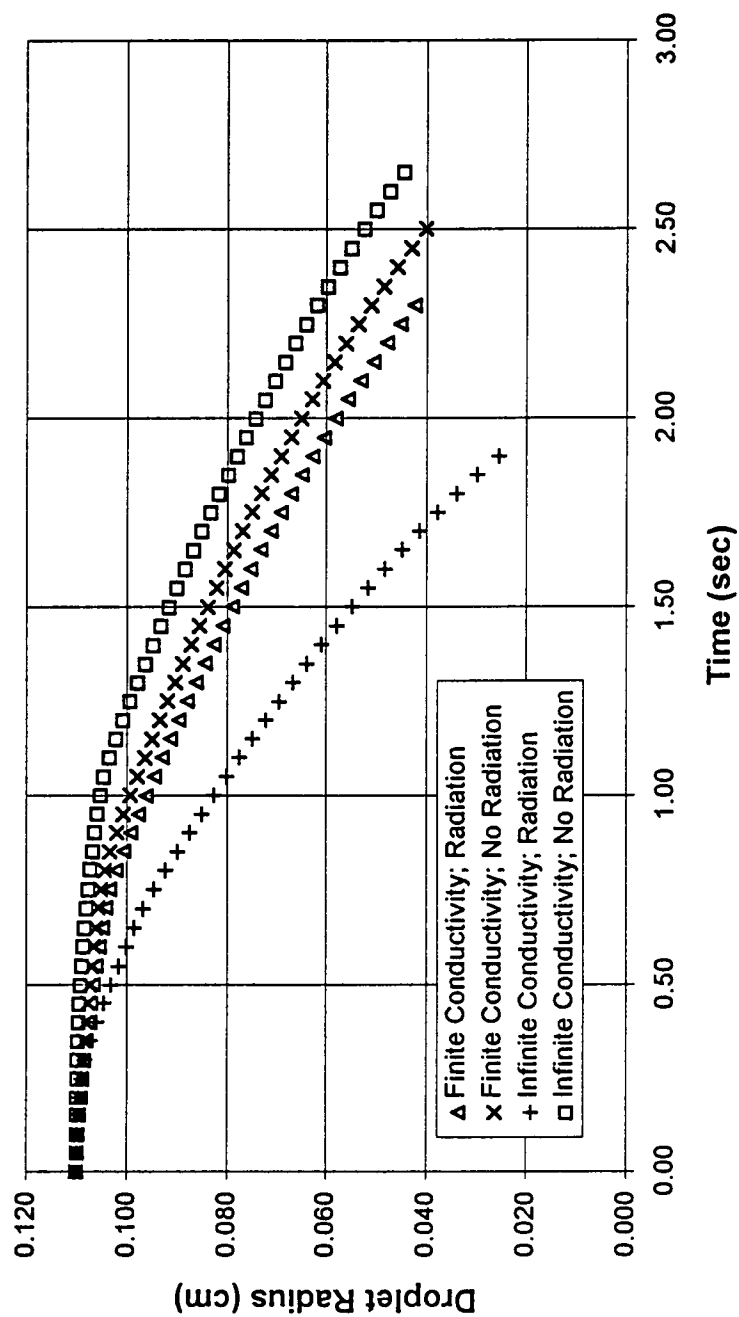


Figure 5.75. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

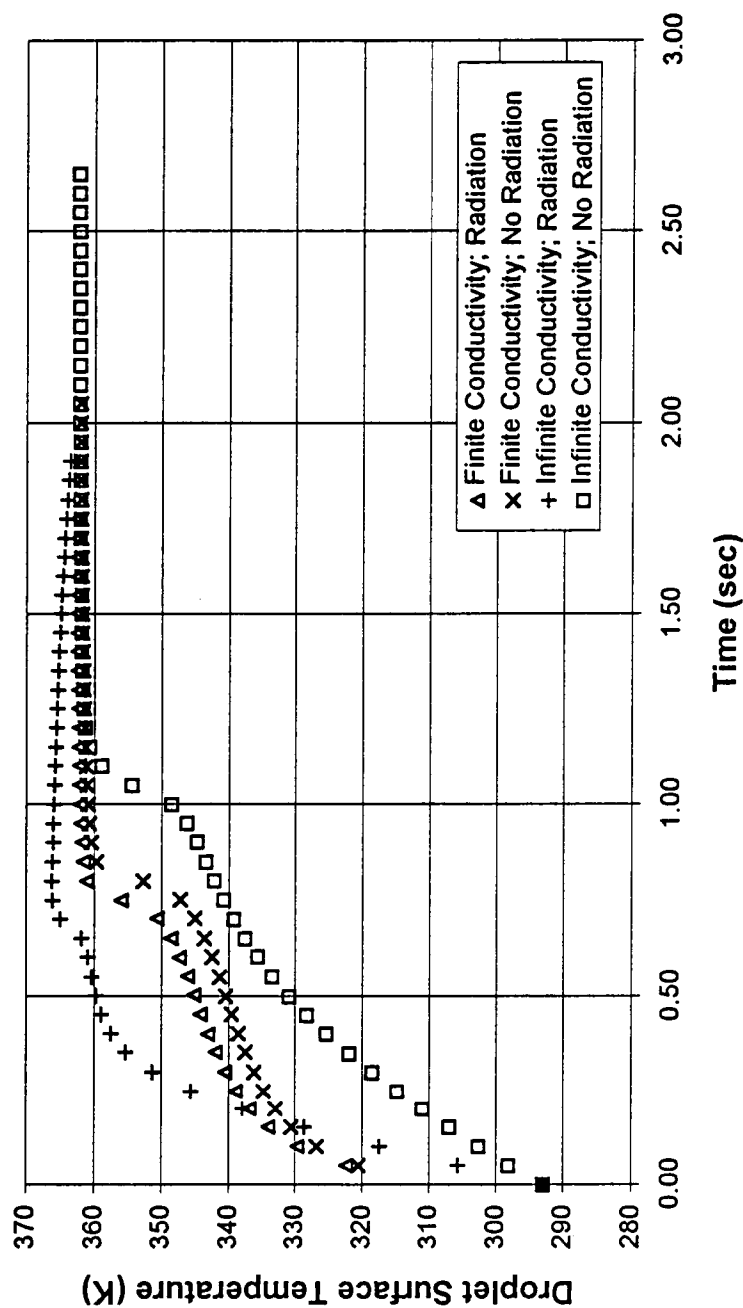


Figure 5.76. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

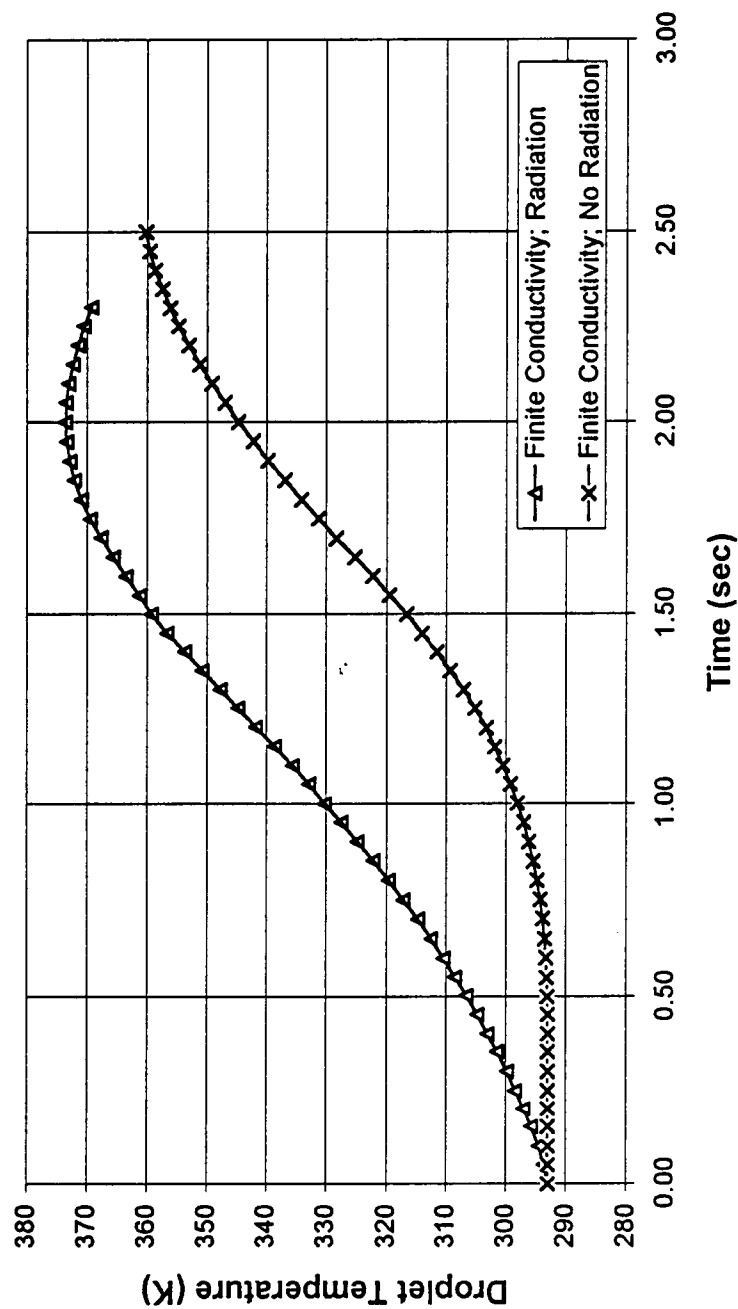


Figure 5.77. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

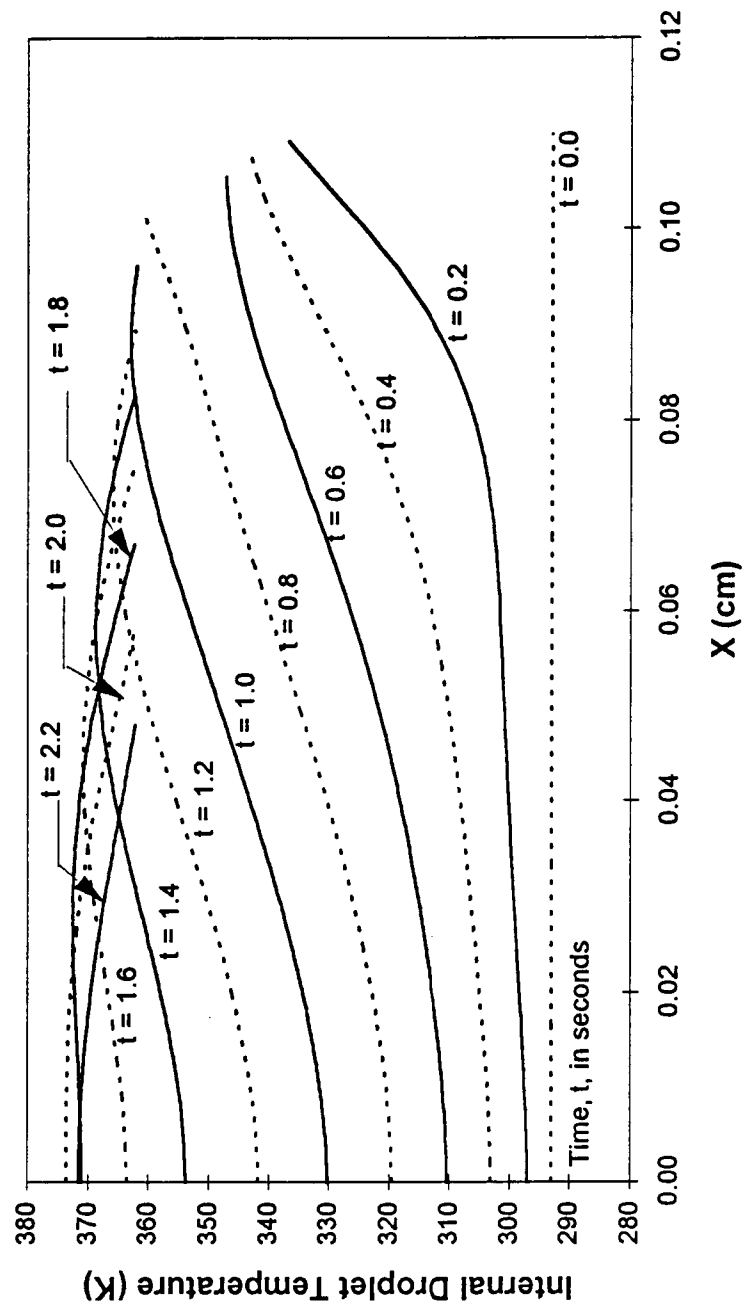


Figure 5.78. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K with Incident Radiation.

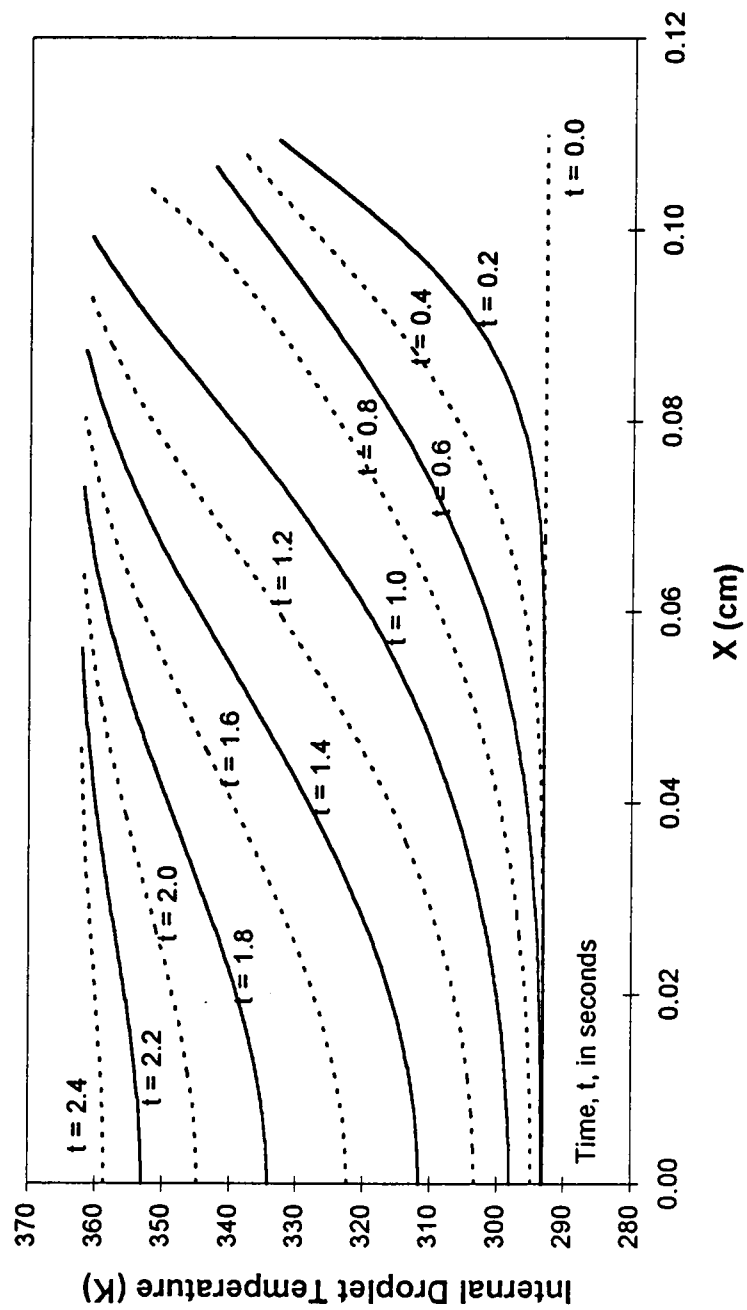


Figure 5.79. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K without Incident Radiation.

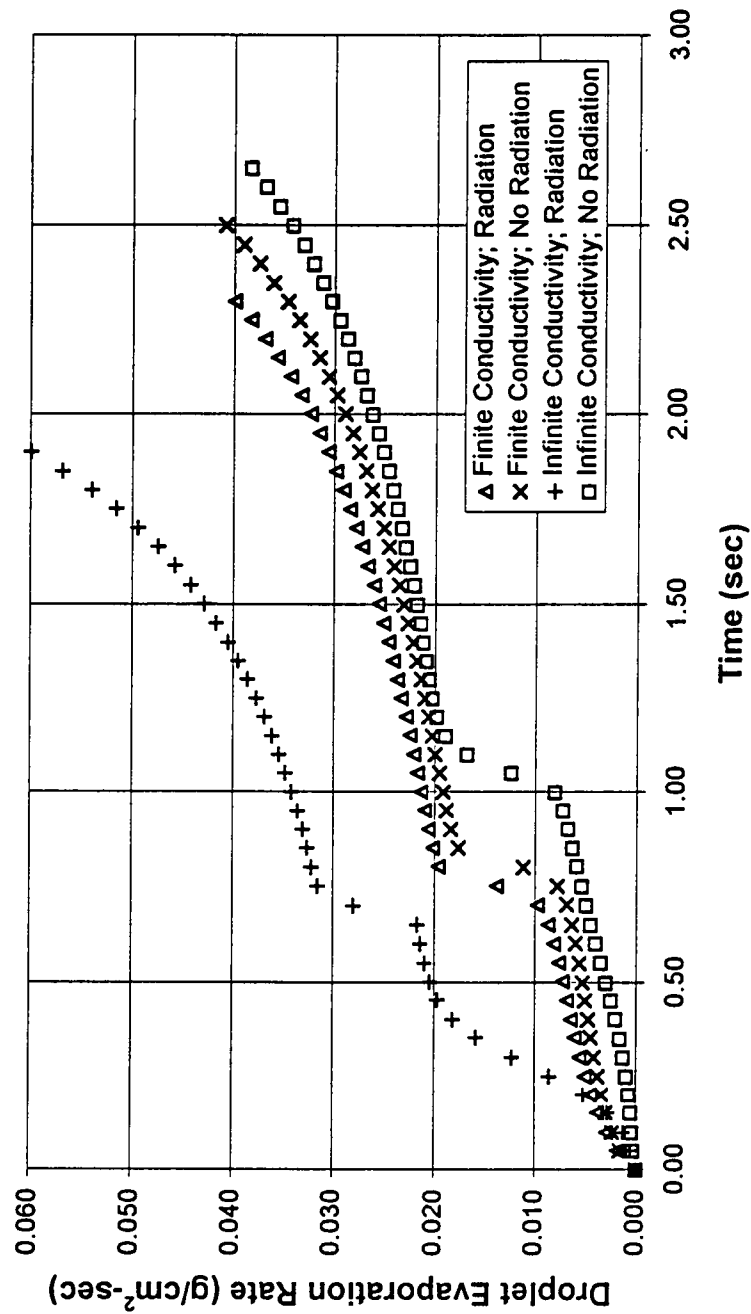


Figure 5.80. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

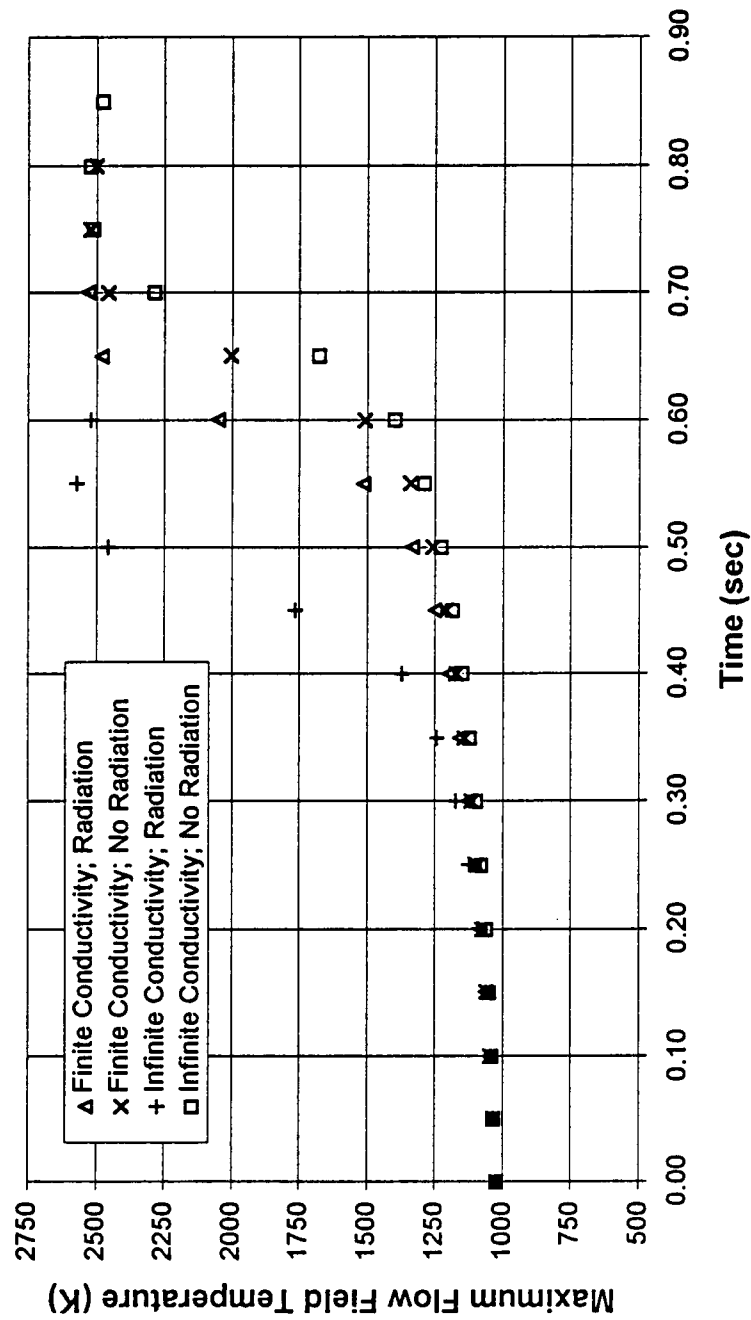


Figure 5.81. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

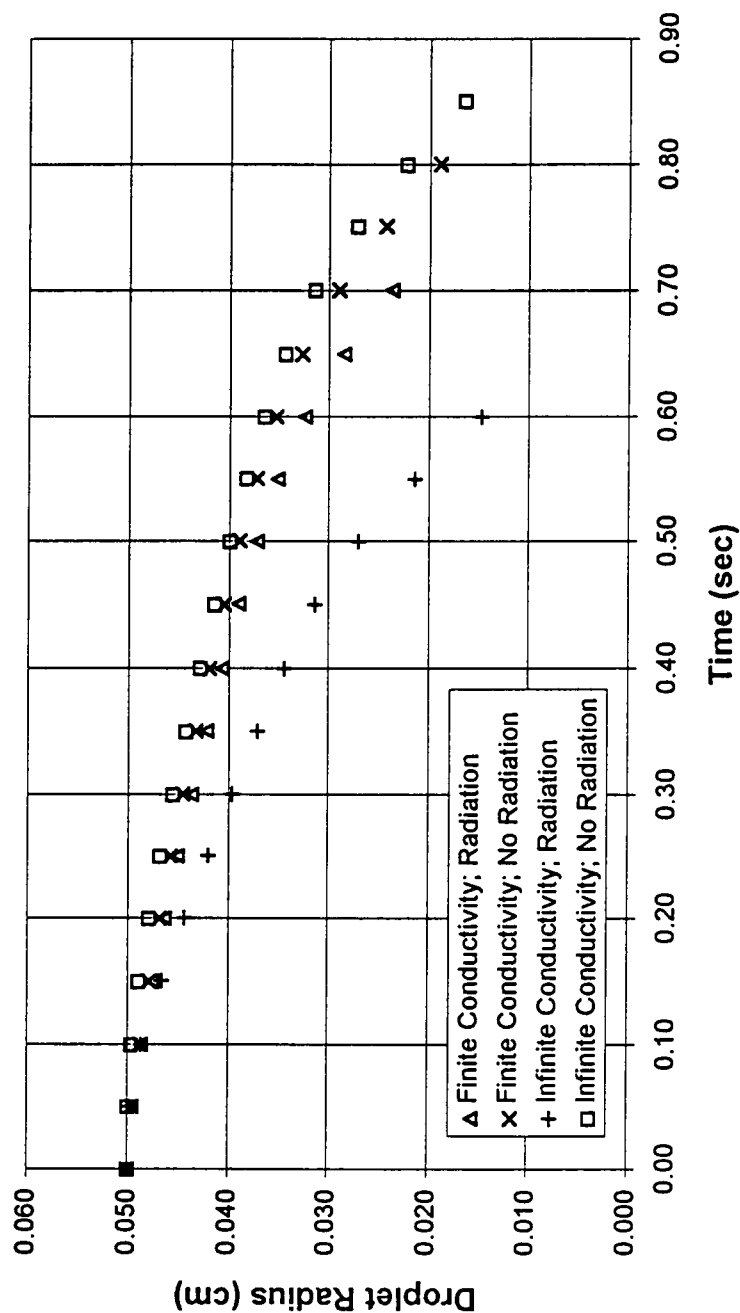


Figure 5.82. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

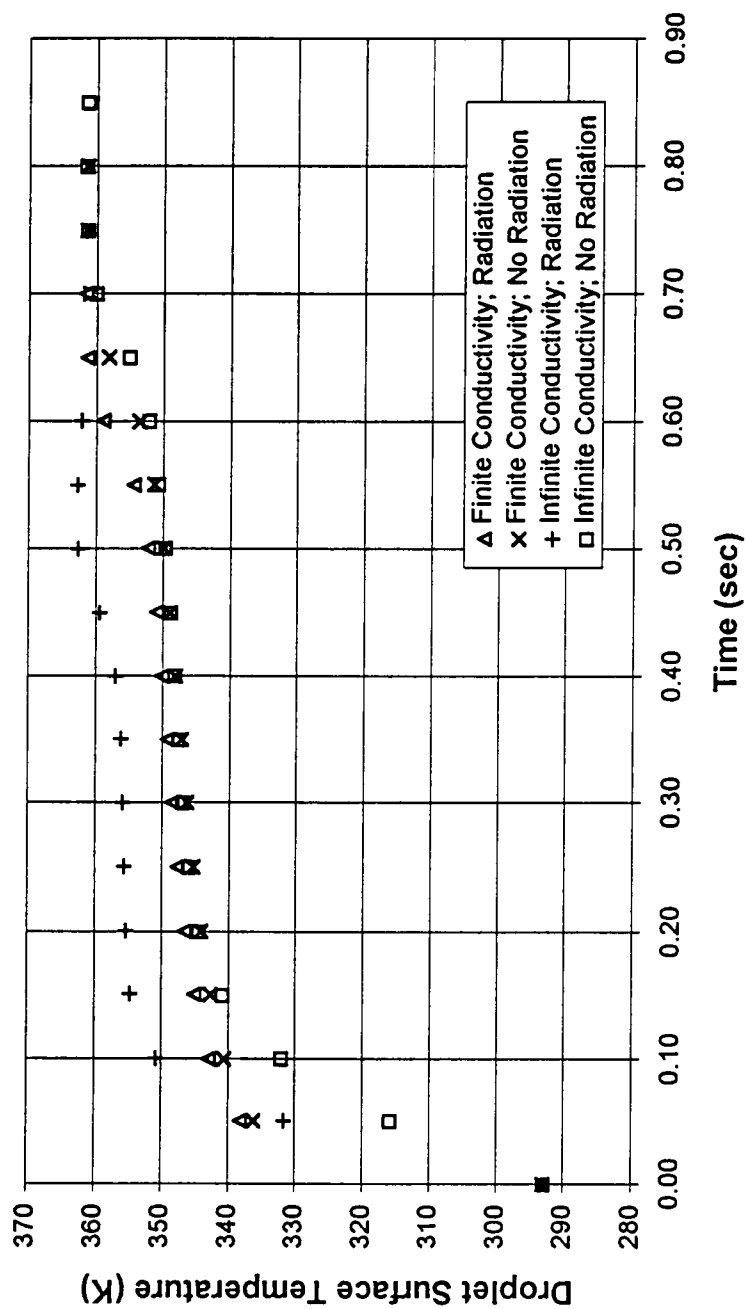


Figure 5.83. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

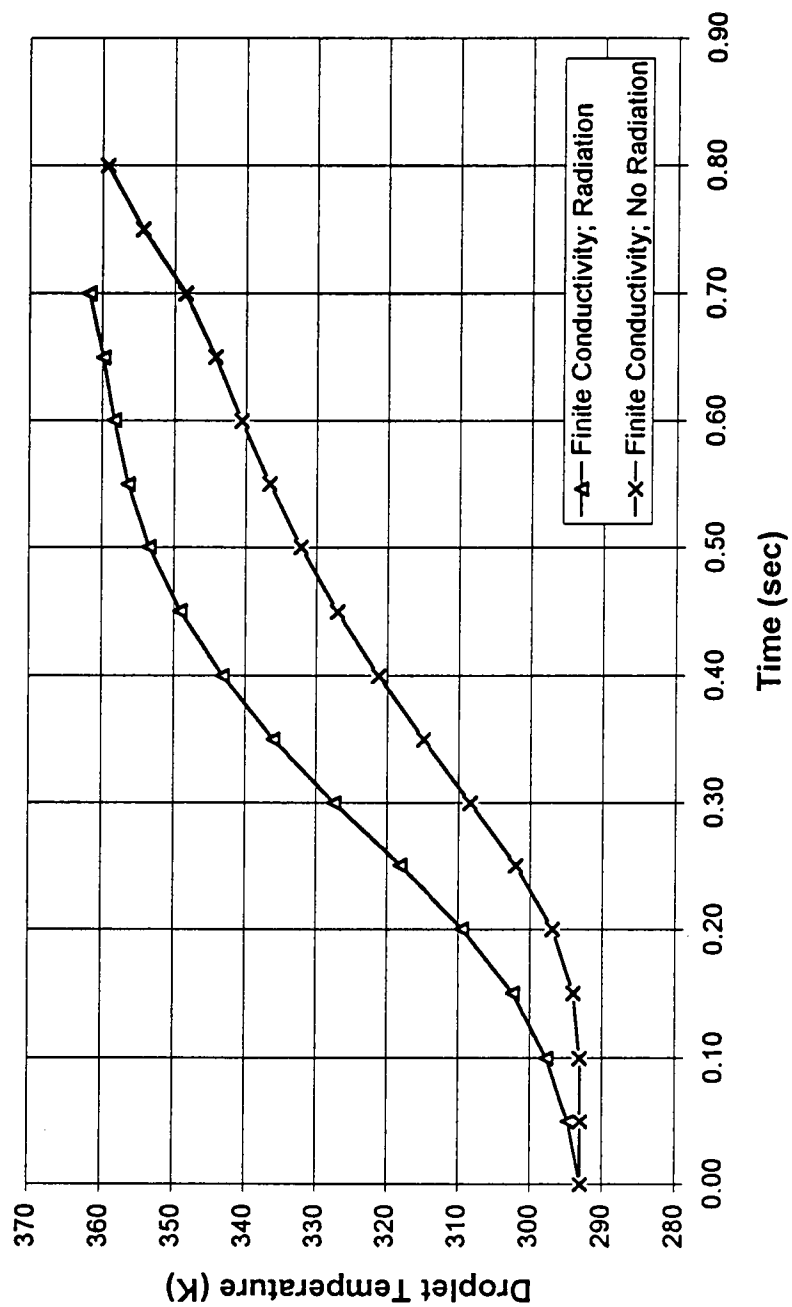


Figure 5.84. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

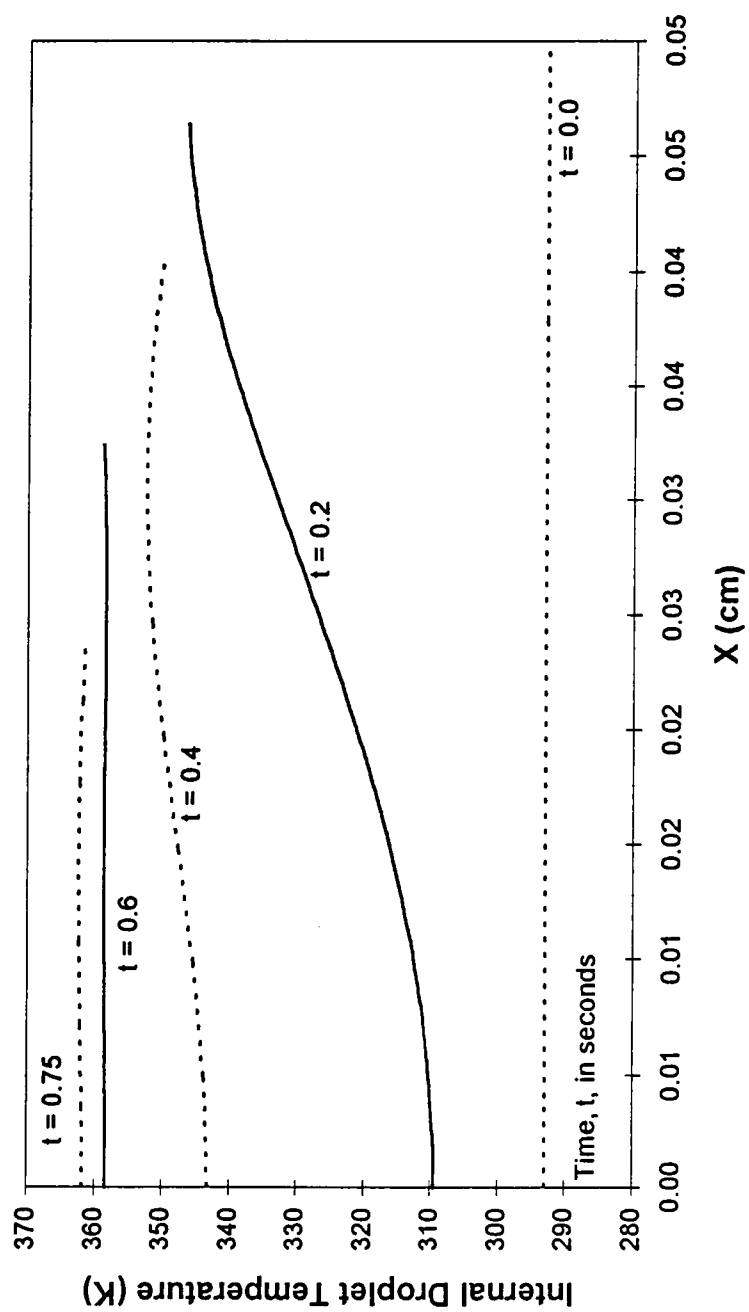


Figure 5.85. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K with Incident Radiation.

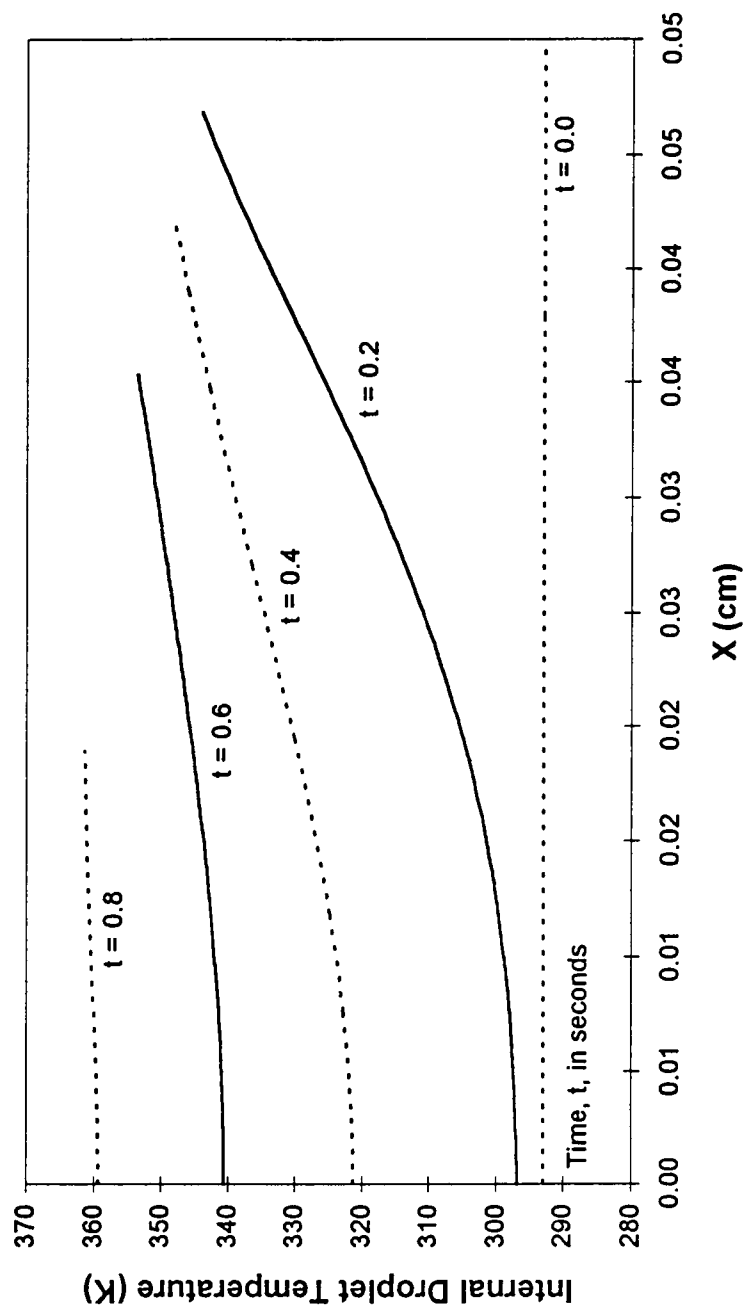


Figure 5.86. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K without Incident Radiation.

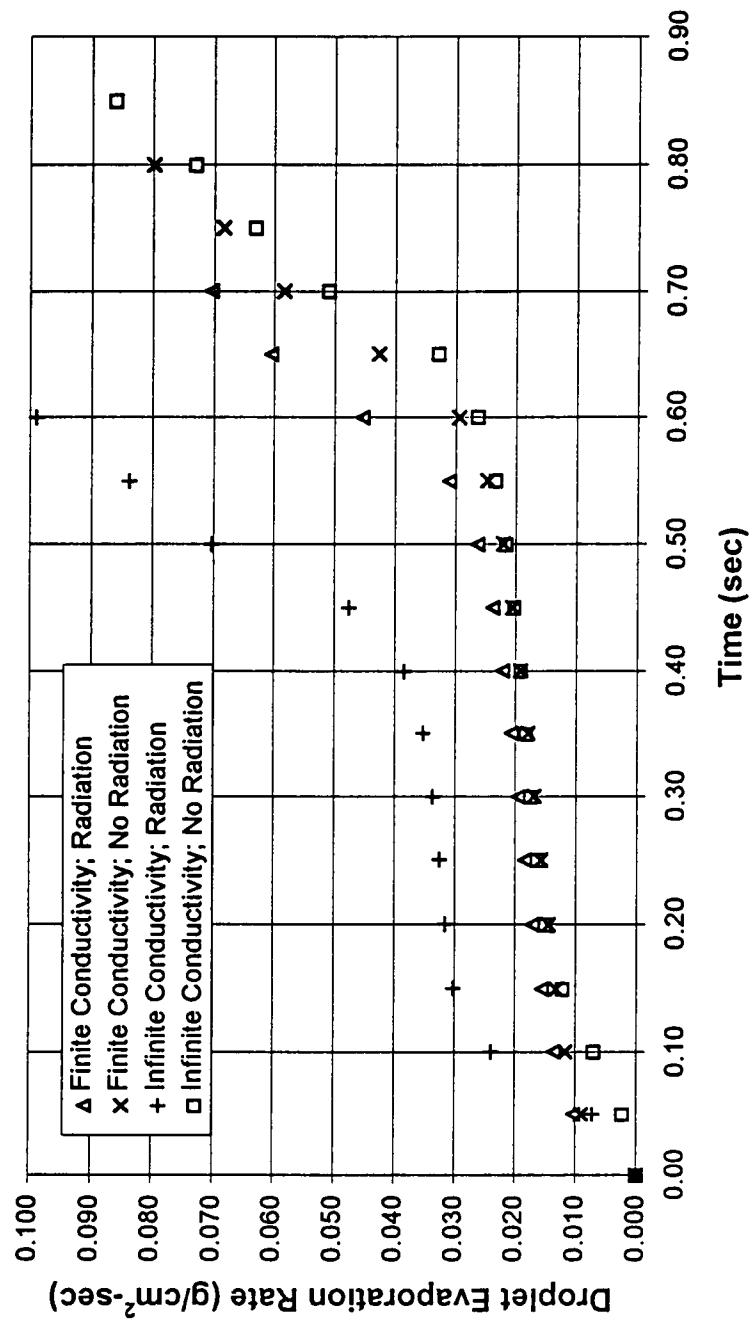


Figure 5.87. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

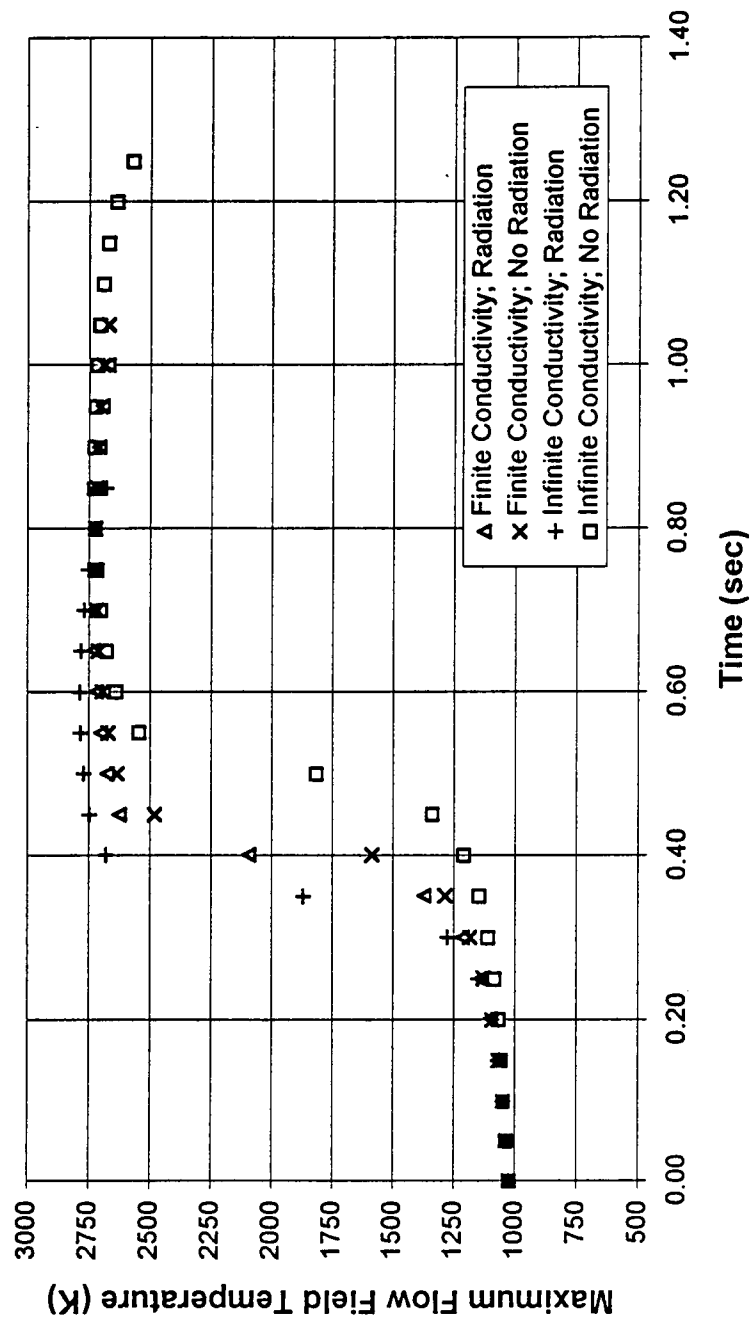


Figure 5.88. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

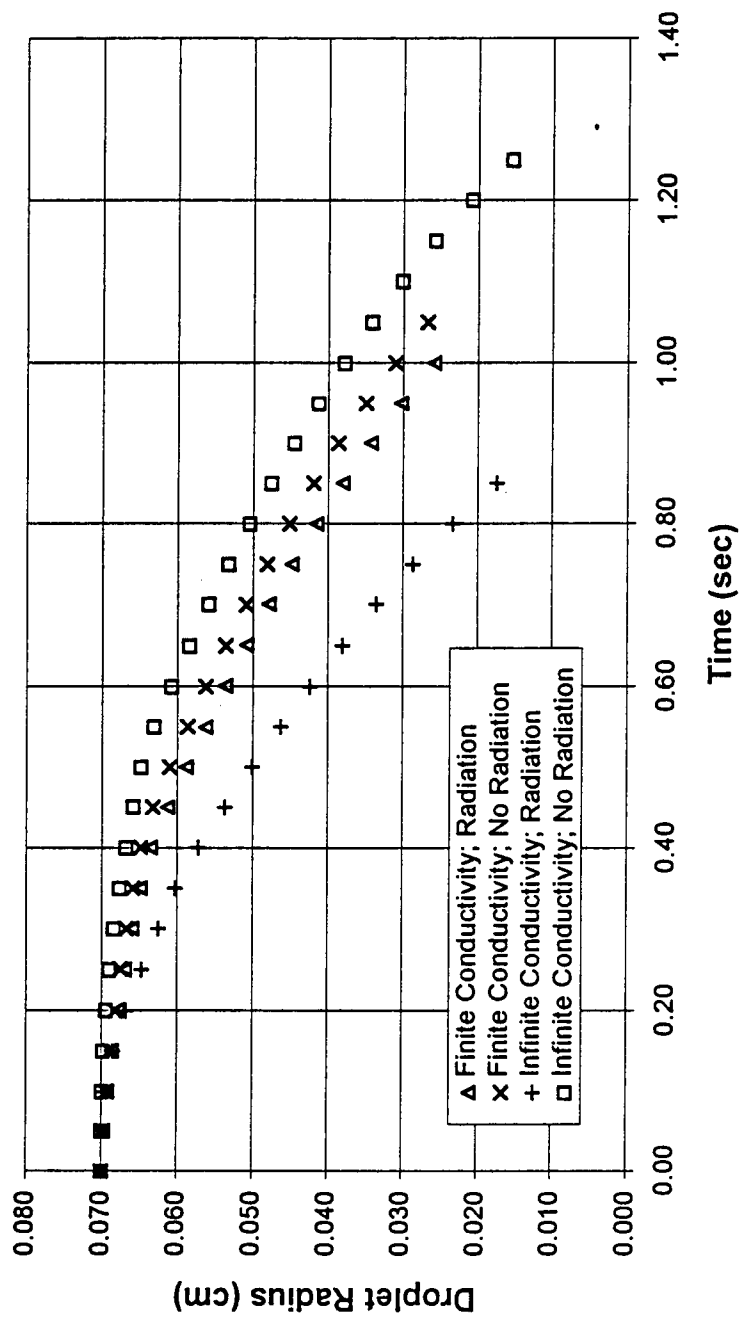


Figure 5.89. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

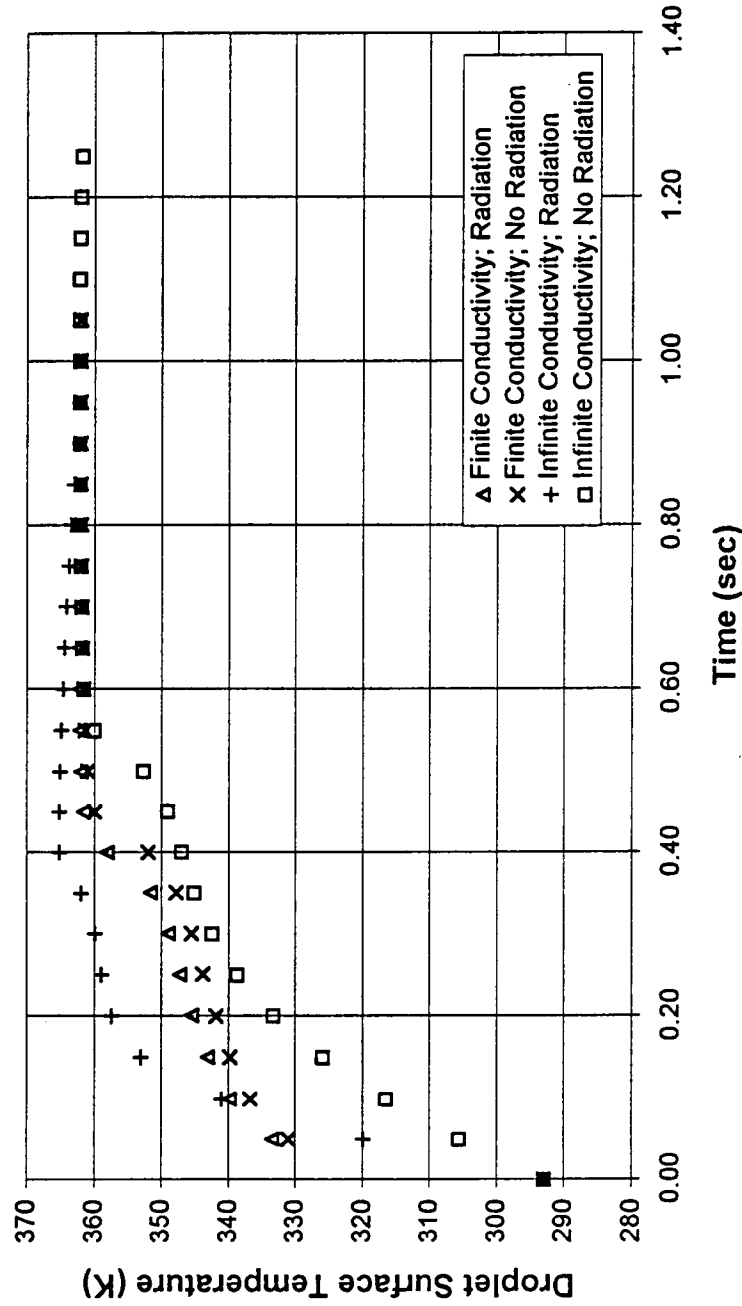


Figure 5.90. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

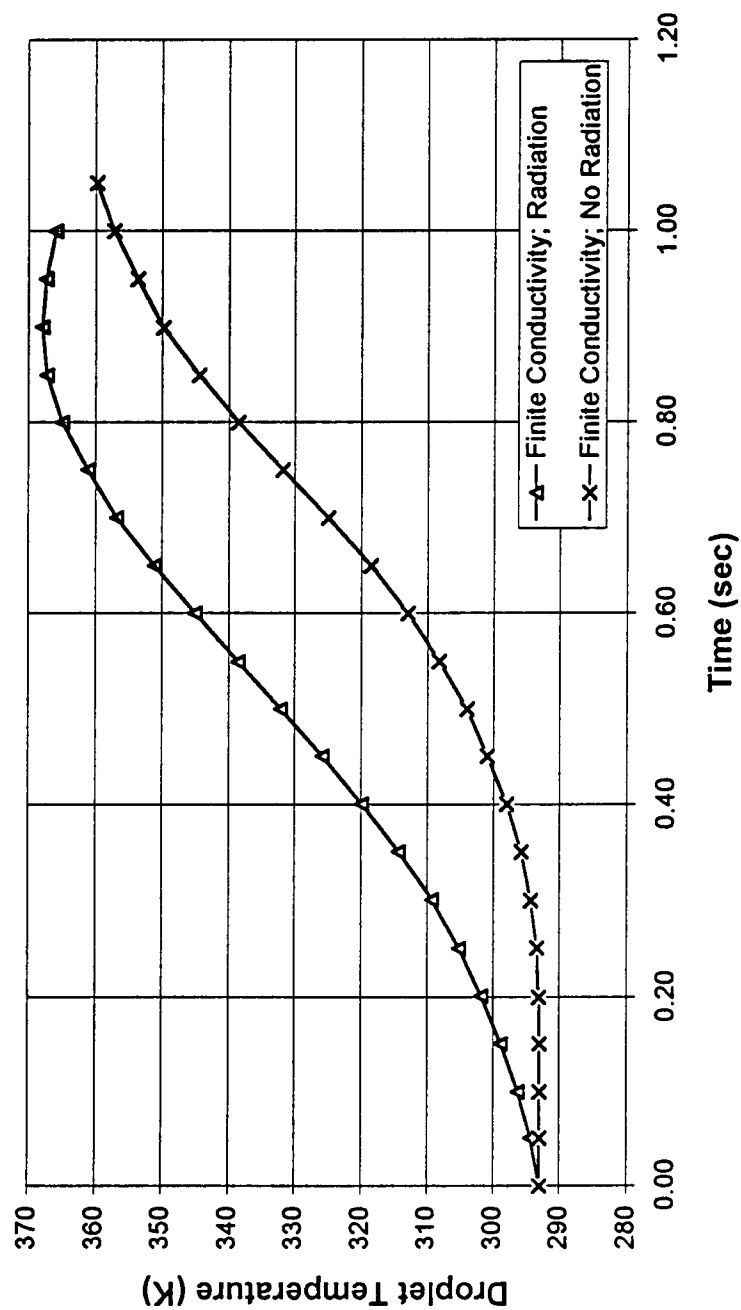


Figure 5.91. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

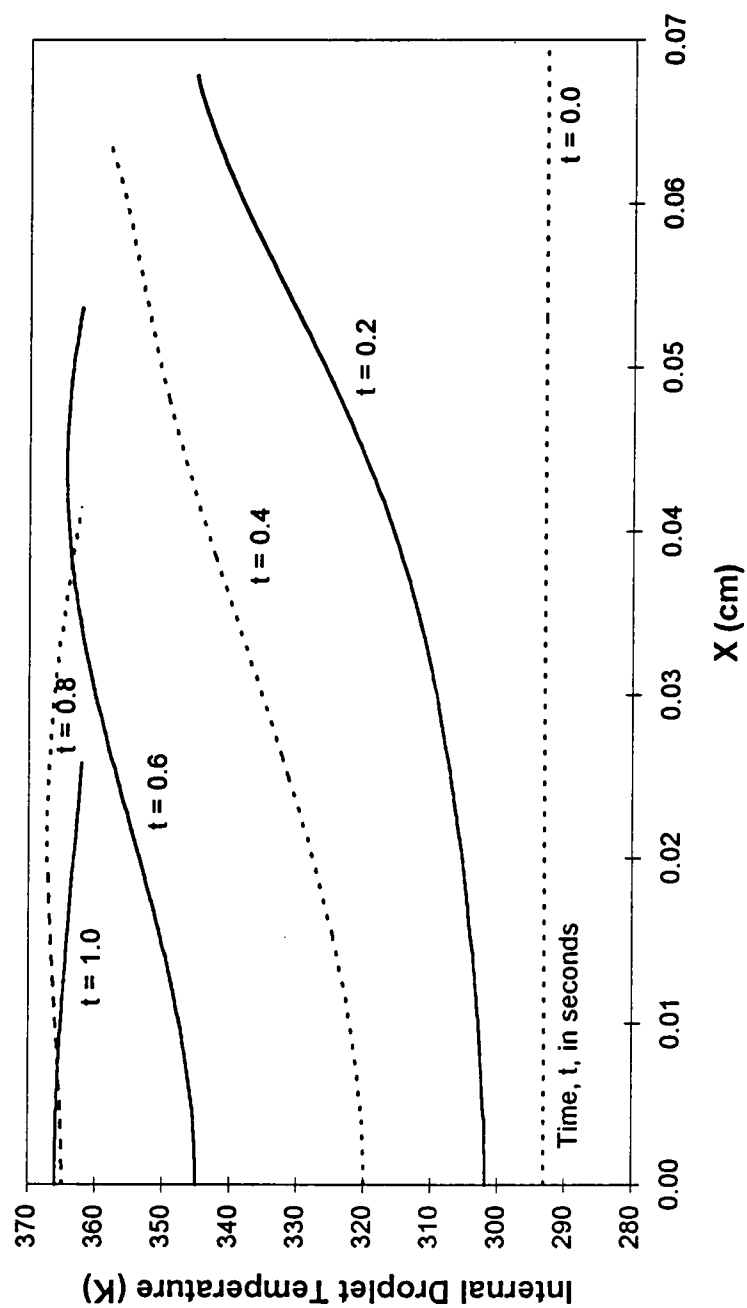


Figure 5.92. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K with Incident Radiation.

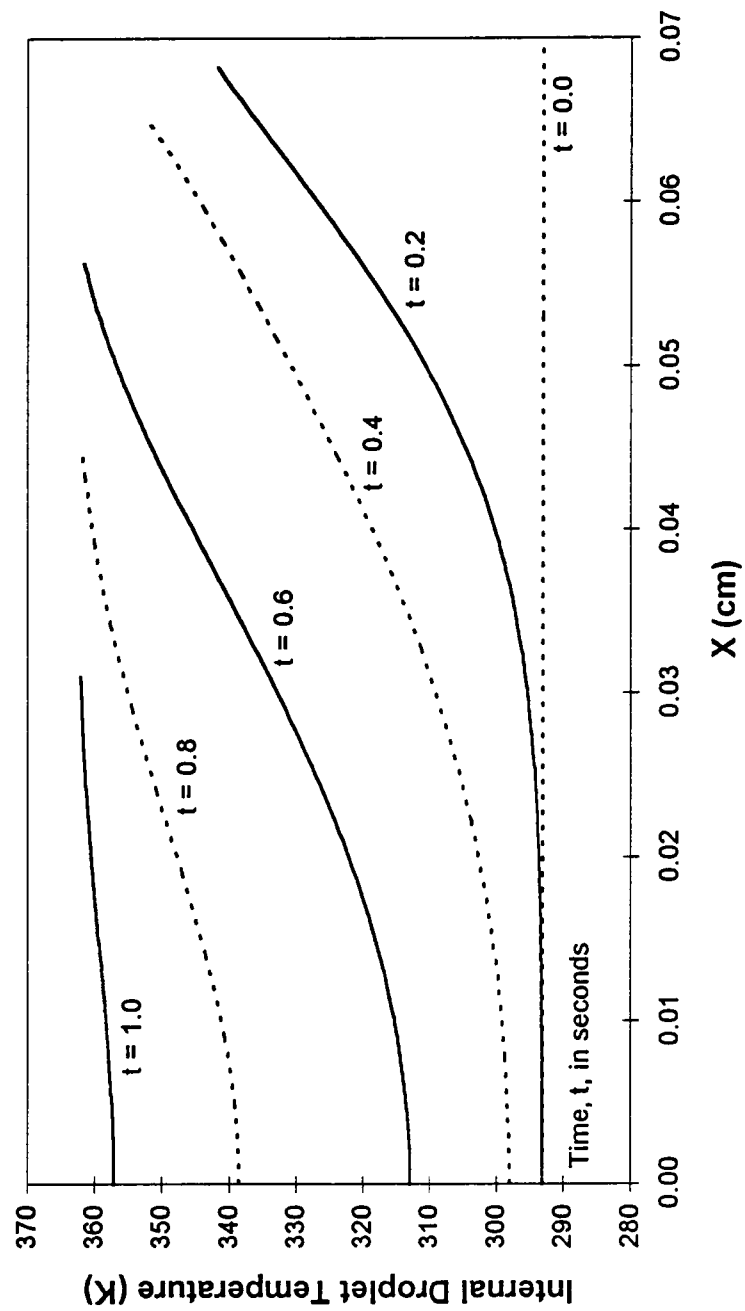


Figure 5.93. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K without Incident Radiation.

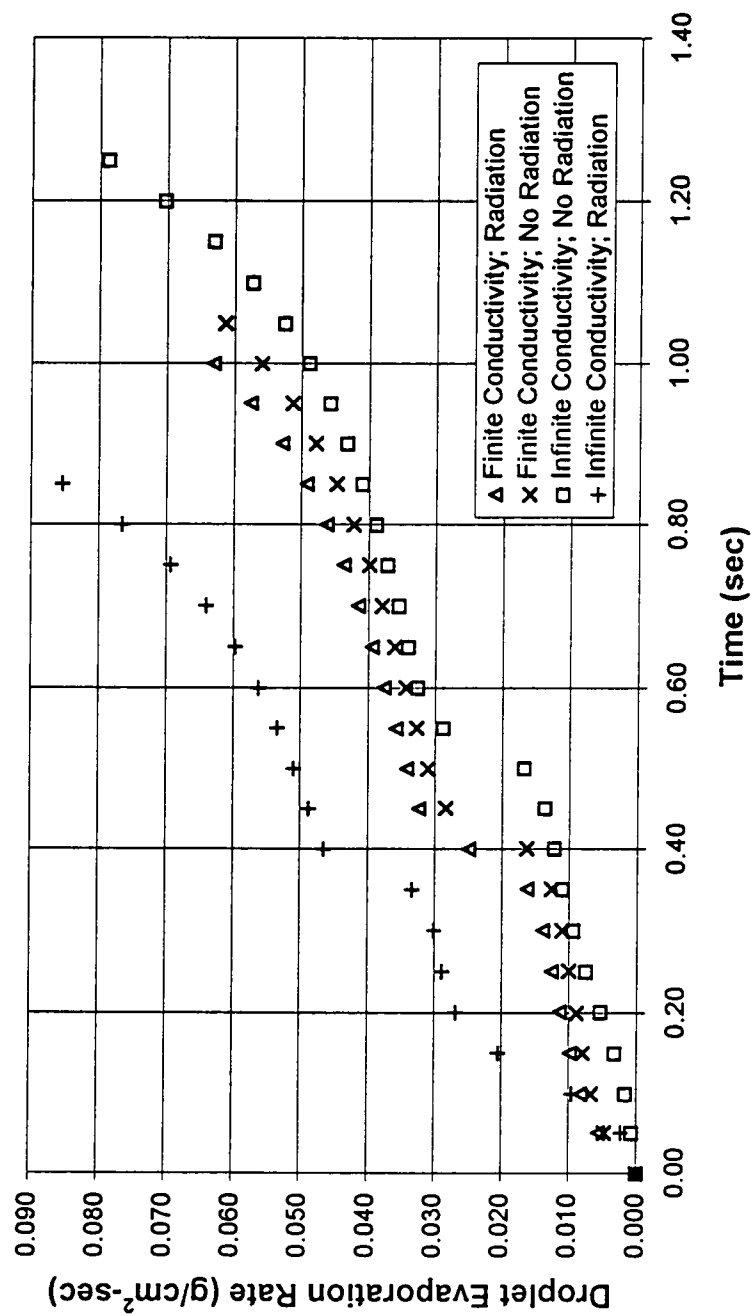


Figure 5.94. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

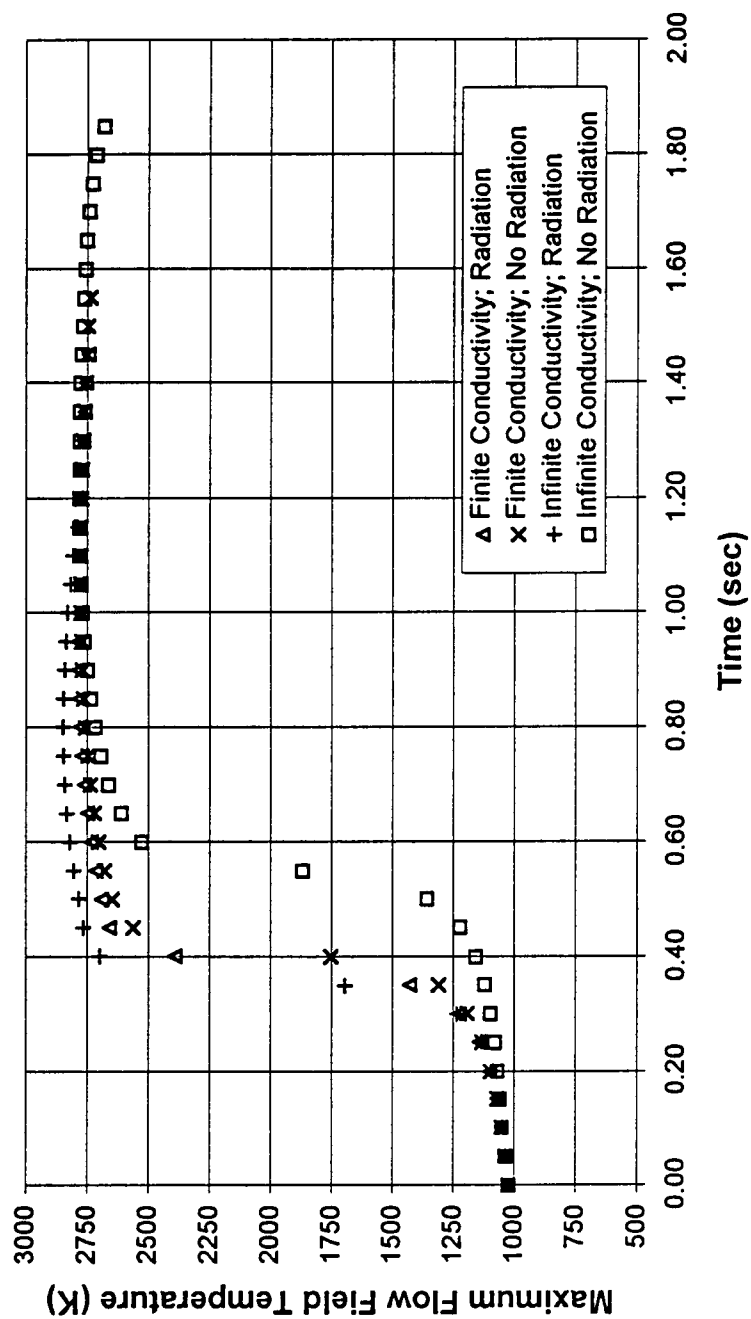


Figure 5.95. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

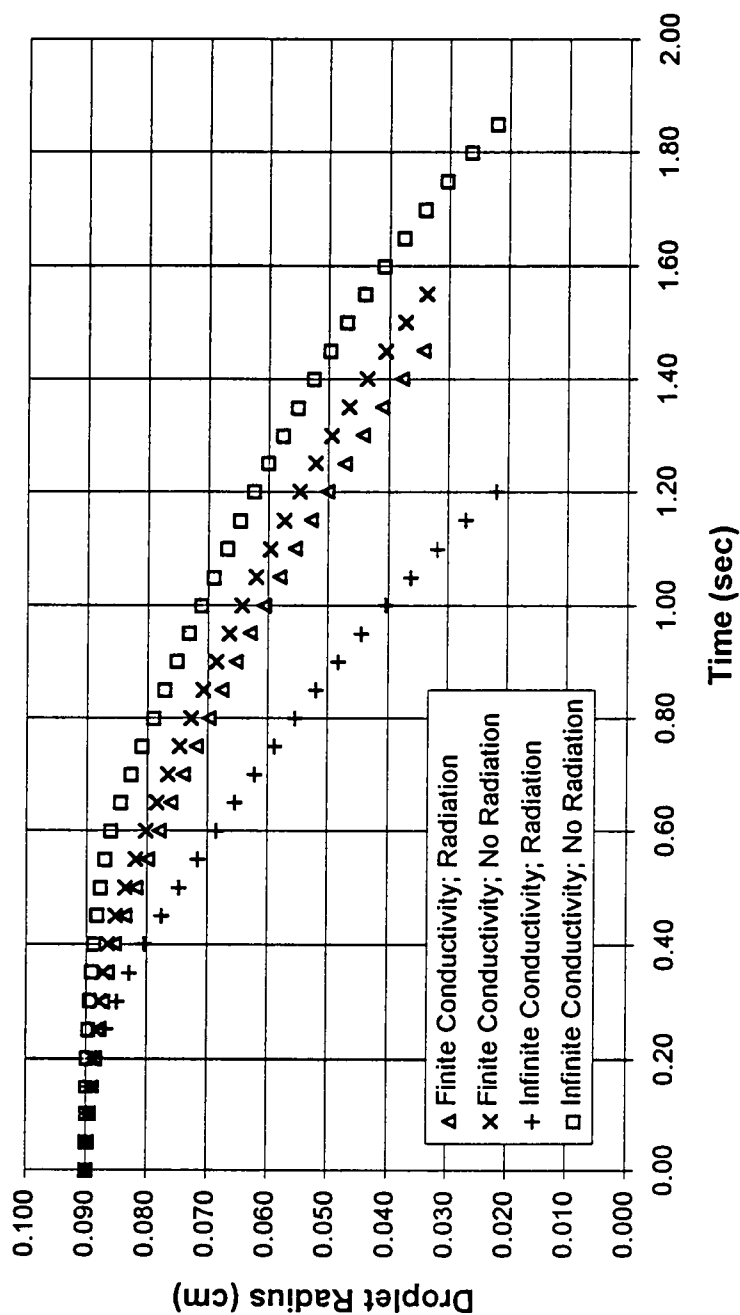


Figure 5.96. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

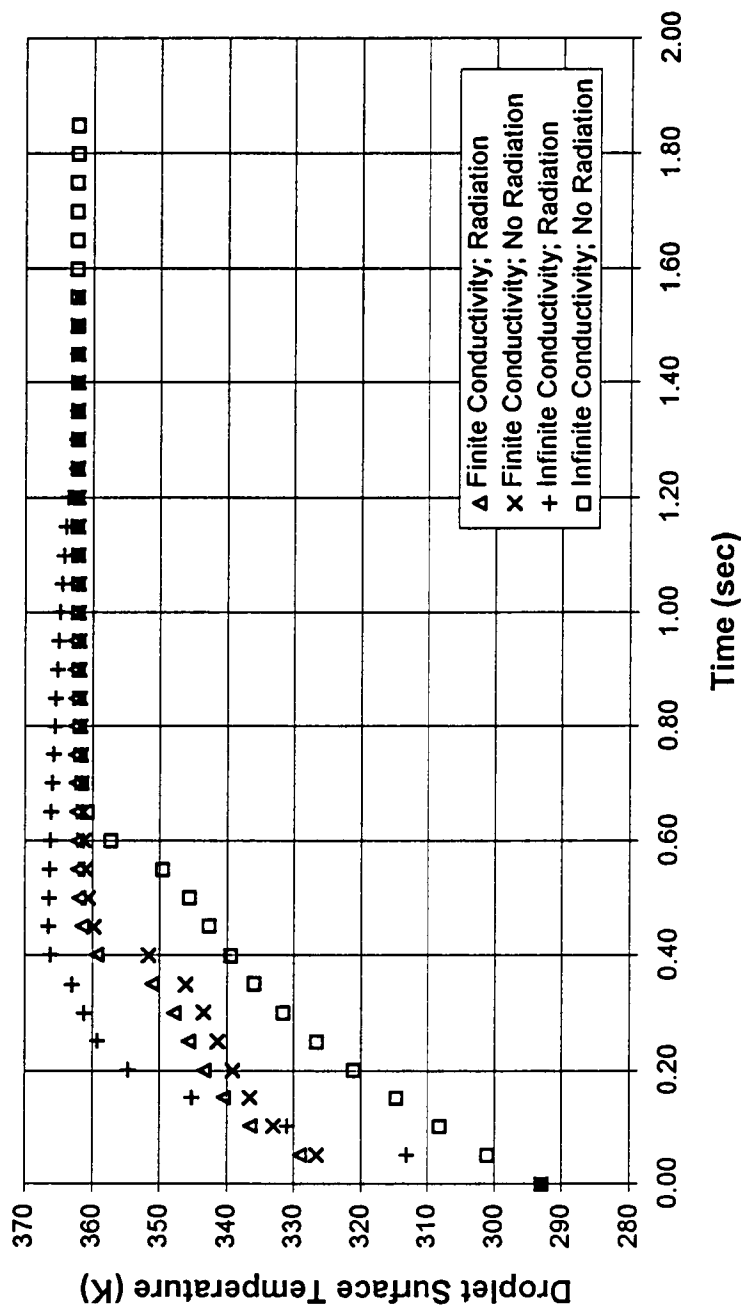


Figure 5.97. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

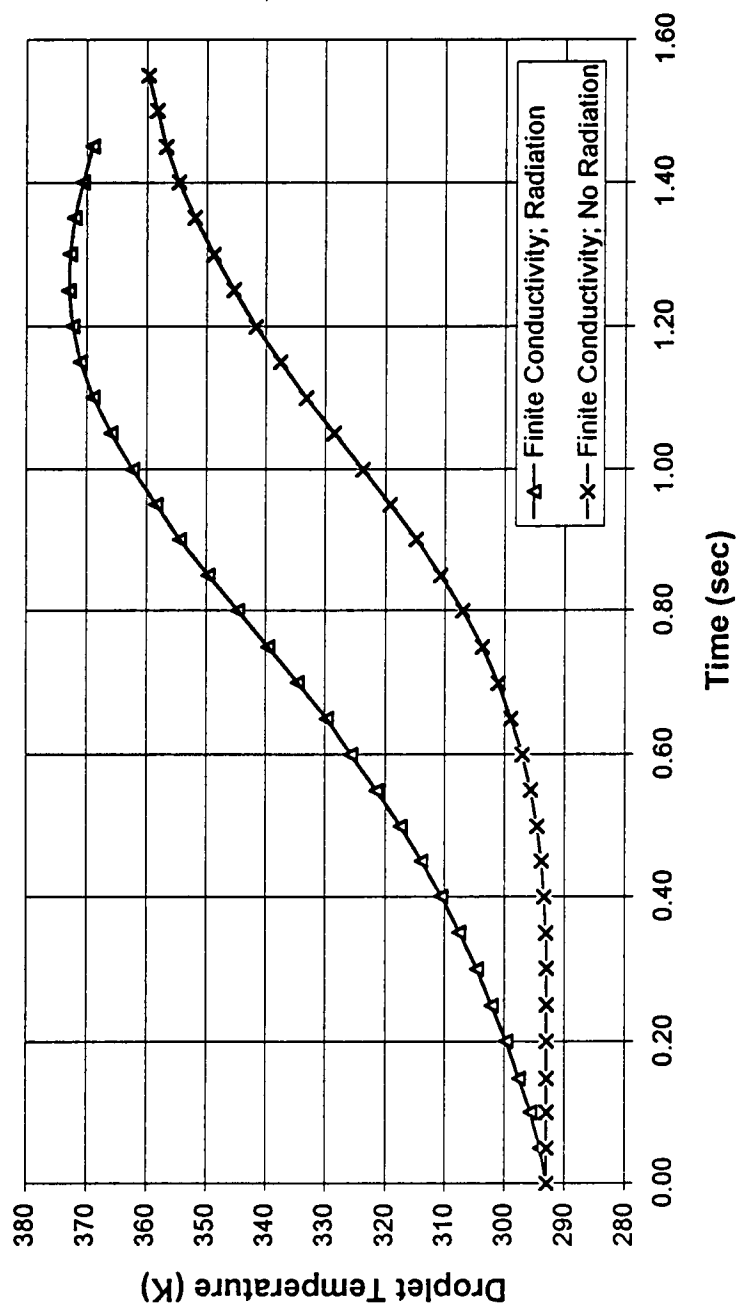


Figure 5.98. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

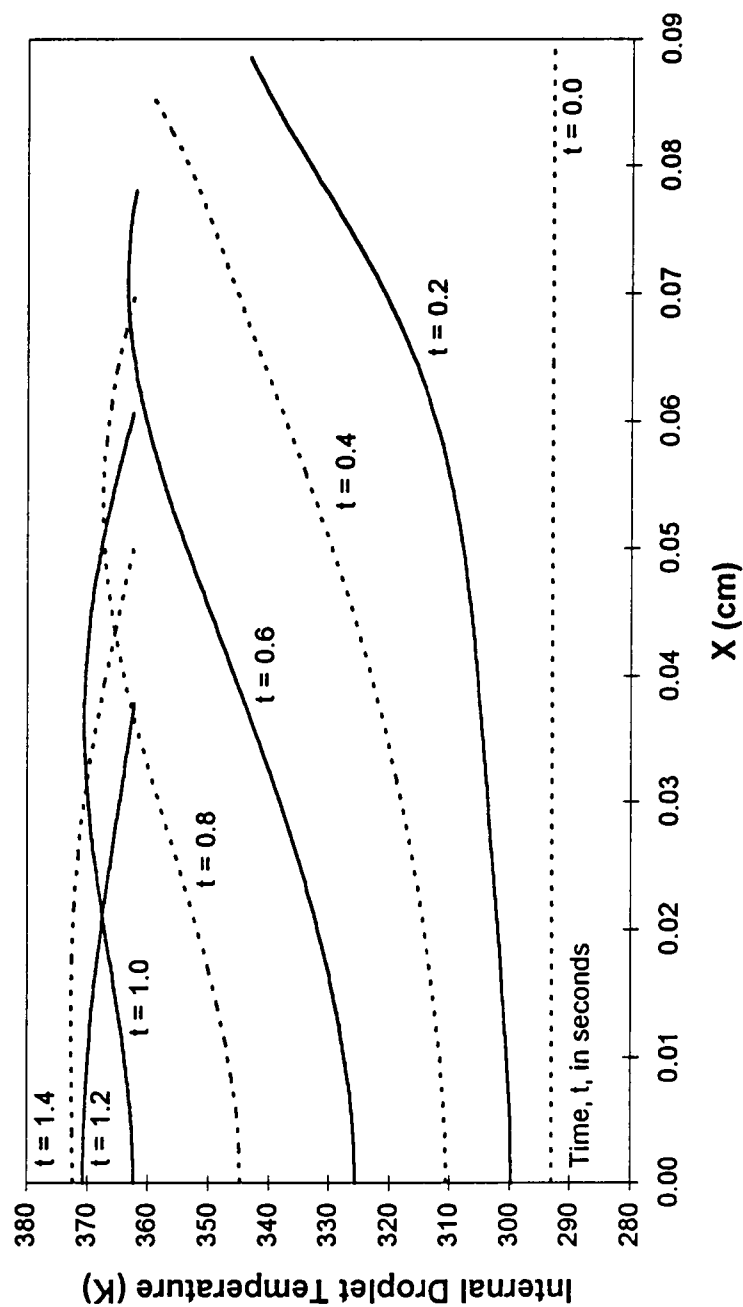


Figure 5.99. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K with Incident Radiation.

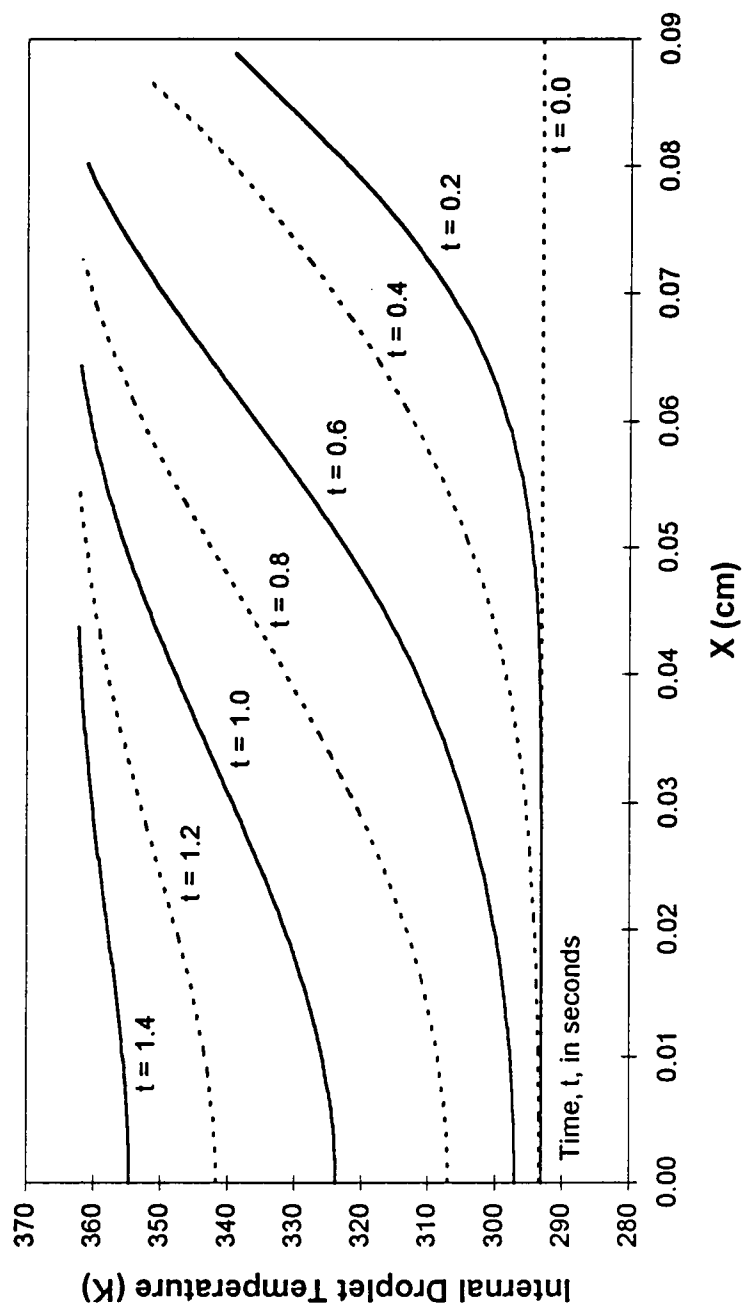


Figure 5.100. Temperature Profiles of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K without Incident Radiation.

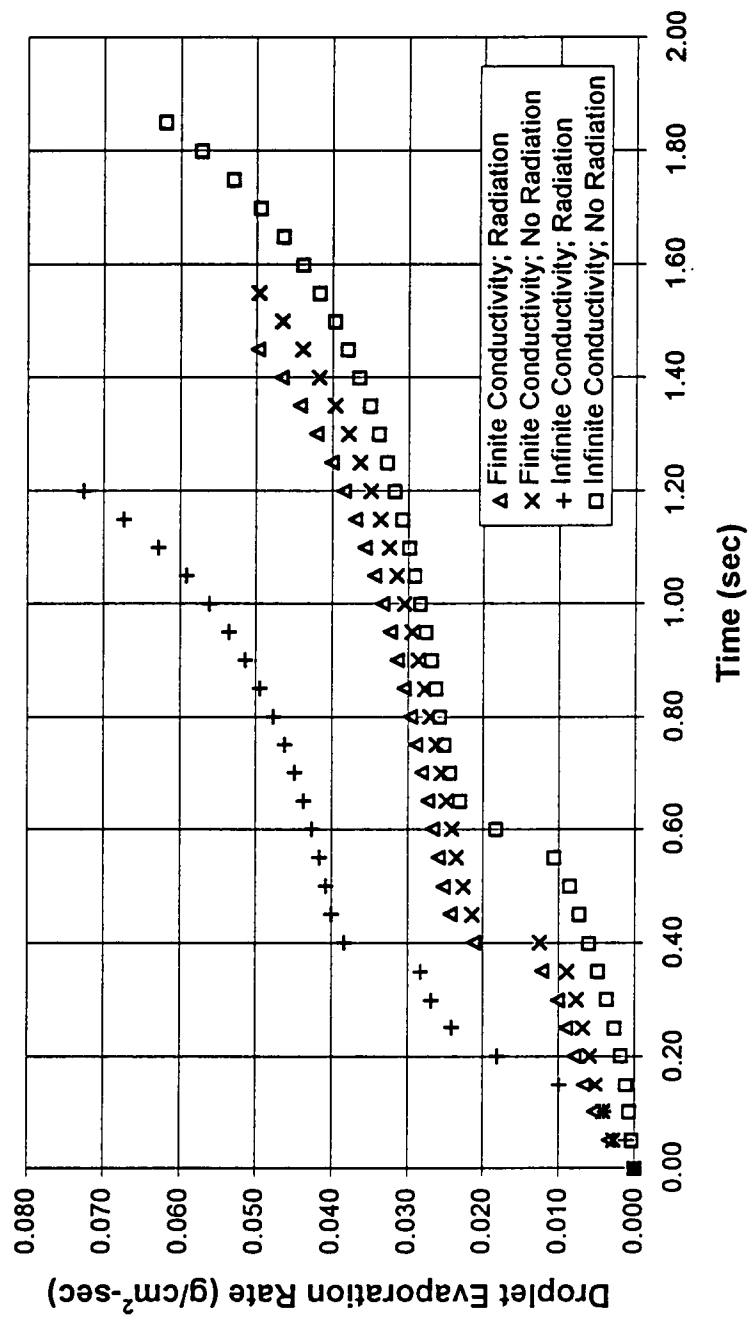


Figure 5.101. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

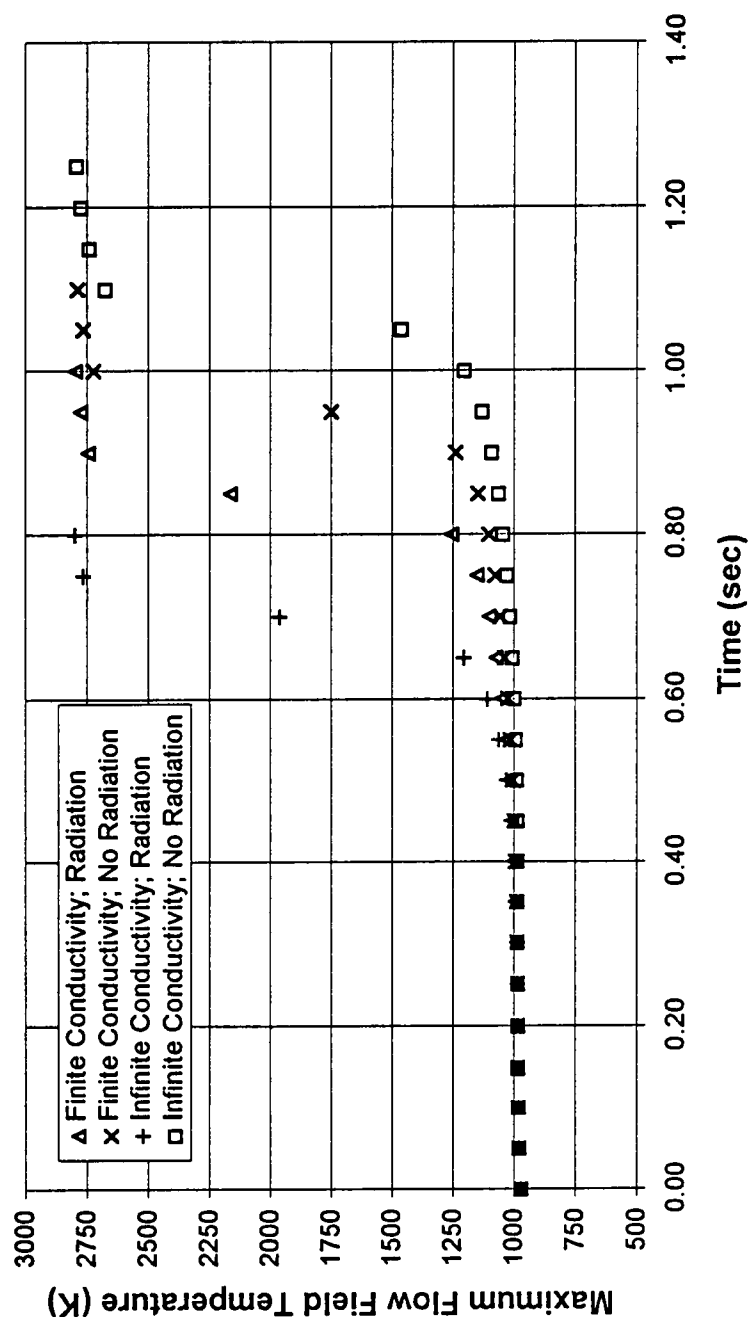


Figure 5.102. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

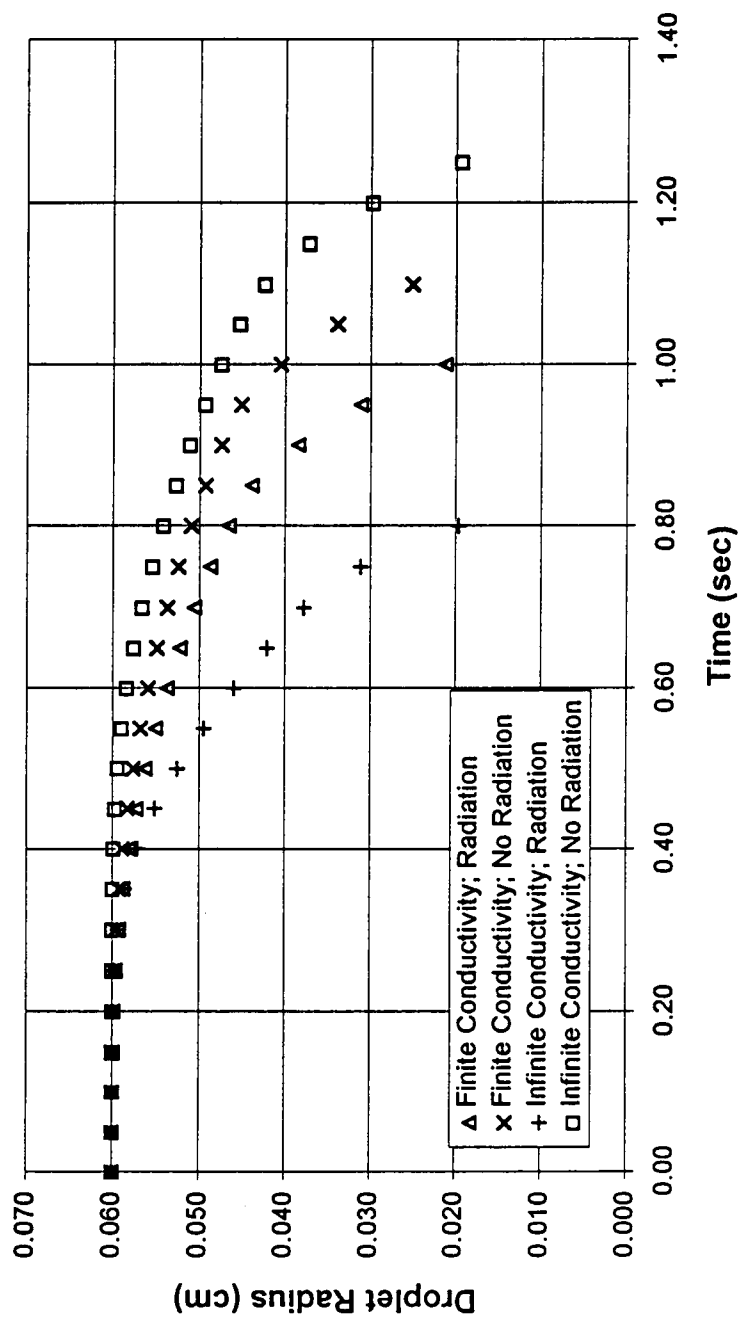


Figure 5.103. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

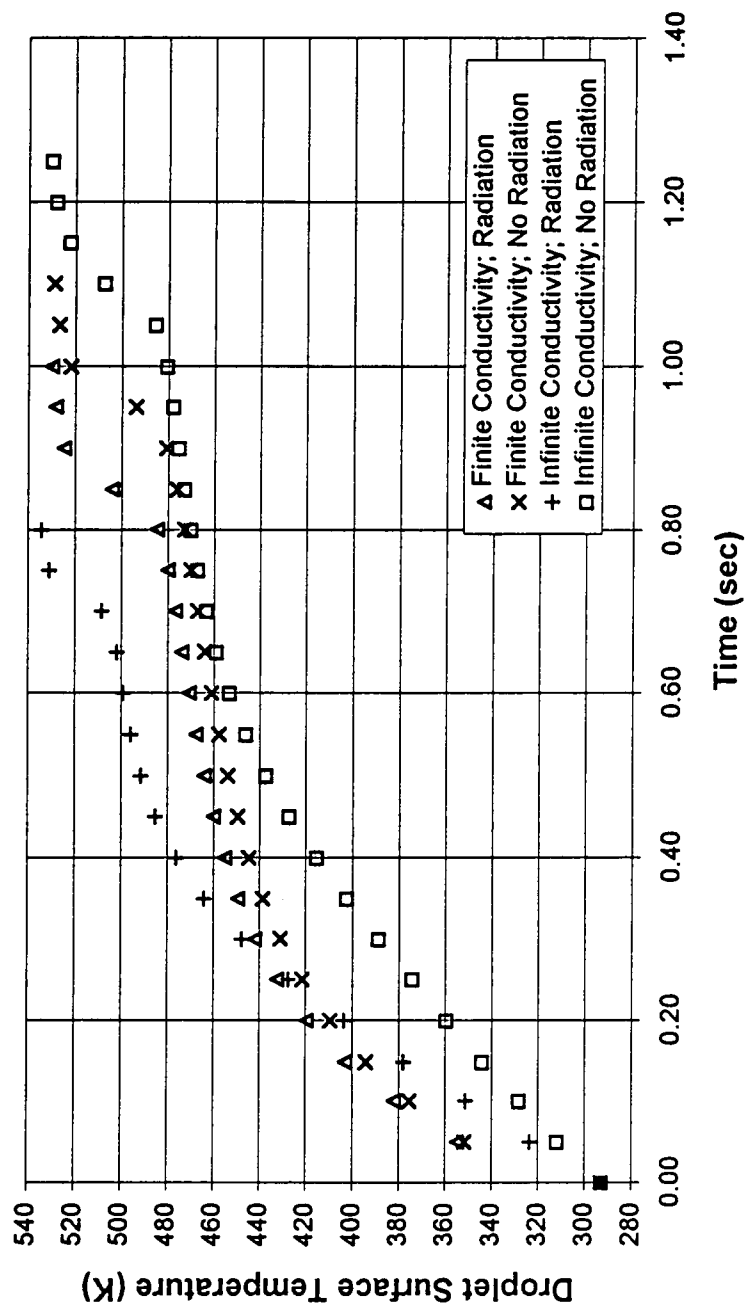


Figure 5.104. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

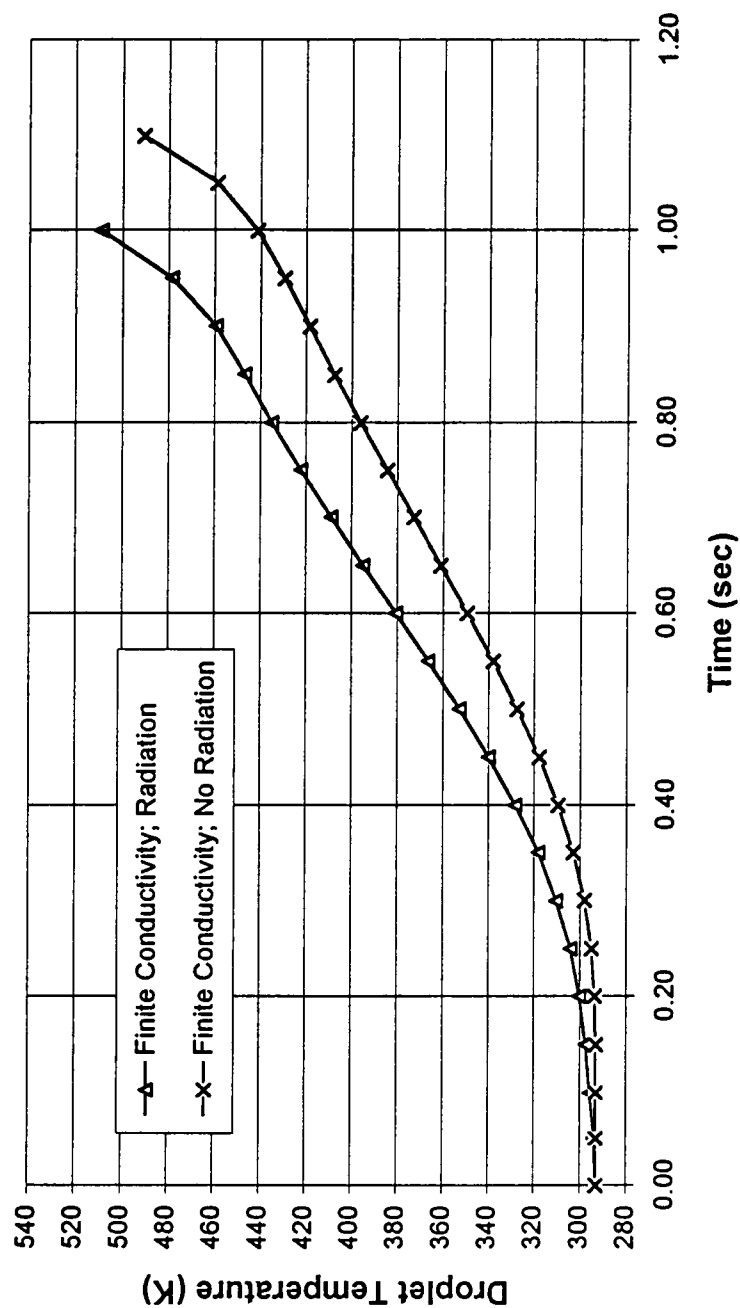


Figure 5.105. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

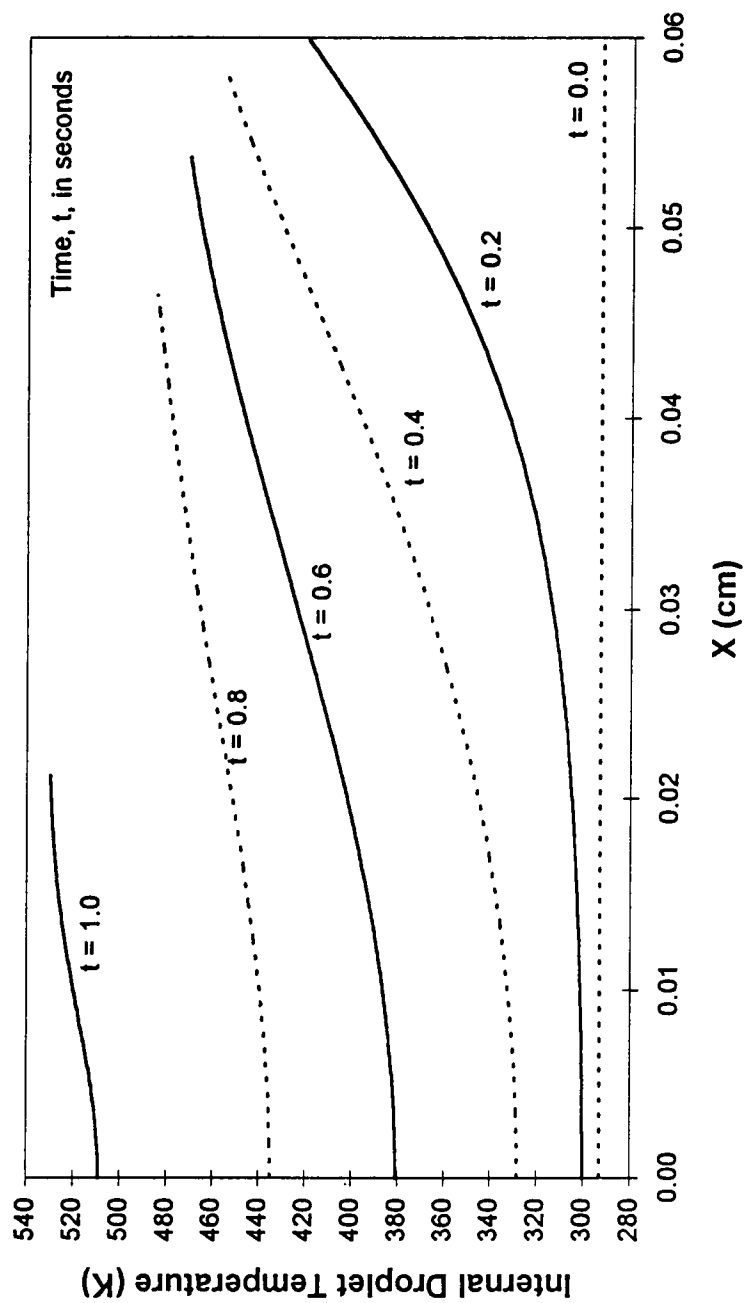


Figure 5.106. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K with Incident Radiation.

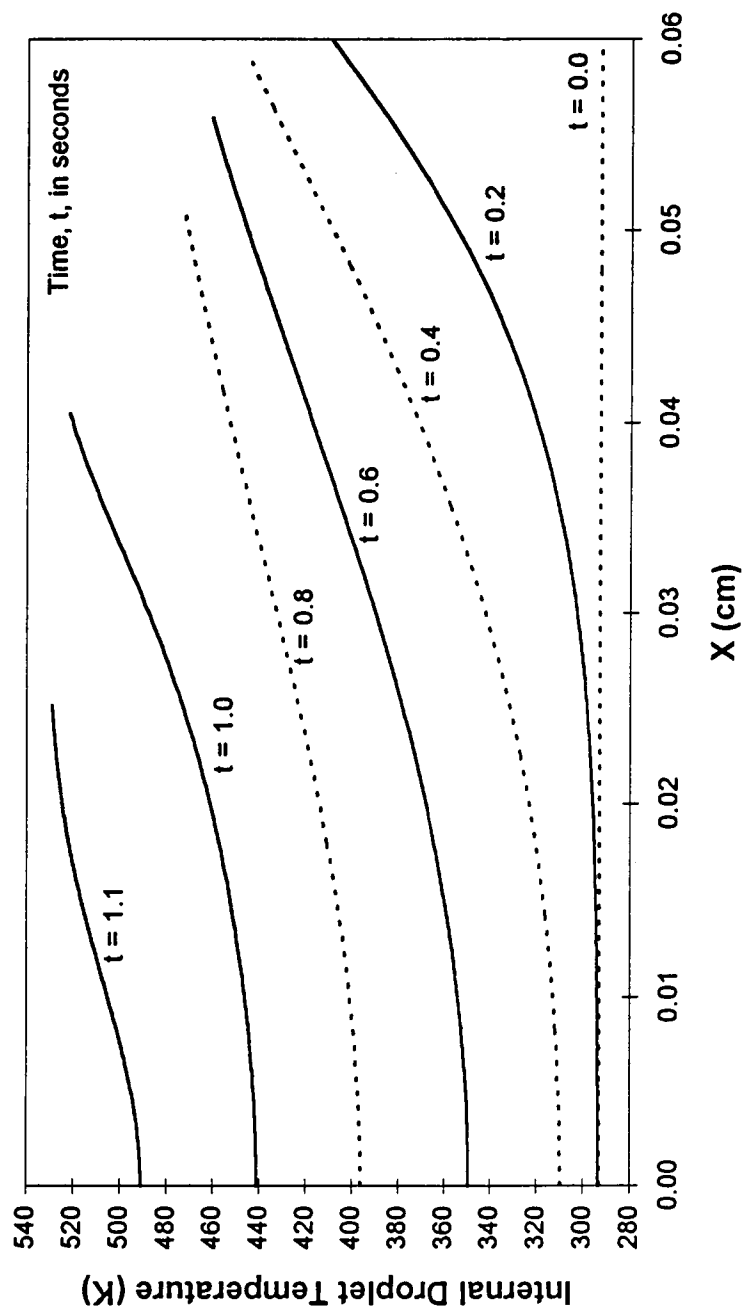


Figure 5.107. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K without Incident Radiation.

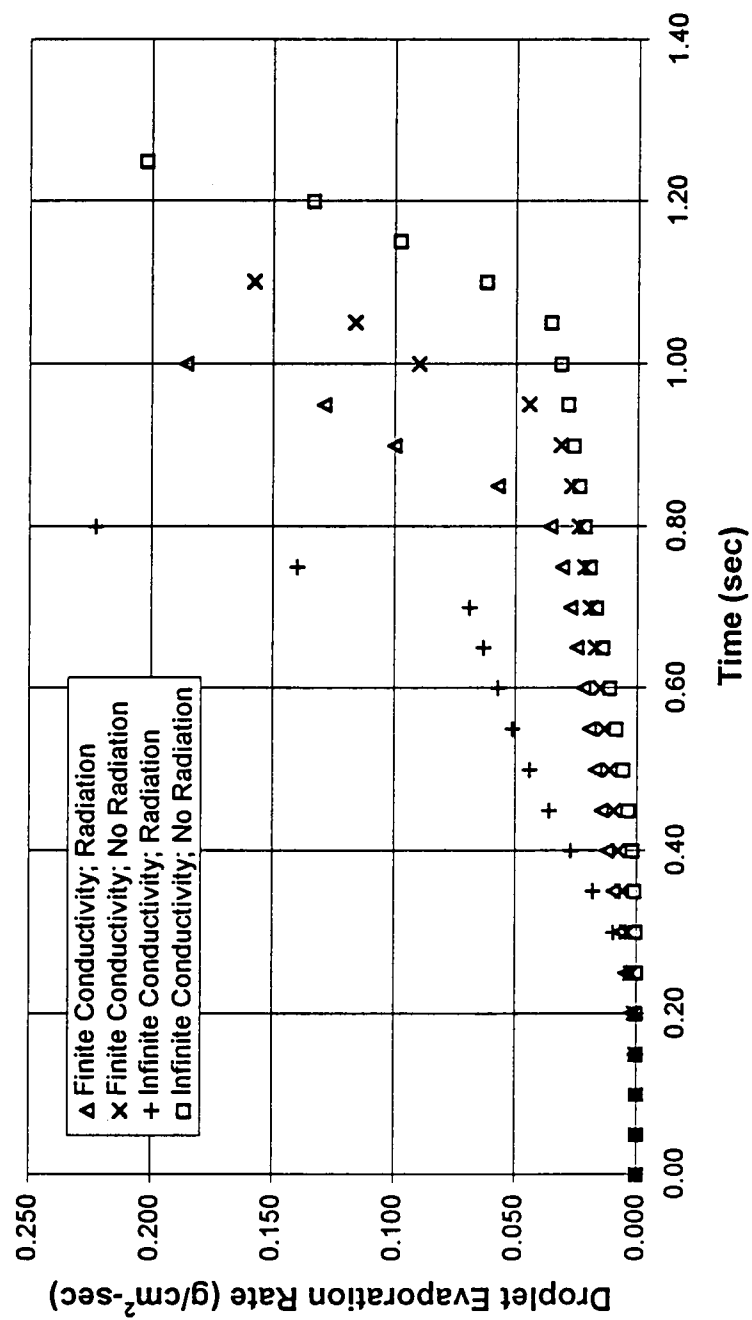


Figure 5.108. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

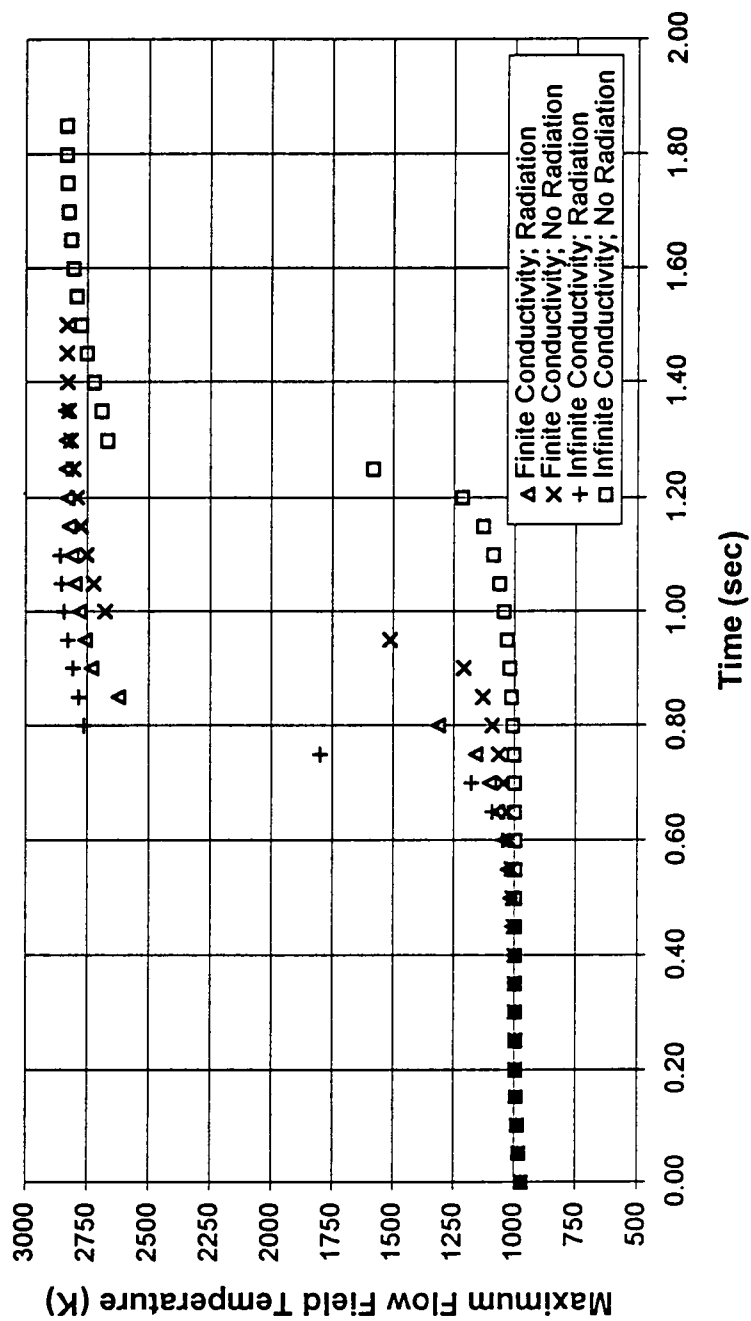


Figure 5.109. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

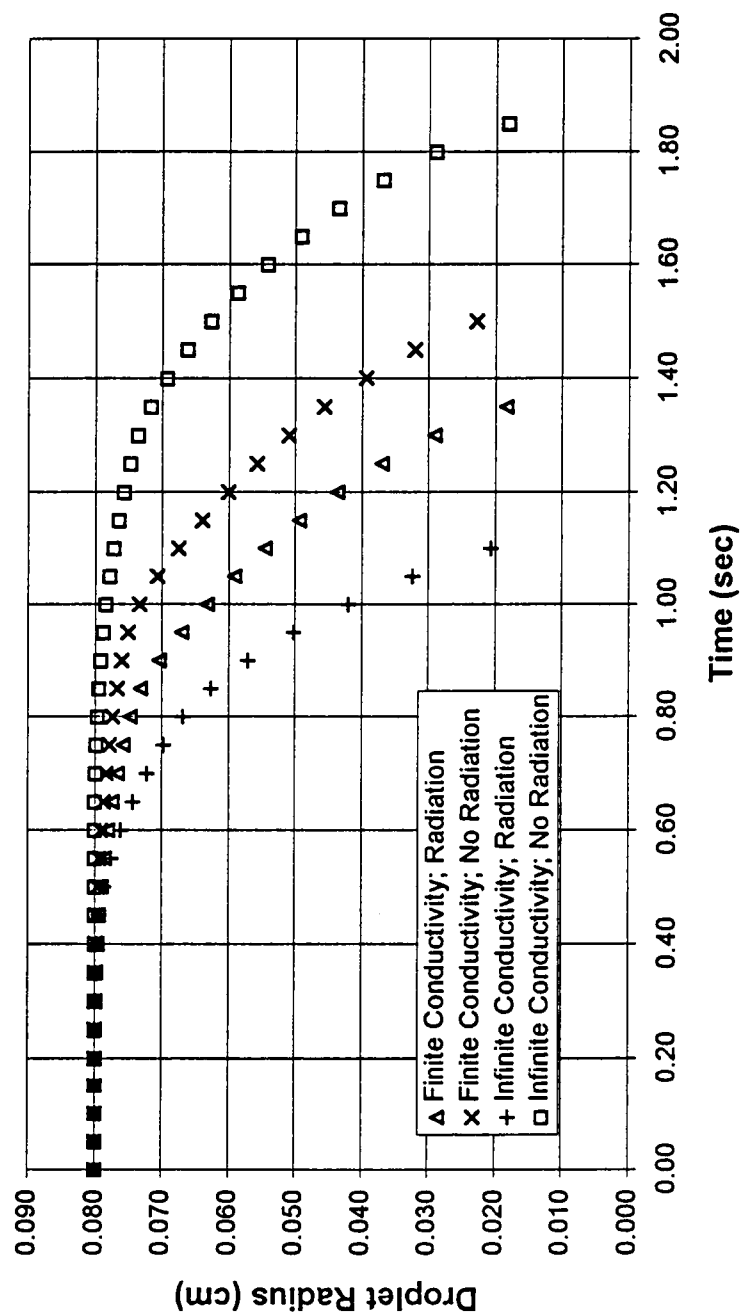


Figure 5.110. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

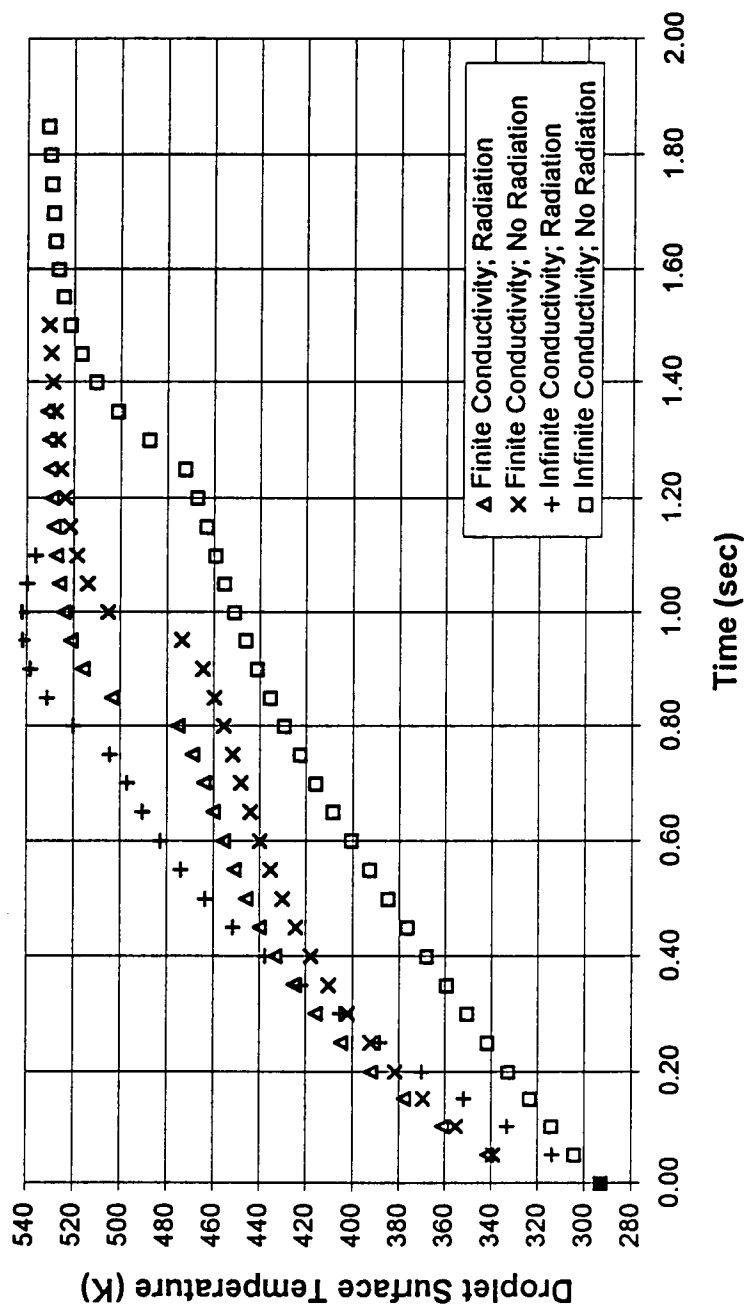


Figure 5.111. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

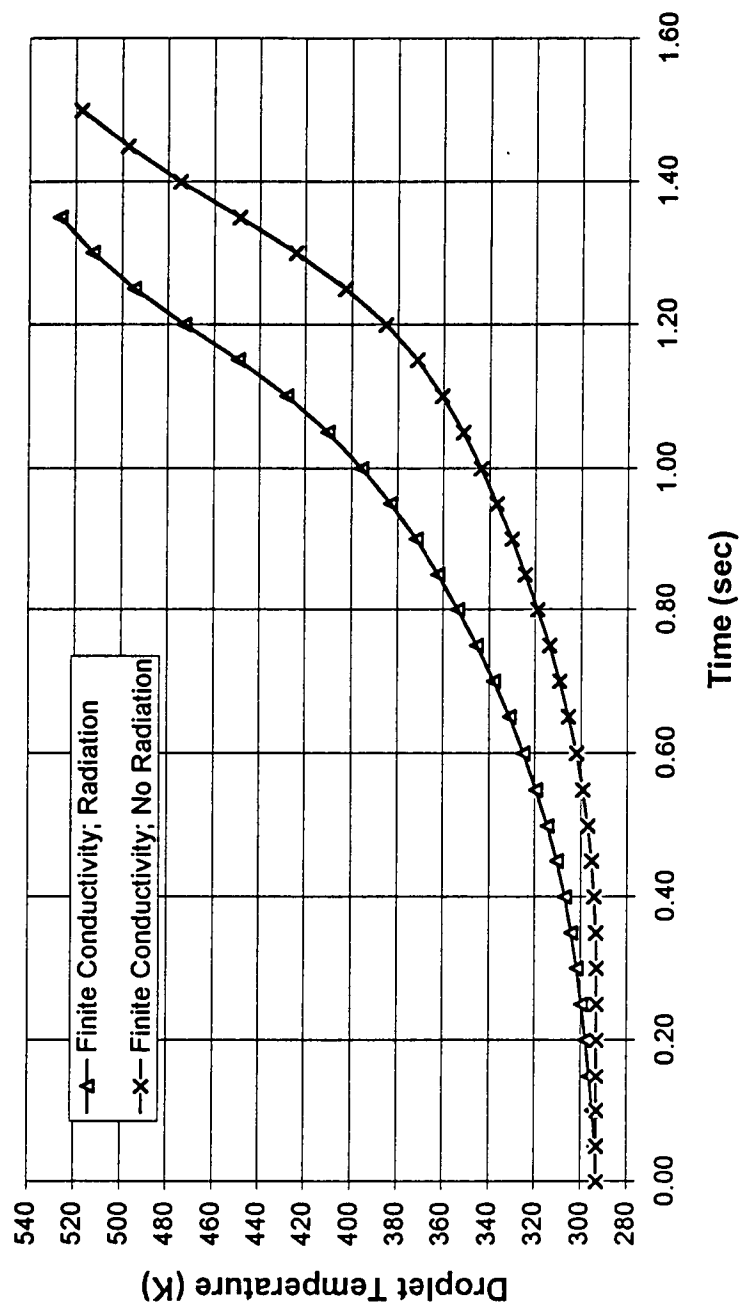


Figure 5.112. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

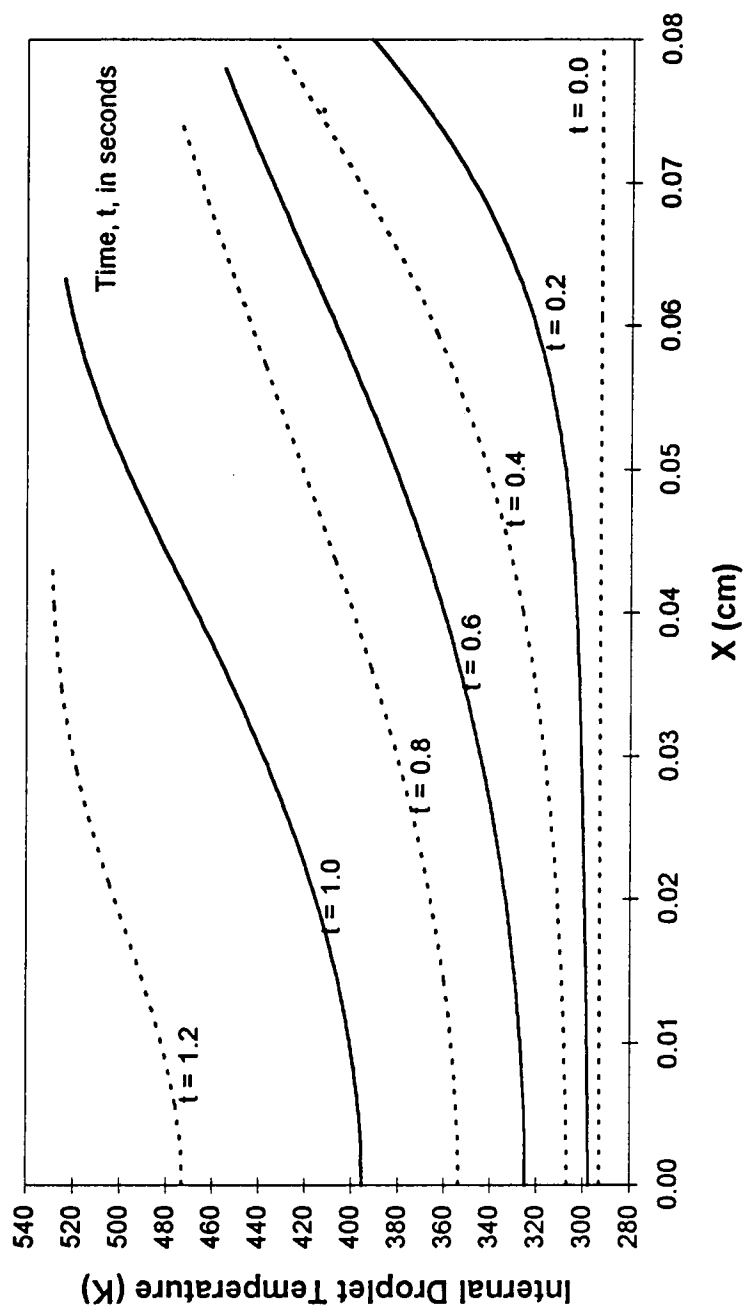


Figure 5.113. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K with Incident Radiation.

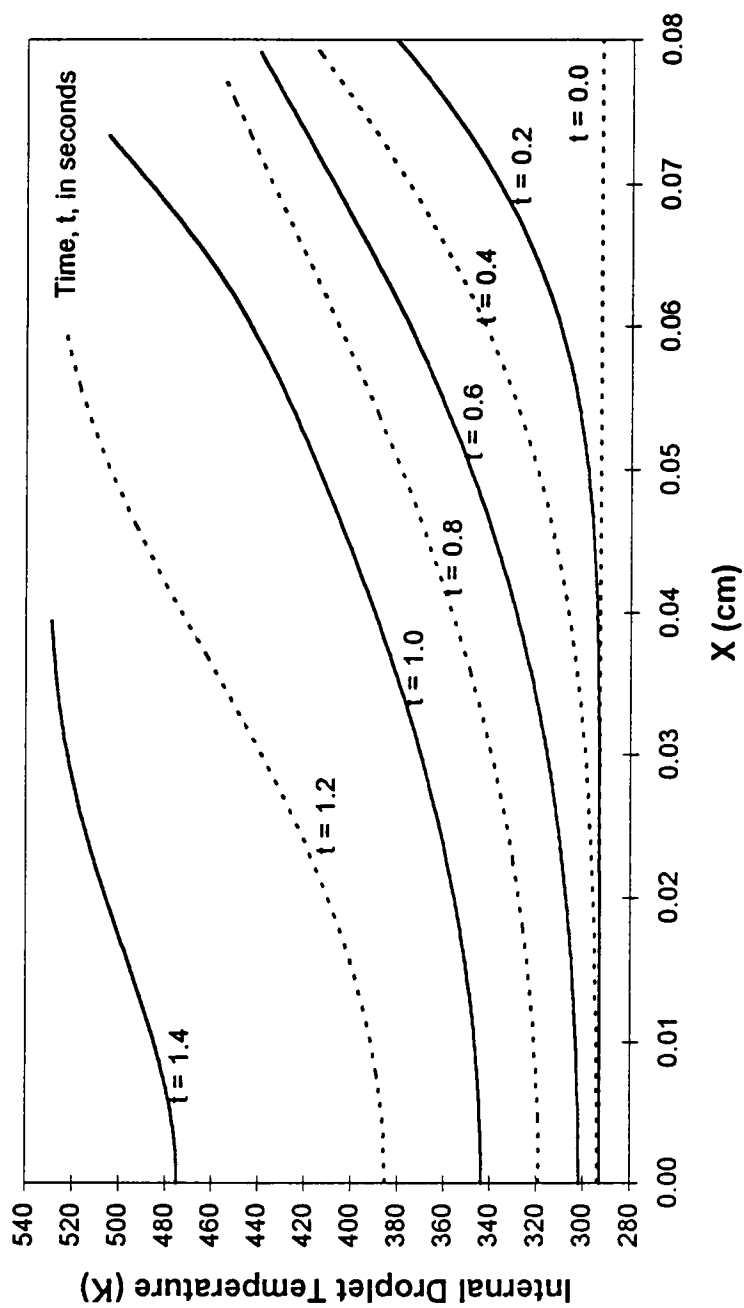


Figure 5.114. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K without Incident Radiation.

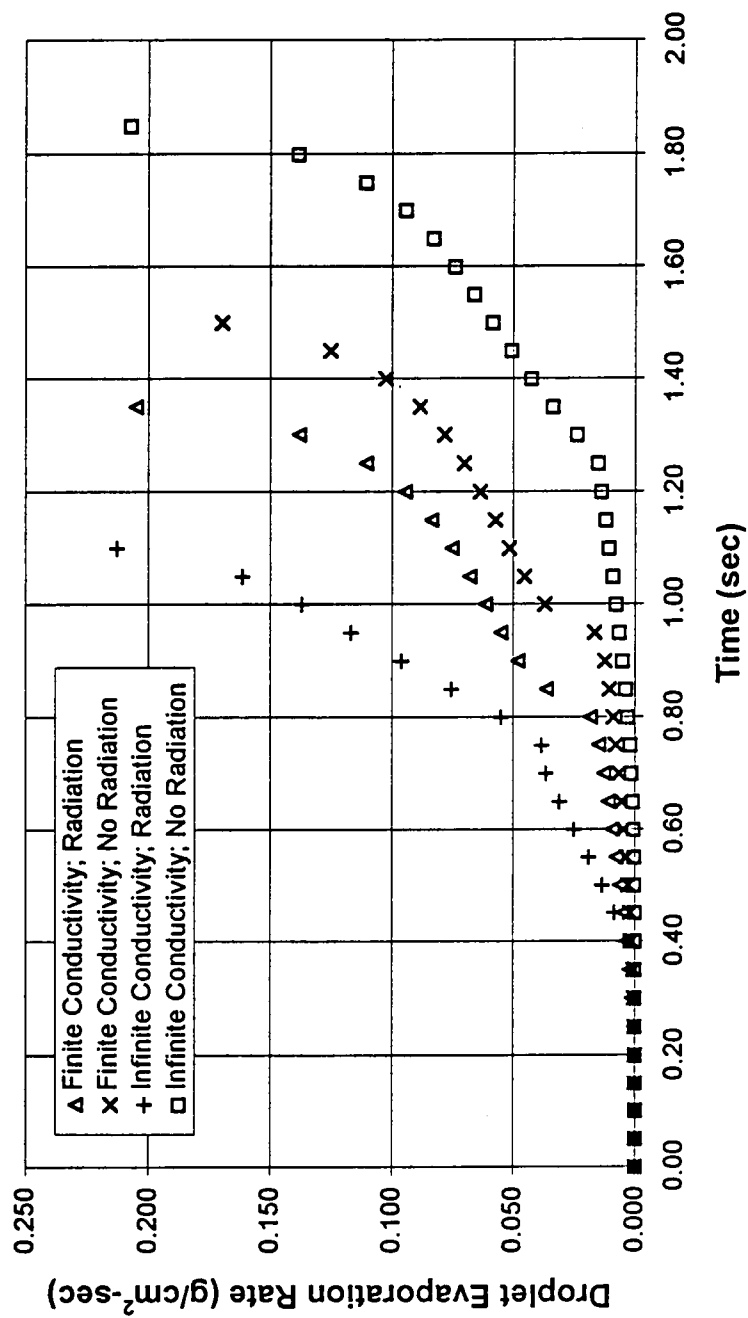


Figure 5.115. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

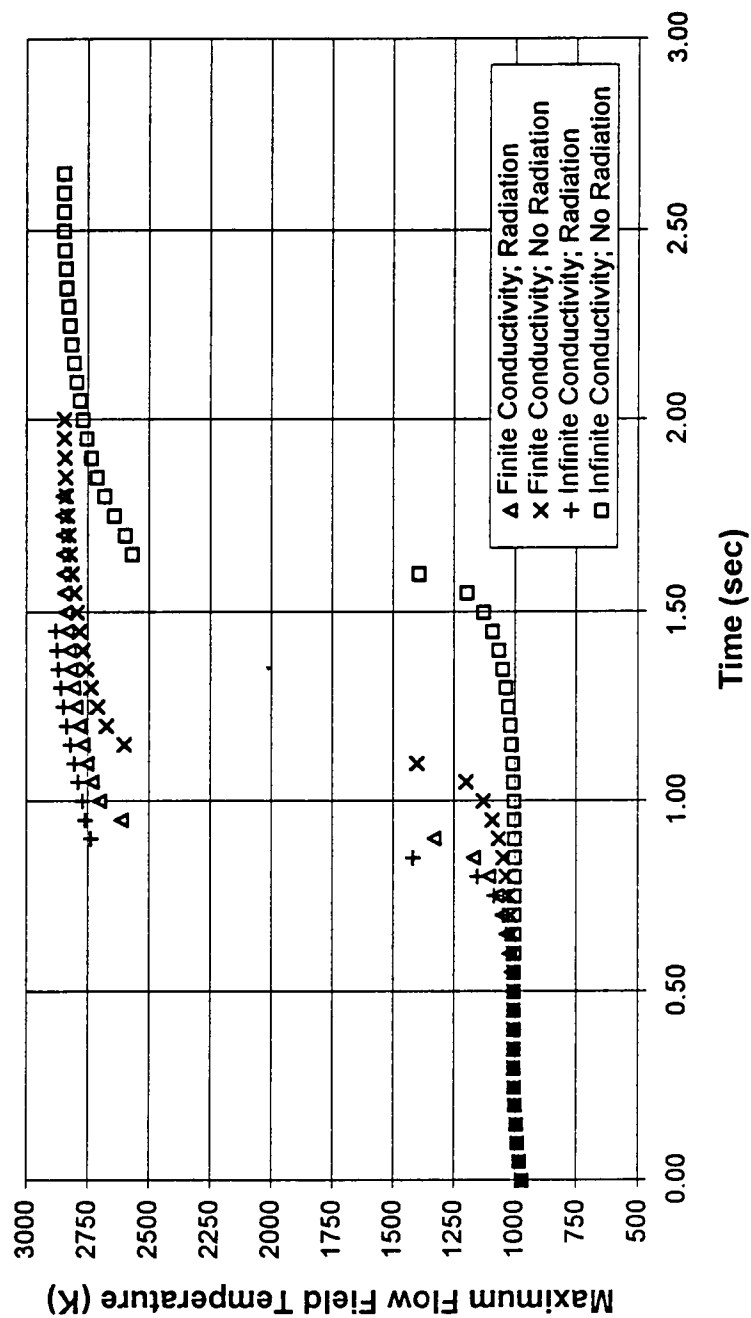


Figure 5.116. Effects of Finite Droplet Conductivity and Radiation on Ignition Delay of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

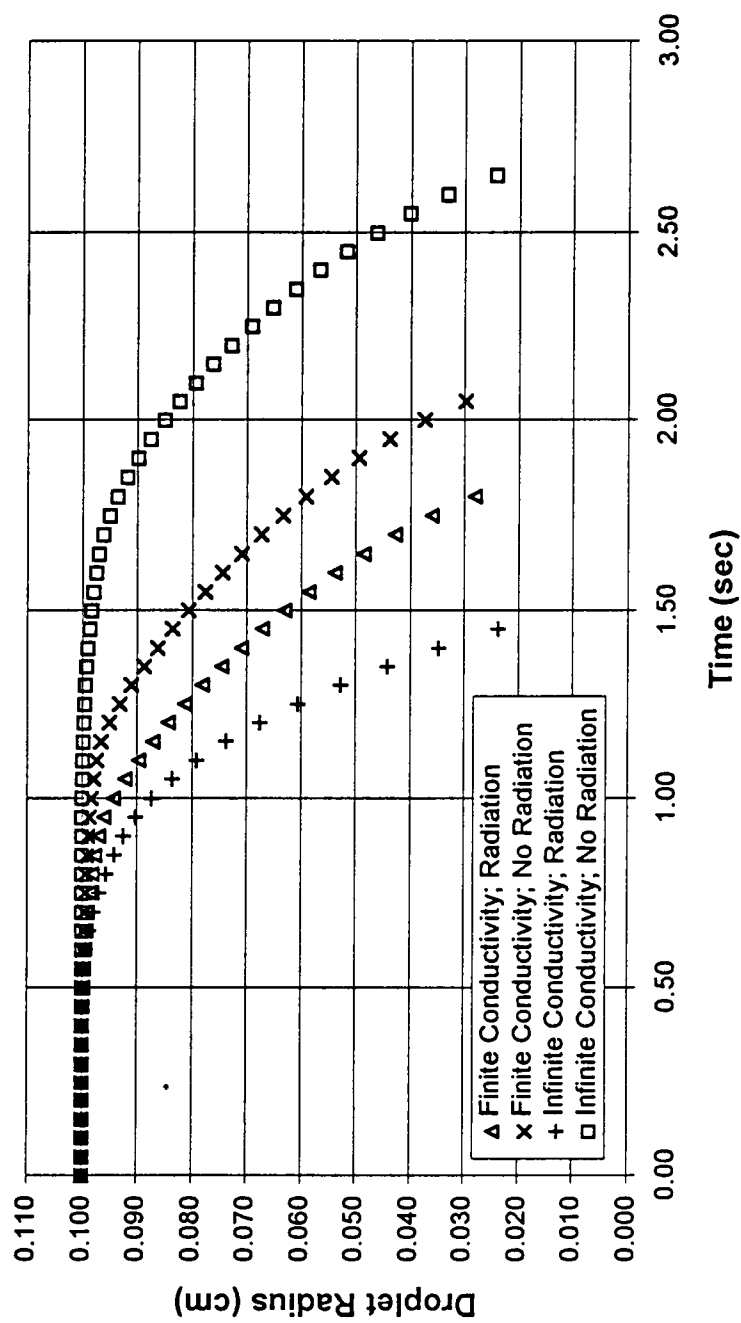


Figure 5.117. Effects of Finite Droplet Conductivity and Radiation on Surface Regression of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

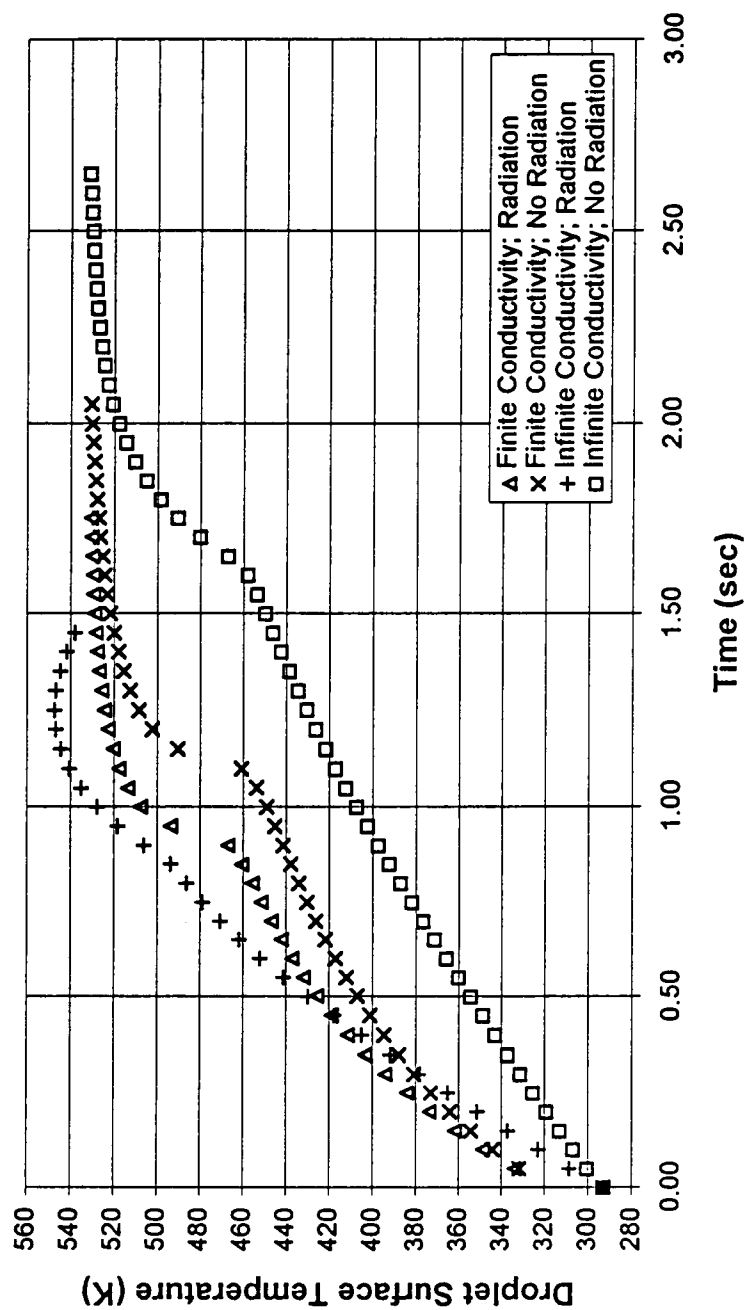


Figure 5.118. Effects of Finite Droplet Conductivity and Radiation on Surface Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

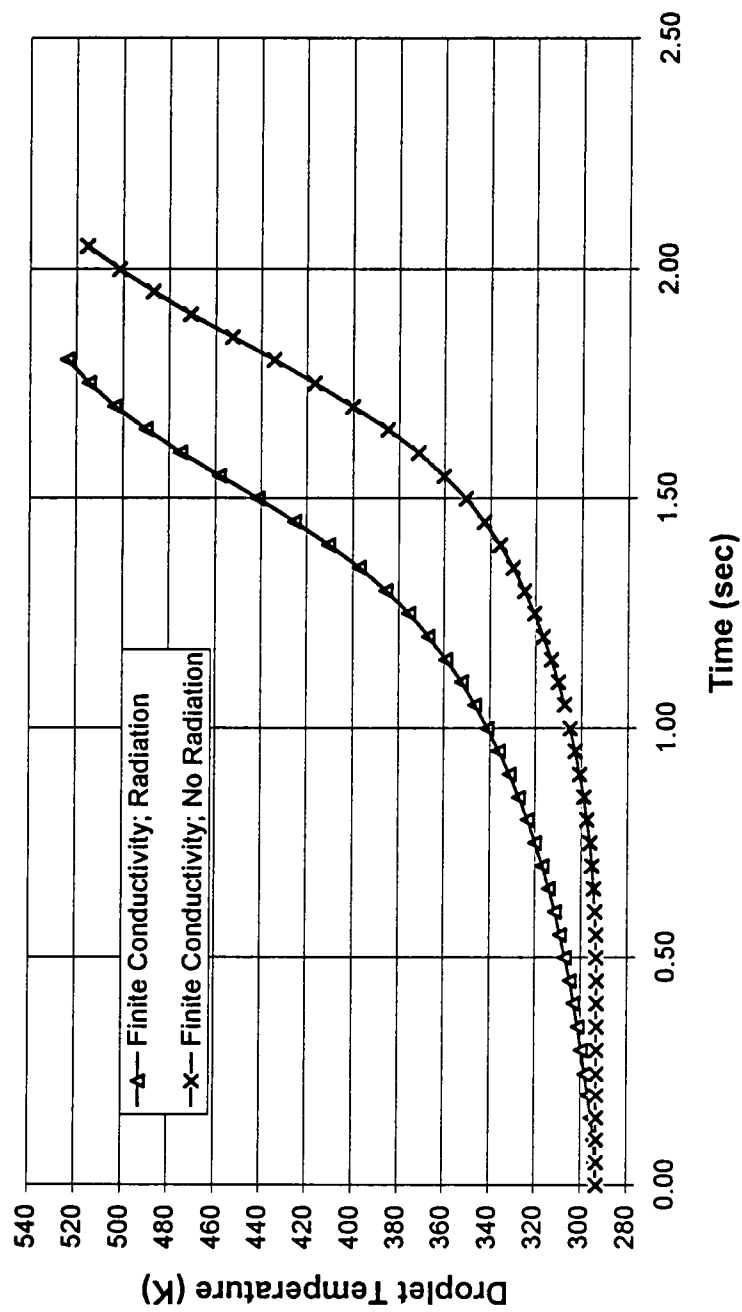


Figure 5.119. Effects of Finite Droplet Conductivity and Radiation on Center Temperature of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

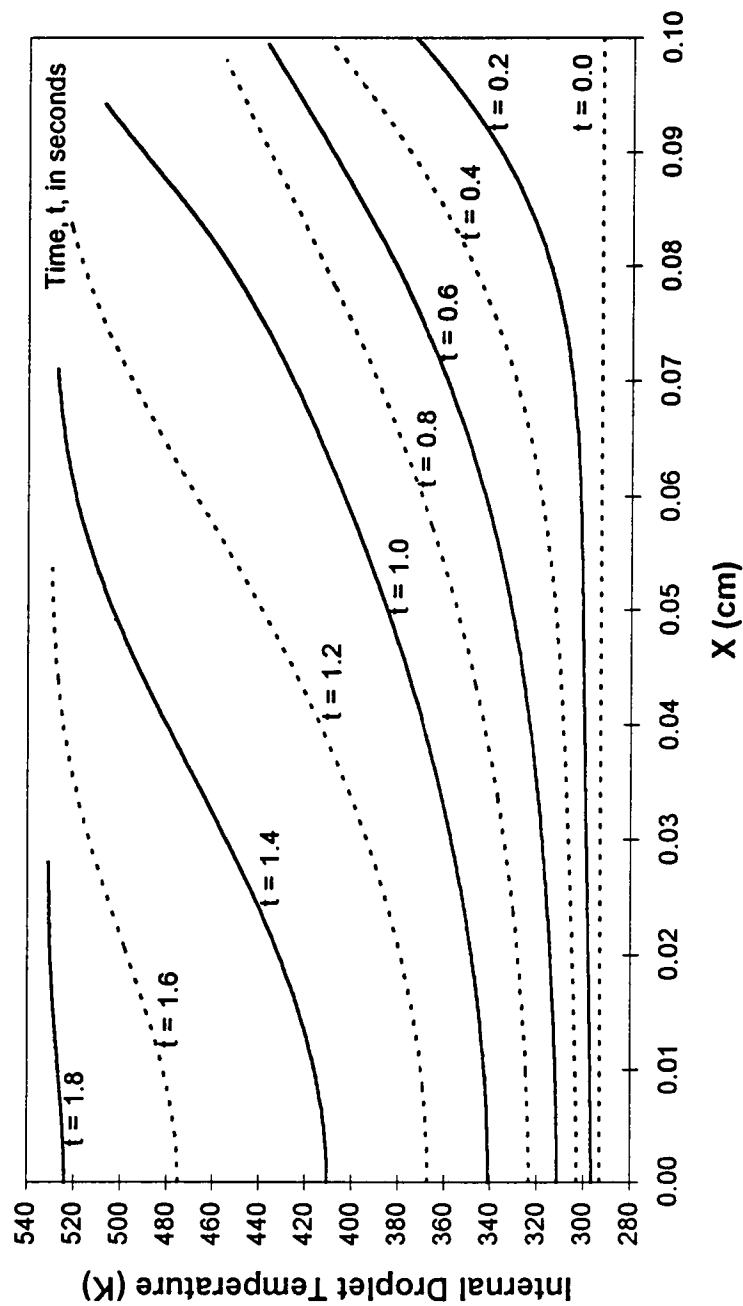


Figure 5.120. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K with Incident Radiation.

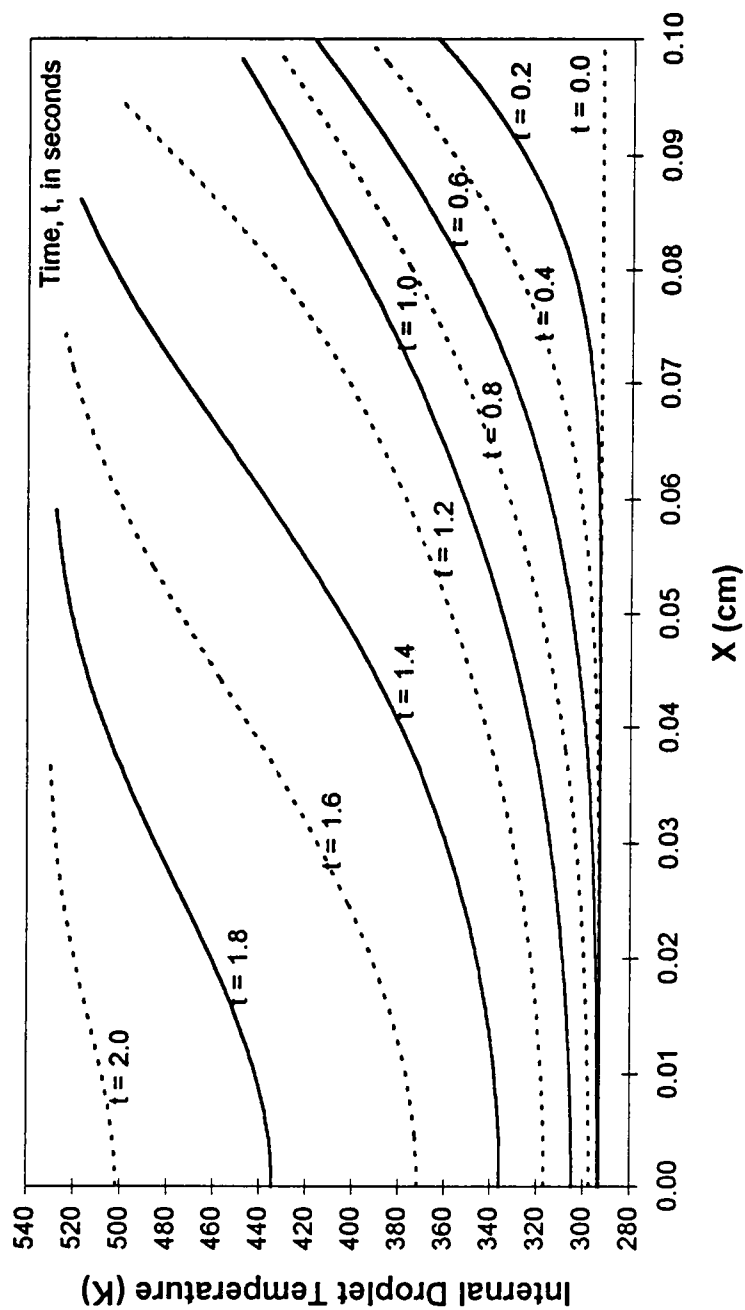


Figure 5.121. Temperature Profiles of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K without Incident Radiation.

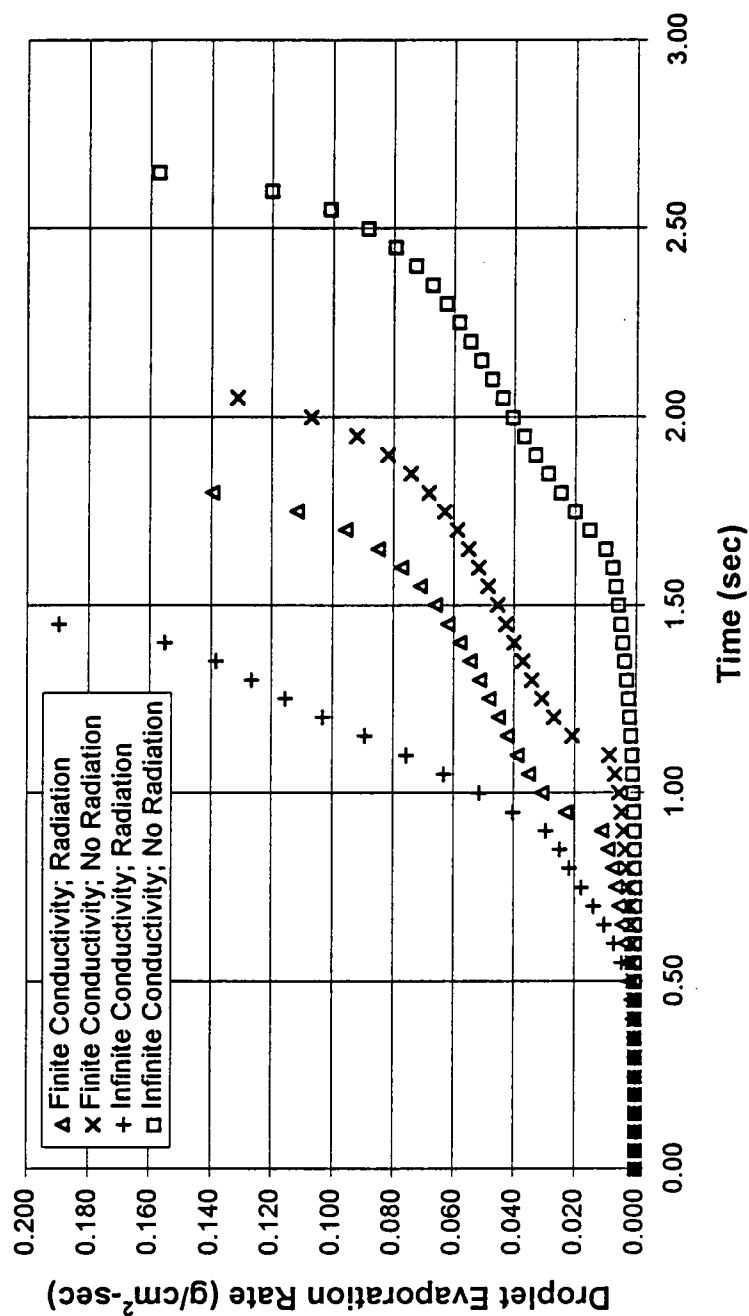


Figure 5.122. Effects of Finite Droplet Conductivity and Radiation on Evaporation Rate of an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

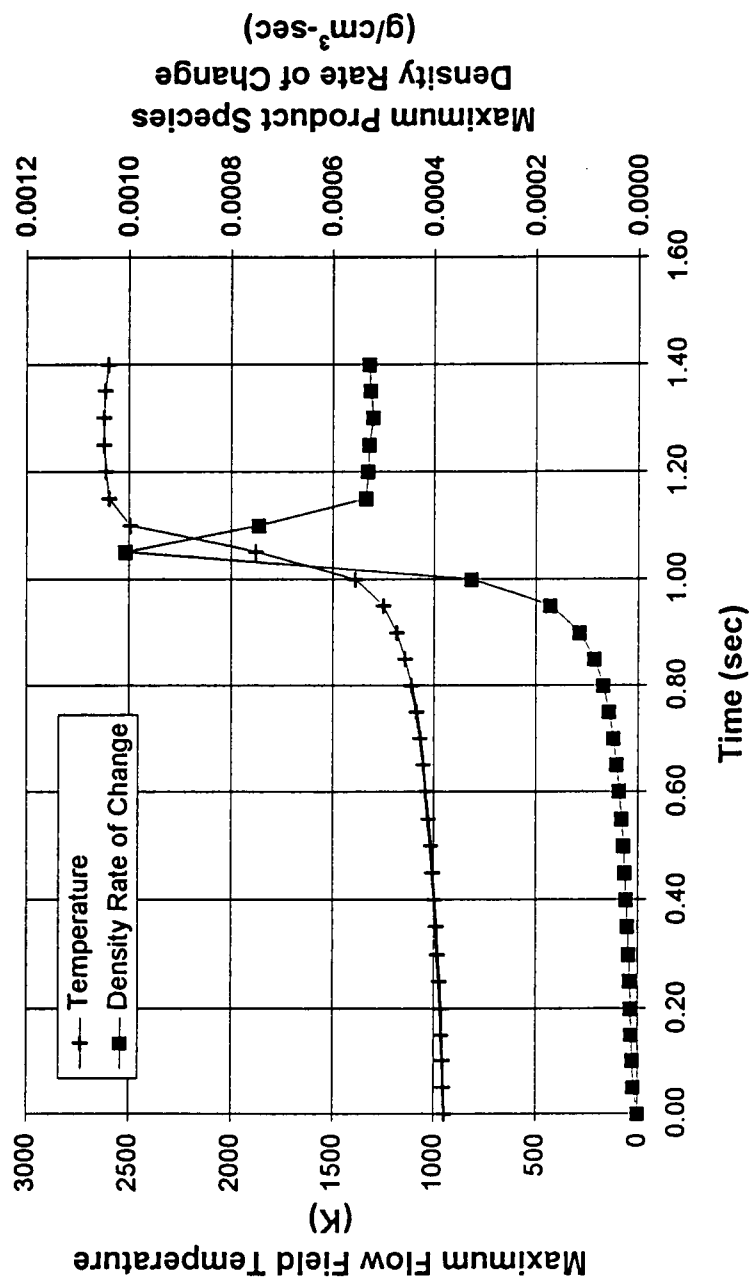


Figure 5.123. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

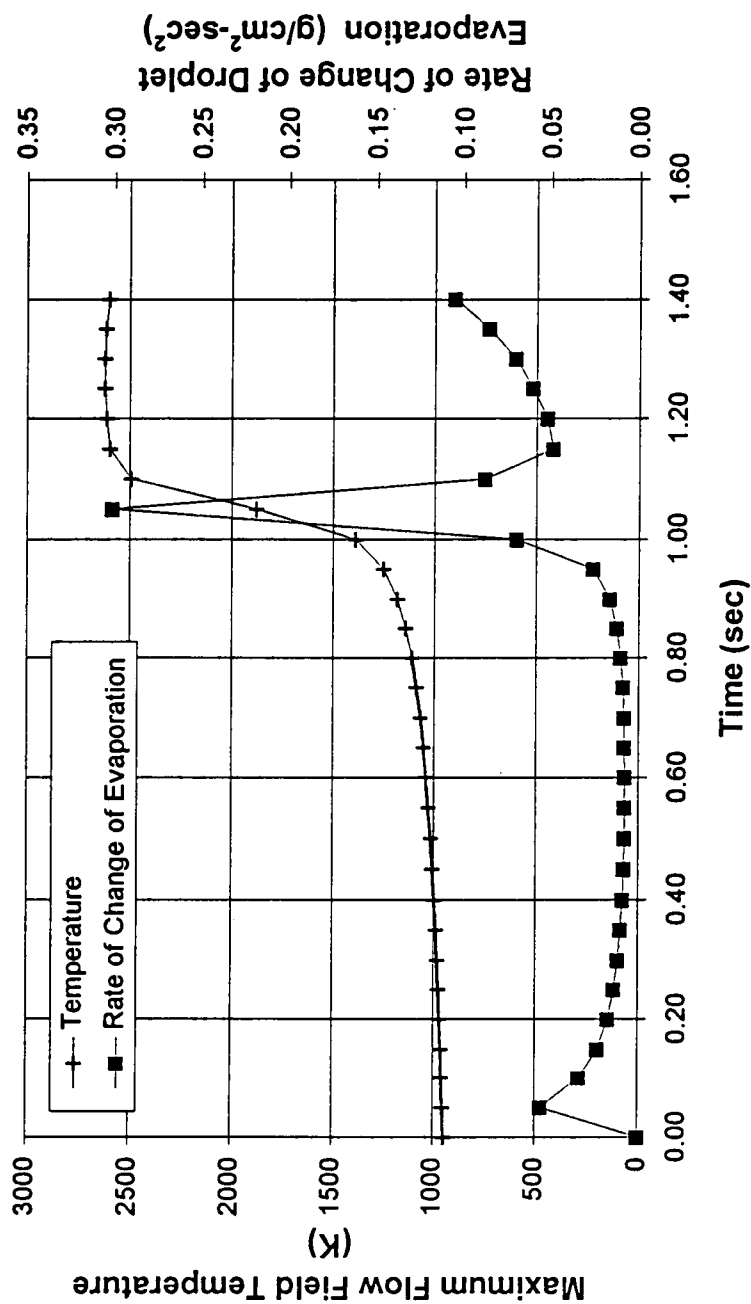


Figure 5.124. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 948 K.

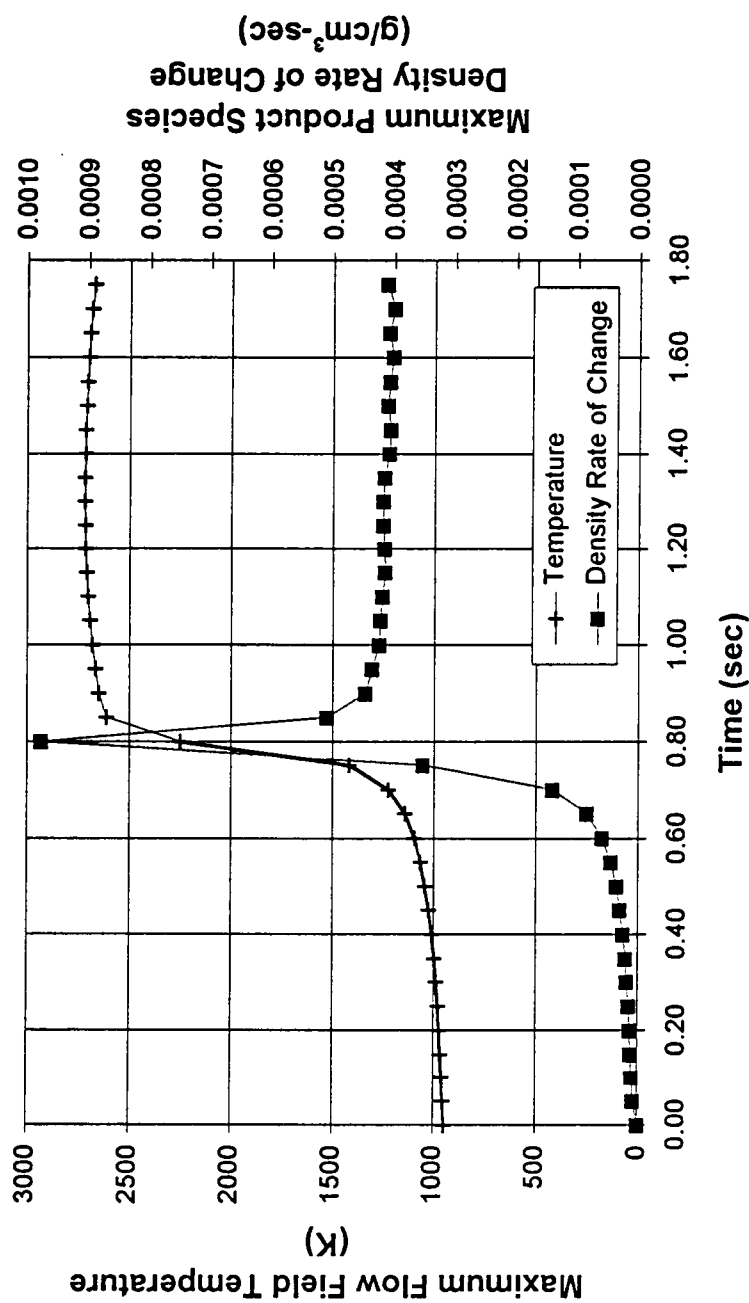


Figure 5.125. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

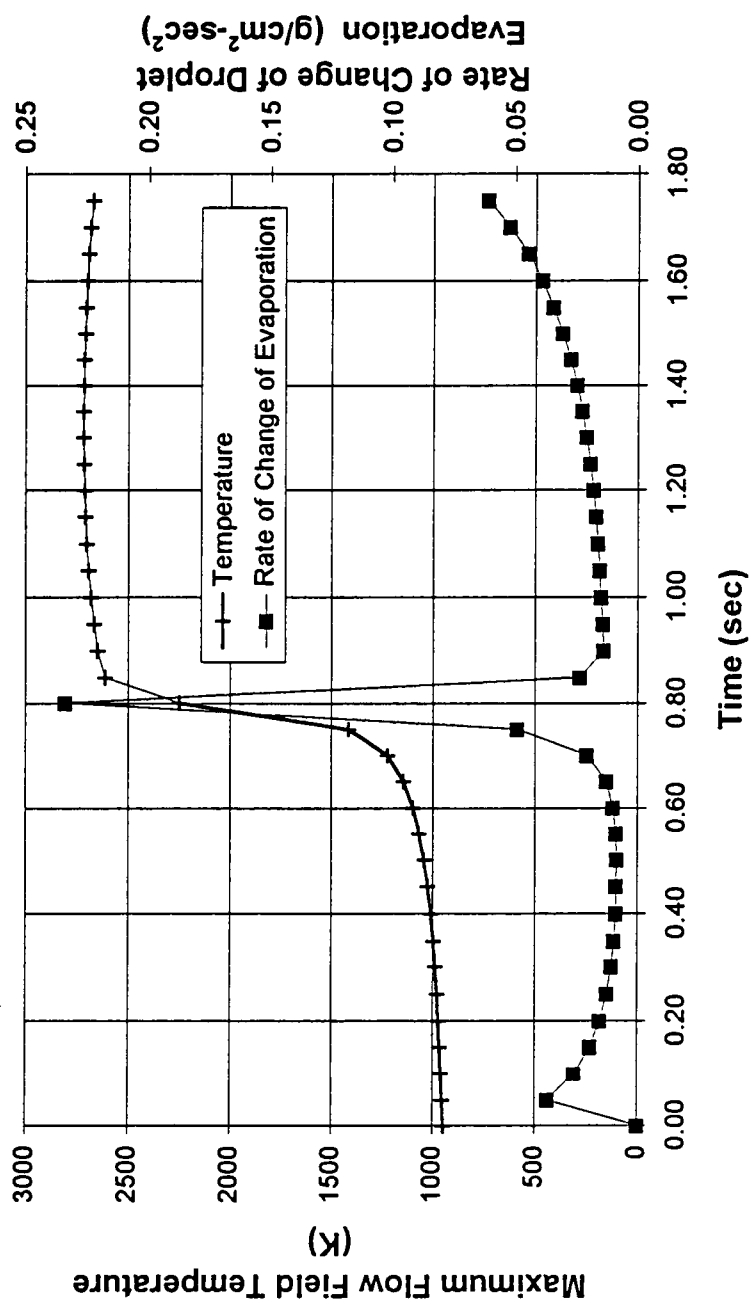


Figure 5.126. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 948 K.

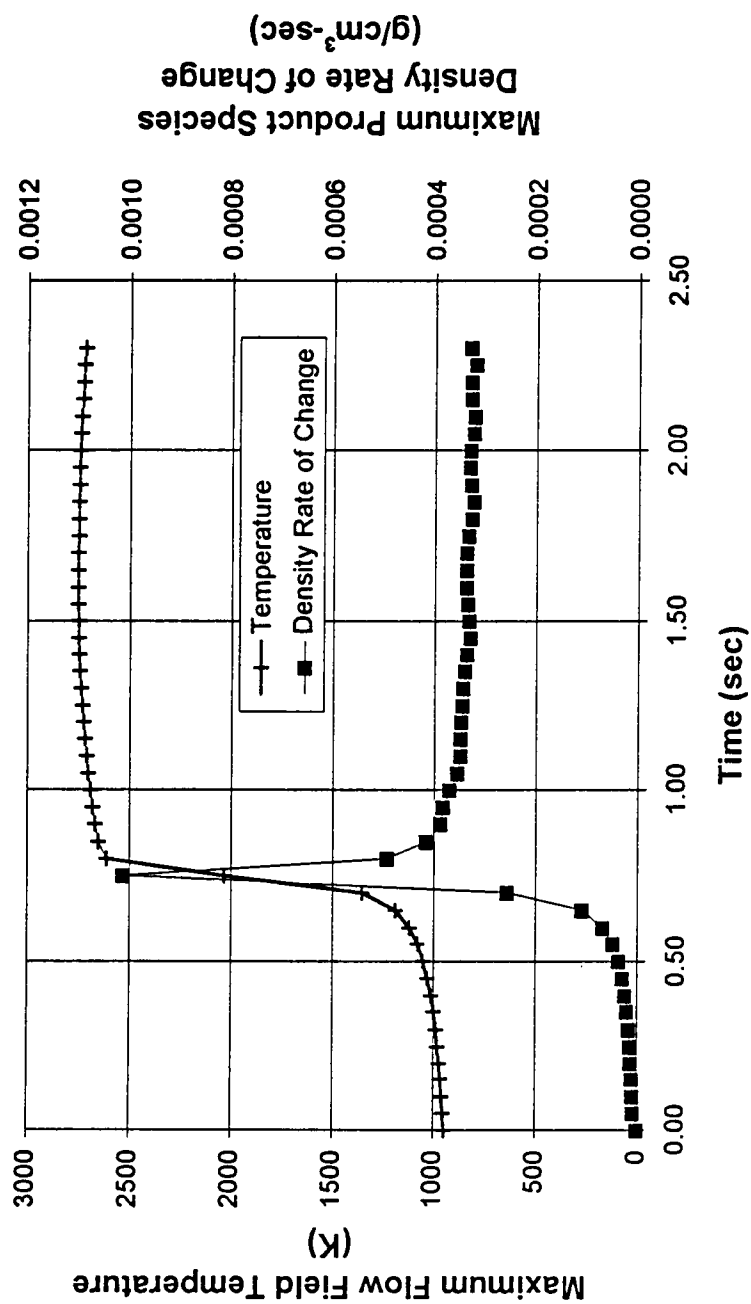


Figure 5.127. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

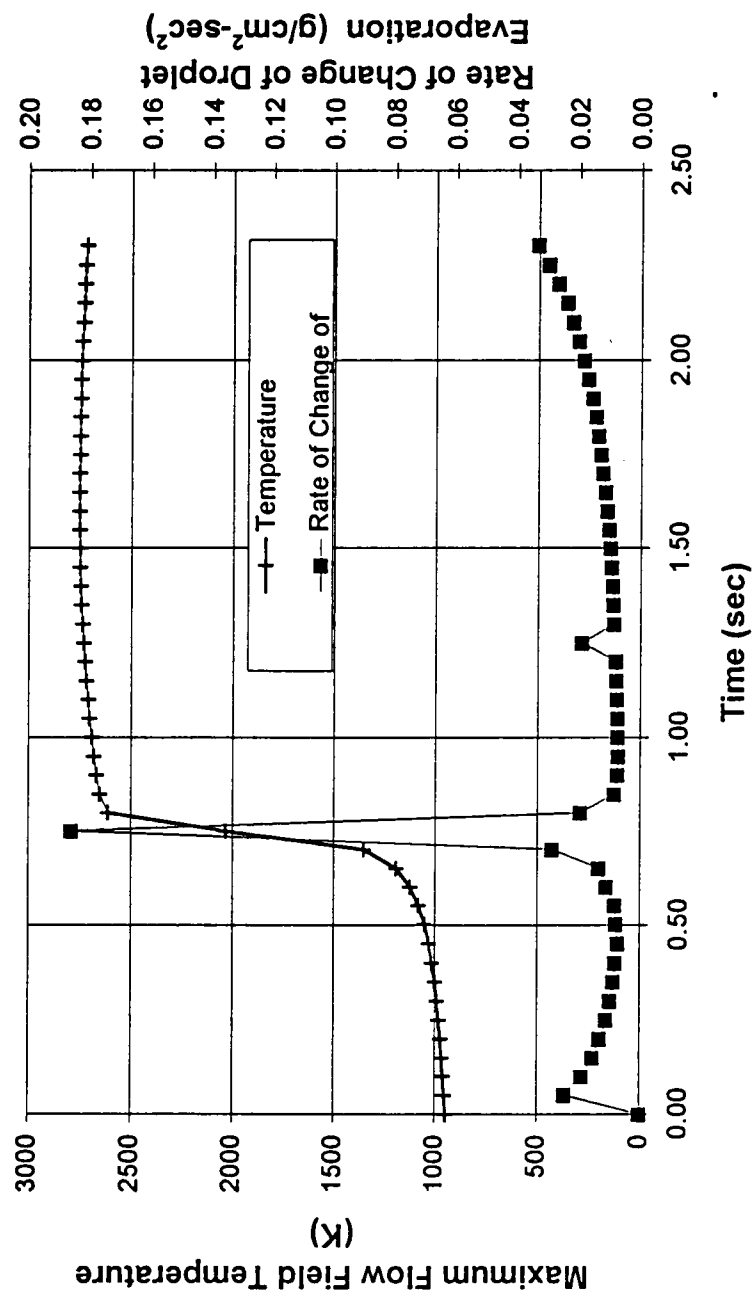


Figure 5.128. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.11 cm in Air at 948 K.

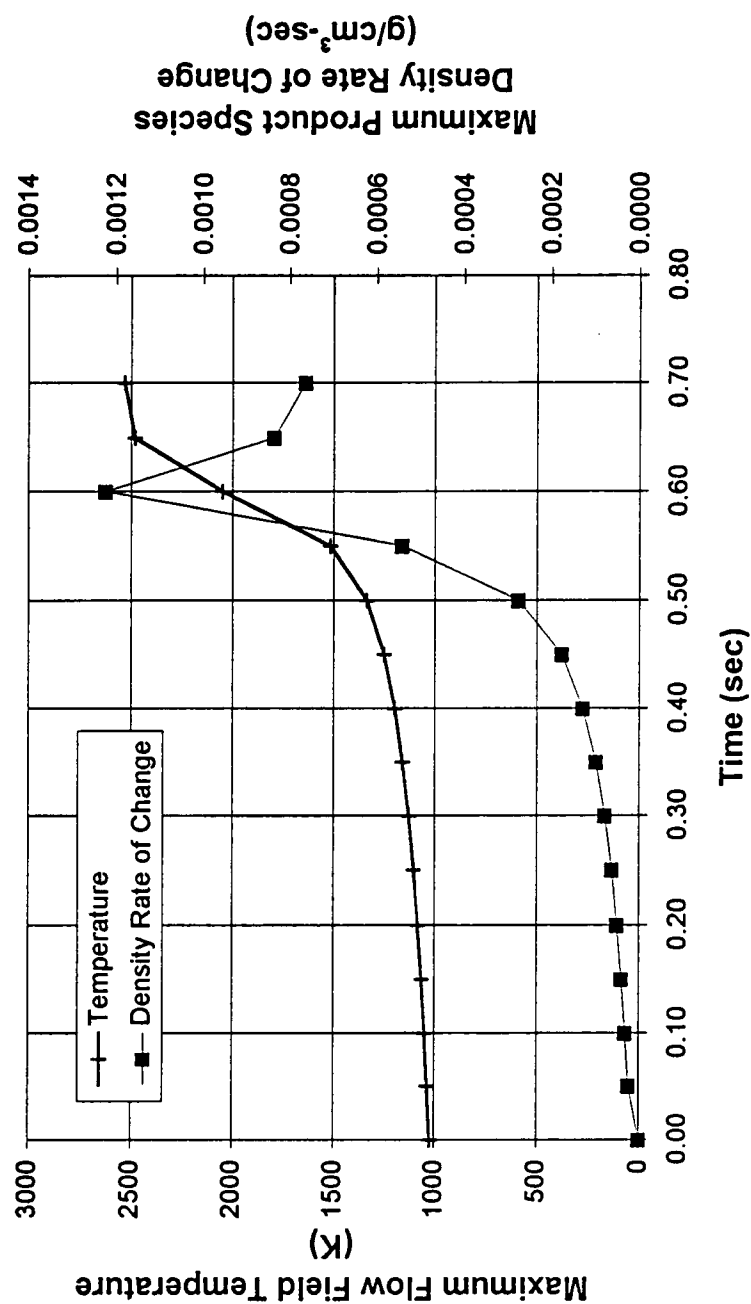


Figure 5.129. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

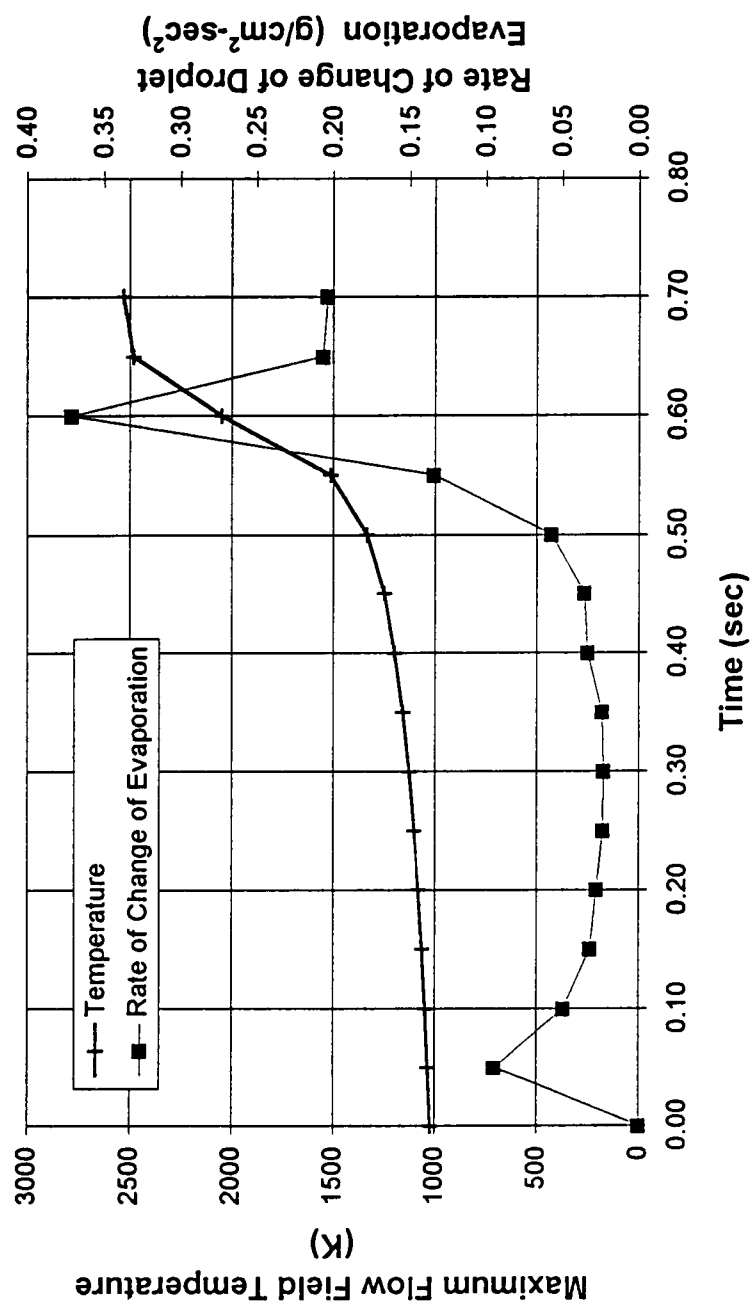


Figure 5.130. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.05 cm in Air at 1023 K.

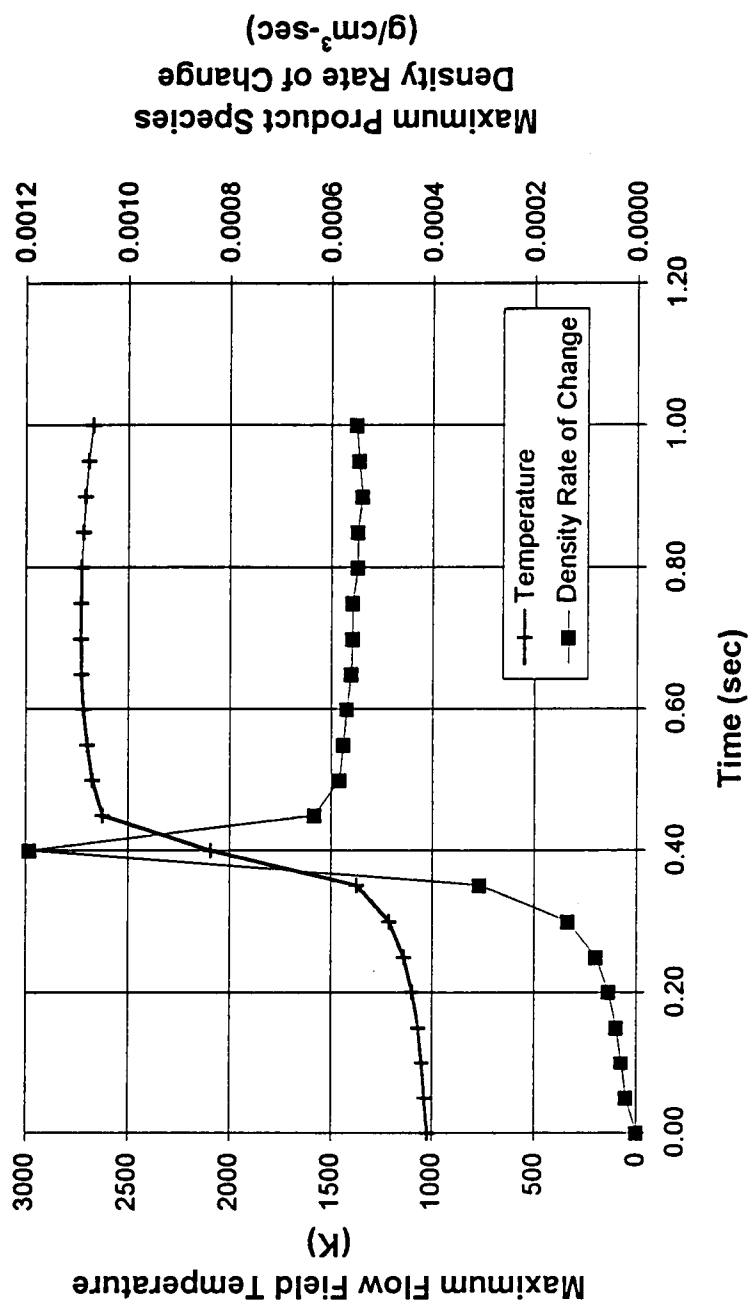


Figure 5.131. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

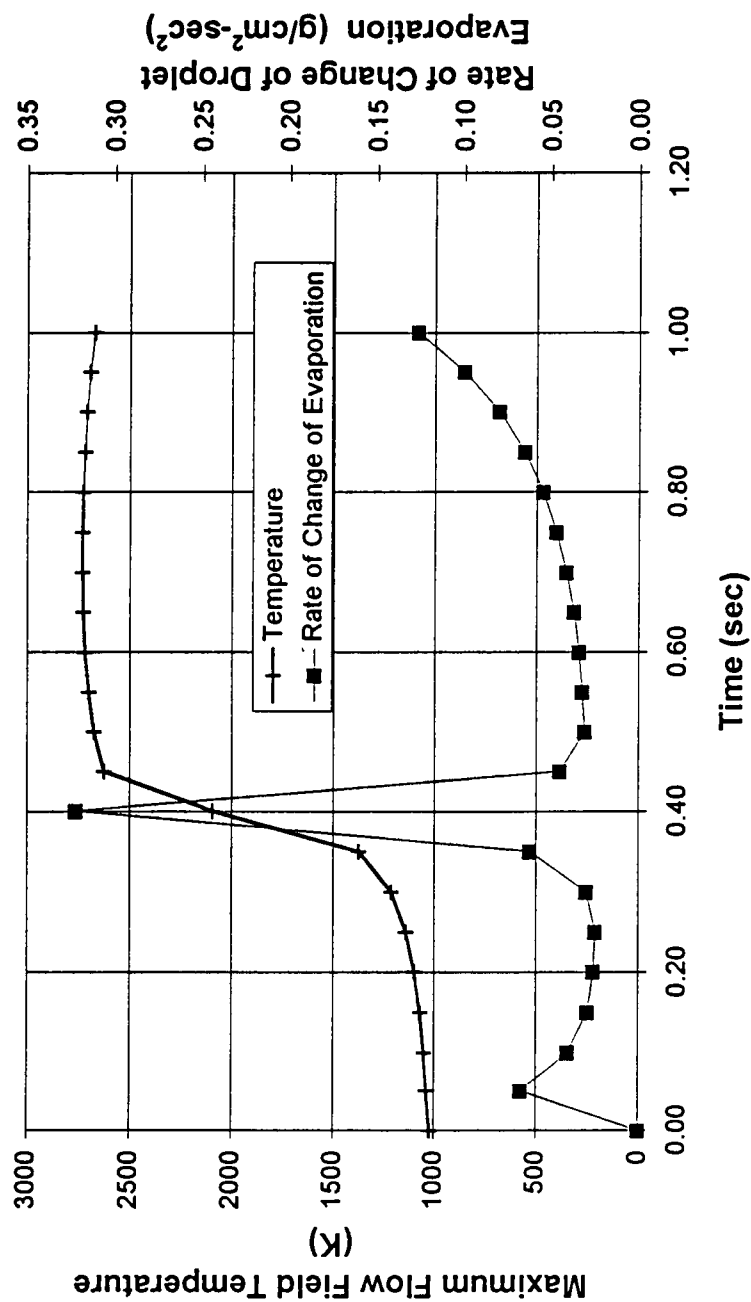


Figure 5.132. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.07 cm in Air at 1023 K.

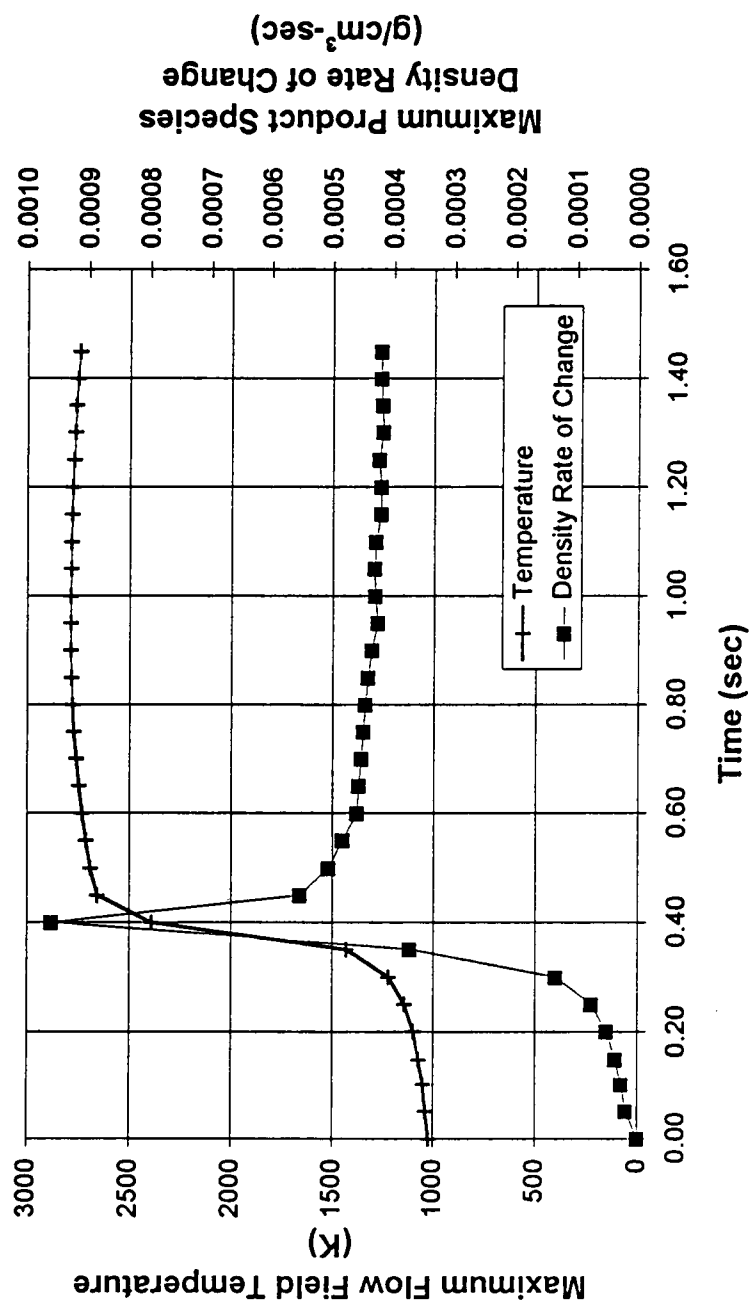


Figure 5.133. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

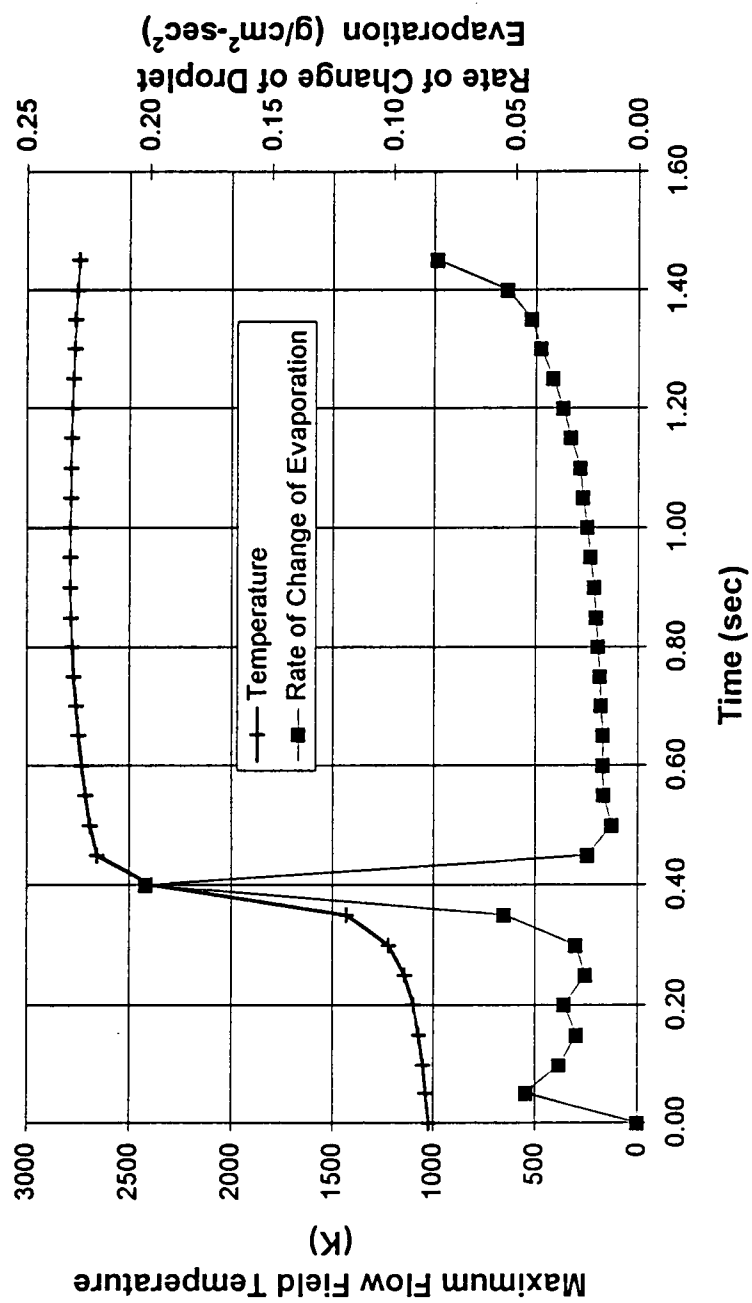


Figure 5.134. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Heptane Droplet with an Initial Radius of 0.09 cm in Air at 1023 K.

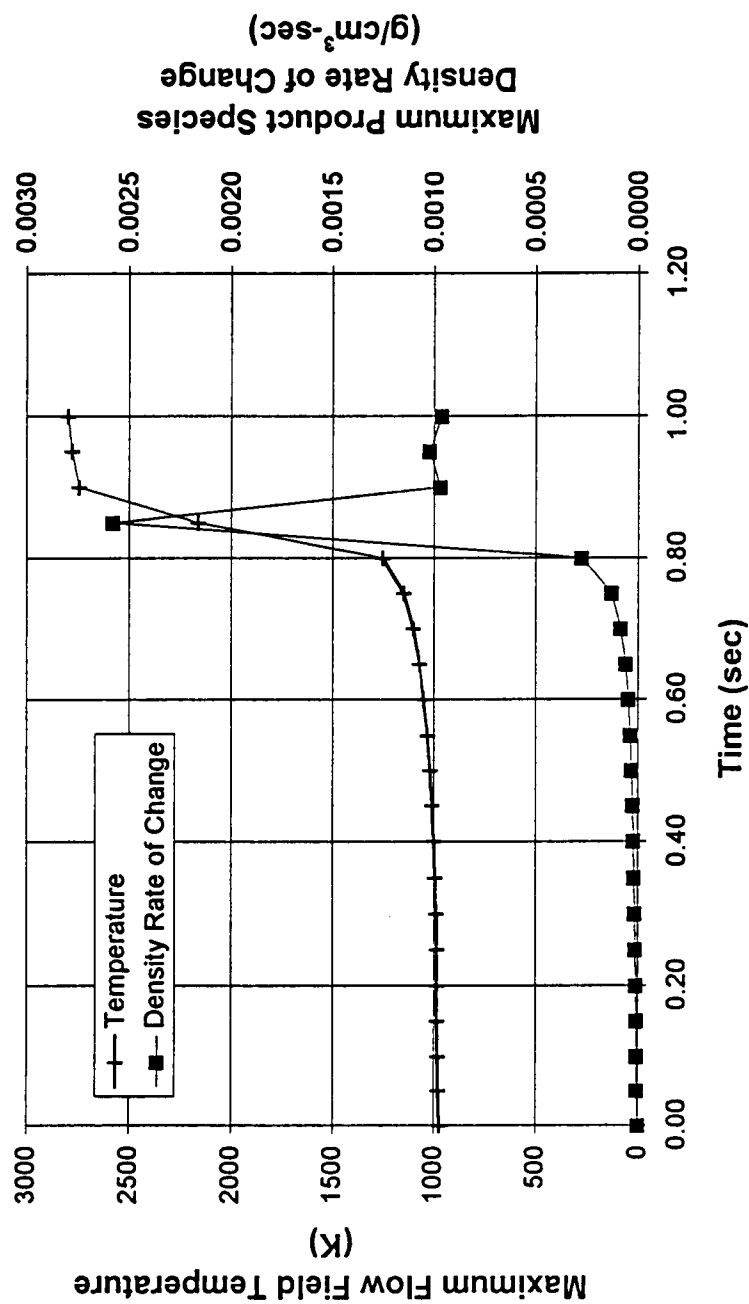


Figure 5.135. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

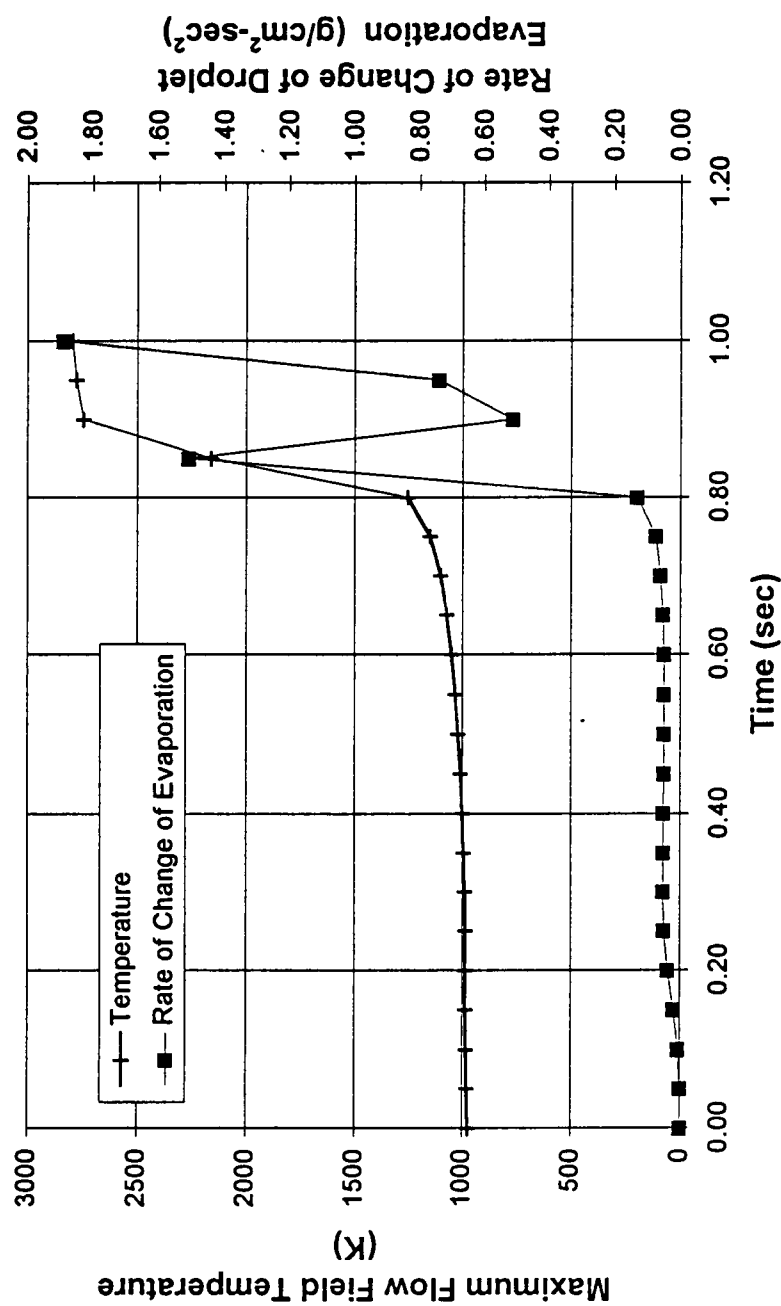


Figure 5.136. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.06 cm in Air at 973 K.

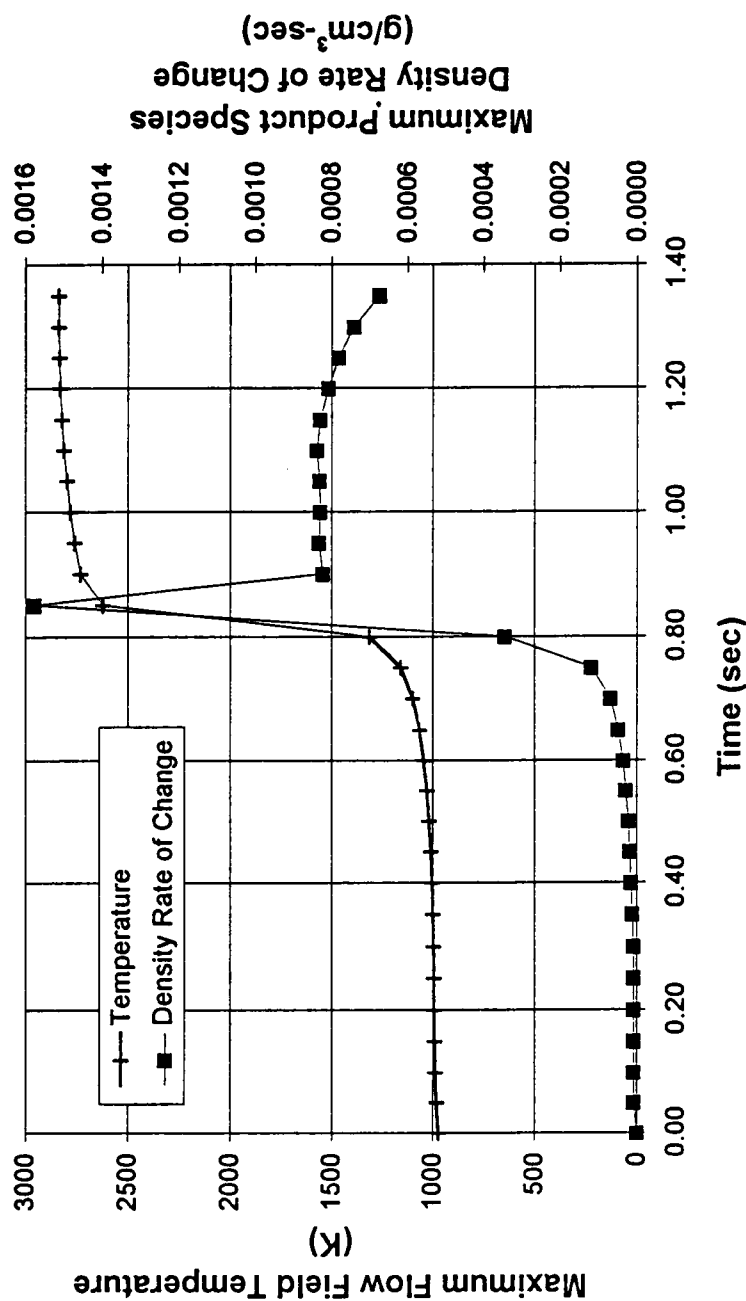


Figure 5.137. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

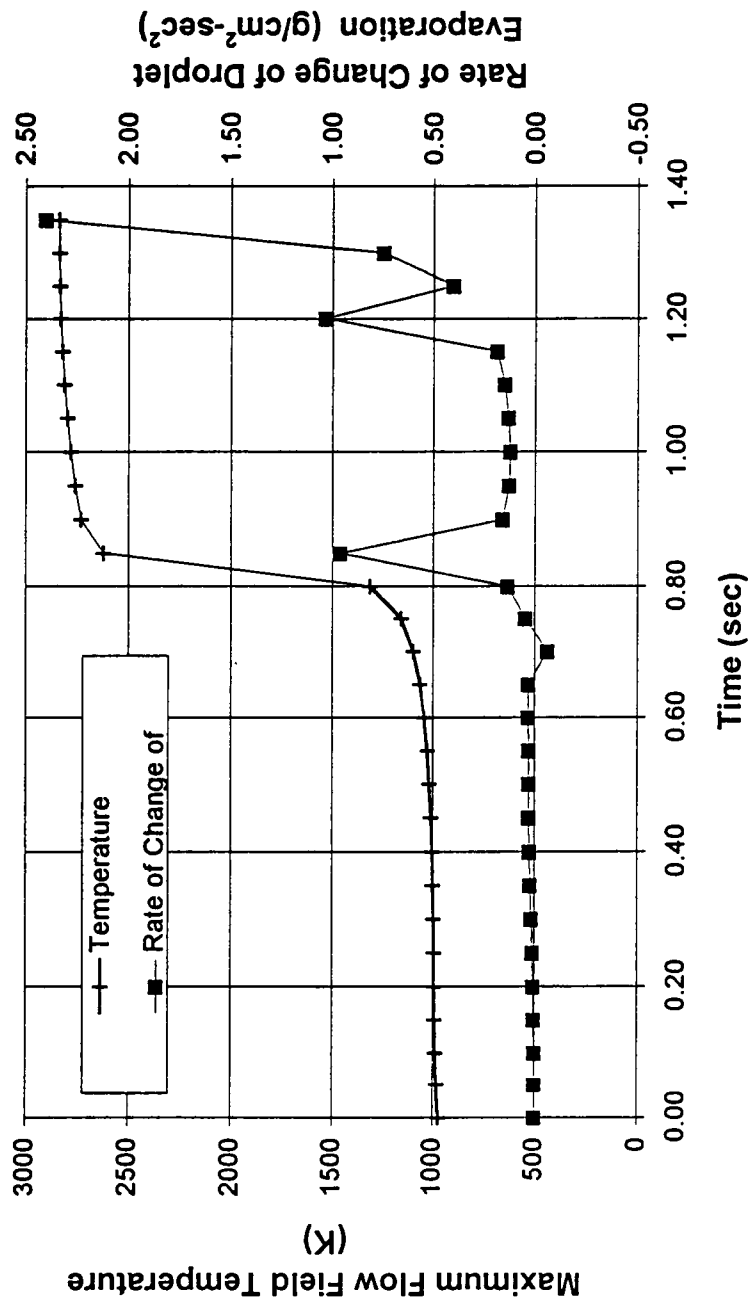


Figure 5.138. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.08 cm in Air at 973 K.

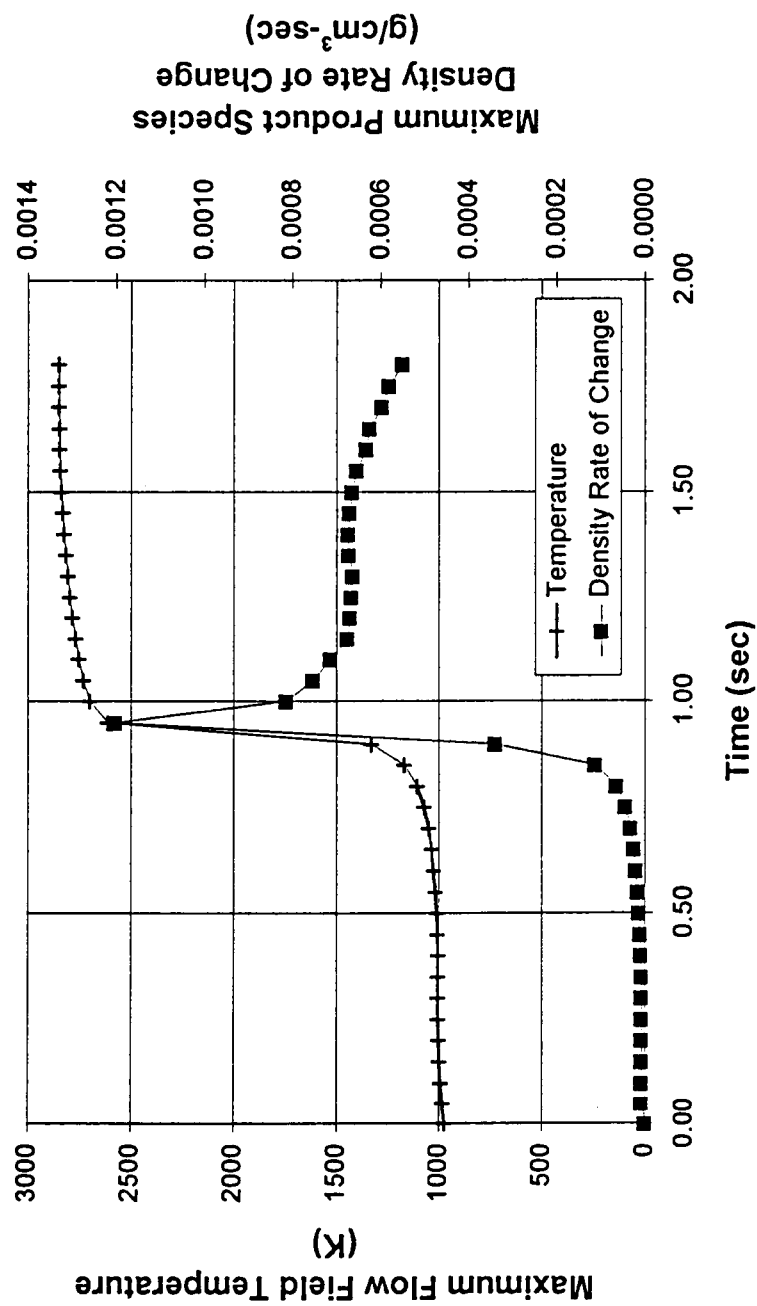


Figure 5.139. Comparison Between Maximum Gaseous Flow Field Temperature and Product Species Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

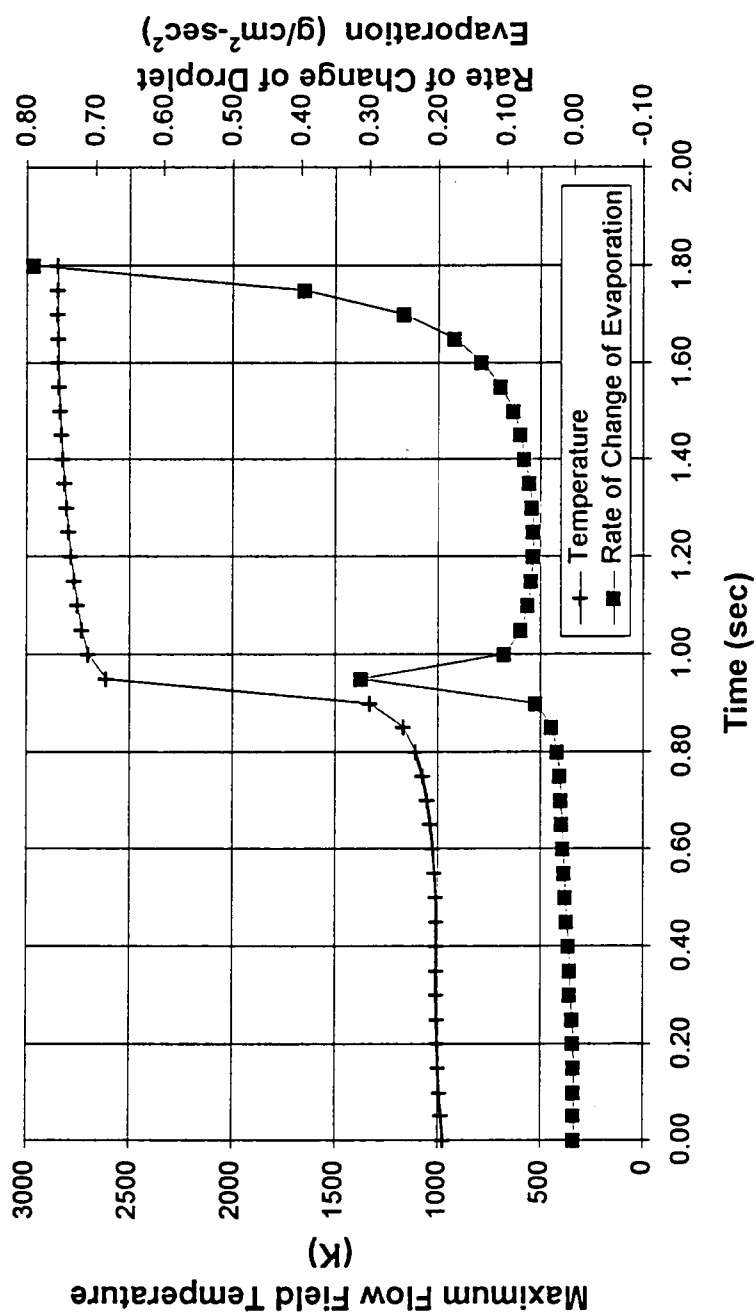


Figure 5.140. Comparison Between Maximum Gaseous Flow Field Temperature and Evaporation Rate of Change for an n-Hexadecane Droplet with an Initial Radius of 0.10 cm in Air at 973 K.

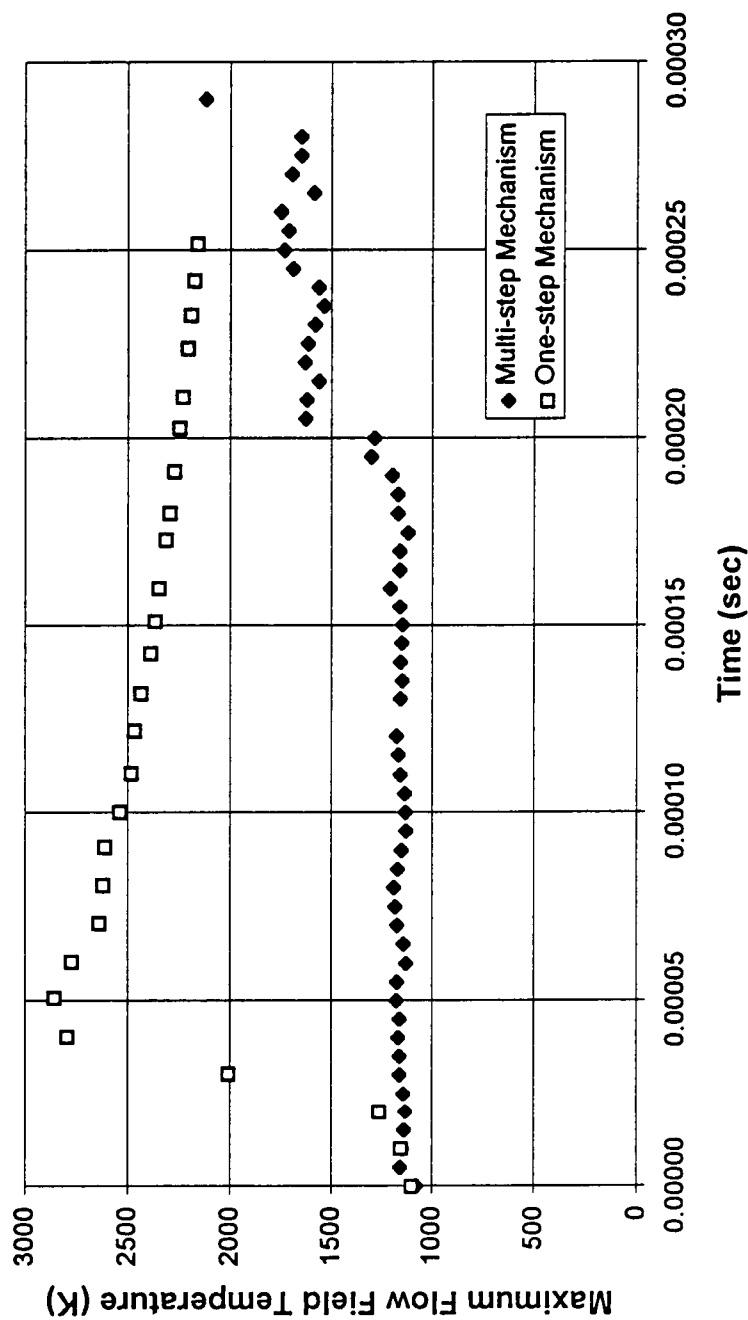


Figure 5.141. Comparison Between Maximum Gaseous Flow Field Temperature of a Multi-step and One-step Chemical Kinetic Mechanism for a Methanol Droplet with an Initial Radius of 0.06 cm in Air at 1080 K.

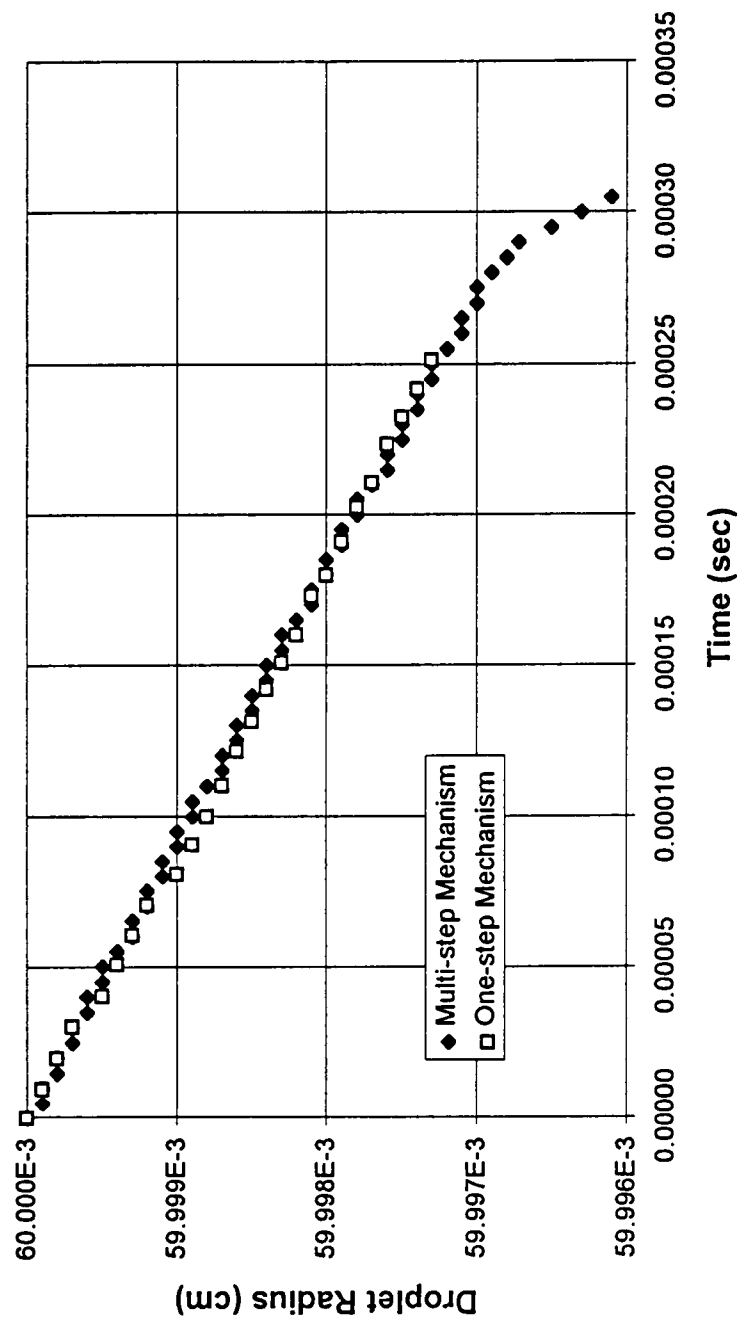


Figure 5.142. Comparison Between Surface Regression of a Multi-step and One-step Chemical Kinetic Mechanism for a Methanol Droplet with an Initial Radius of 0.06 cm in Air at 1080 K.

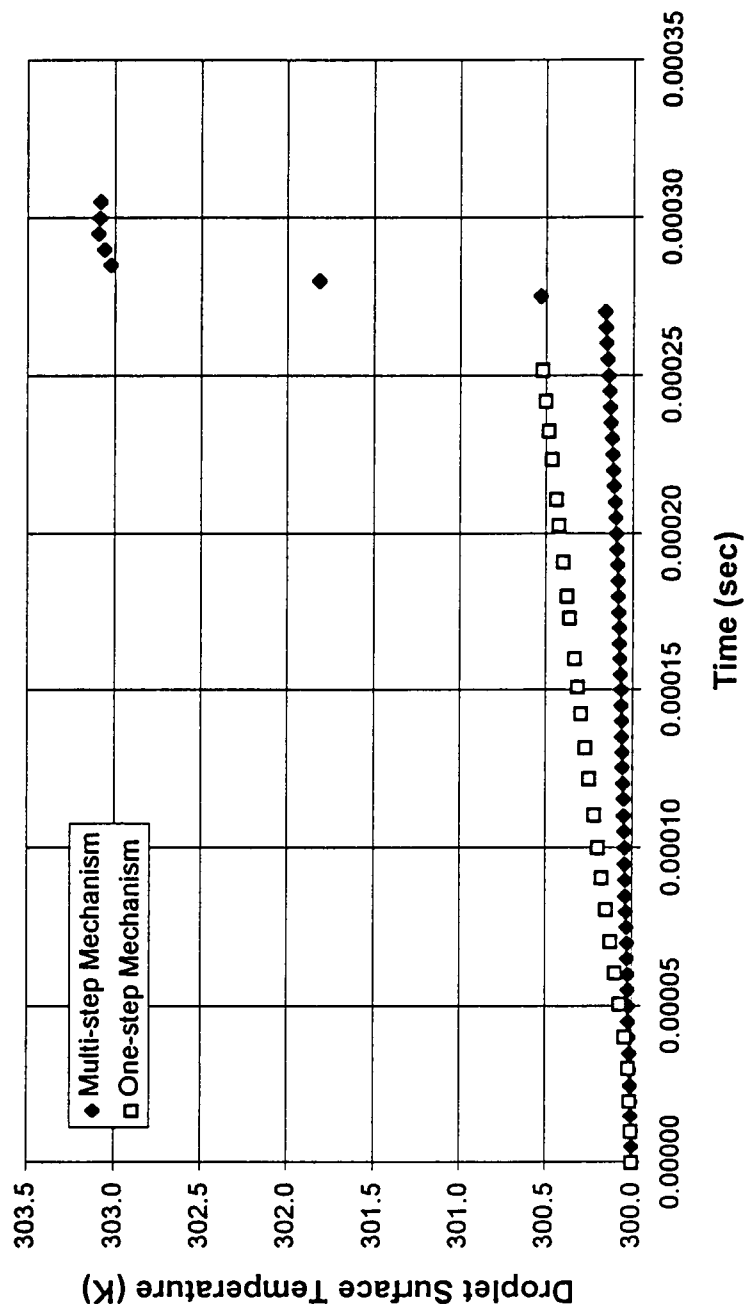


Figure 5.143. Comparison Between Surface Temperature of a Multi-step and One-step Chemical Kinetic Mechanism for a Methanol Droplet with an Initial Radius of 0.06 cm in Air at 1080 K.

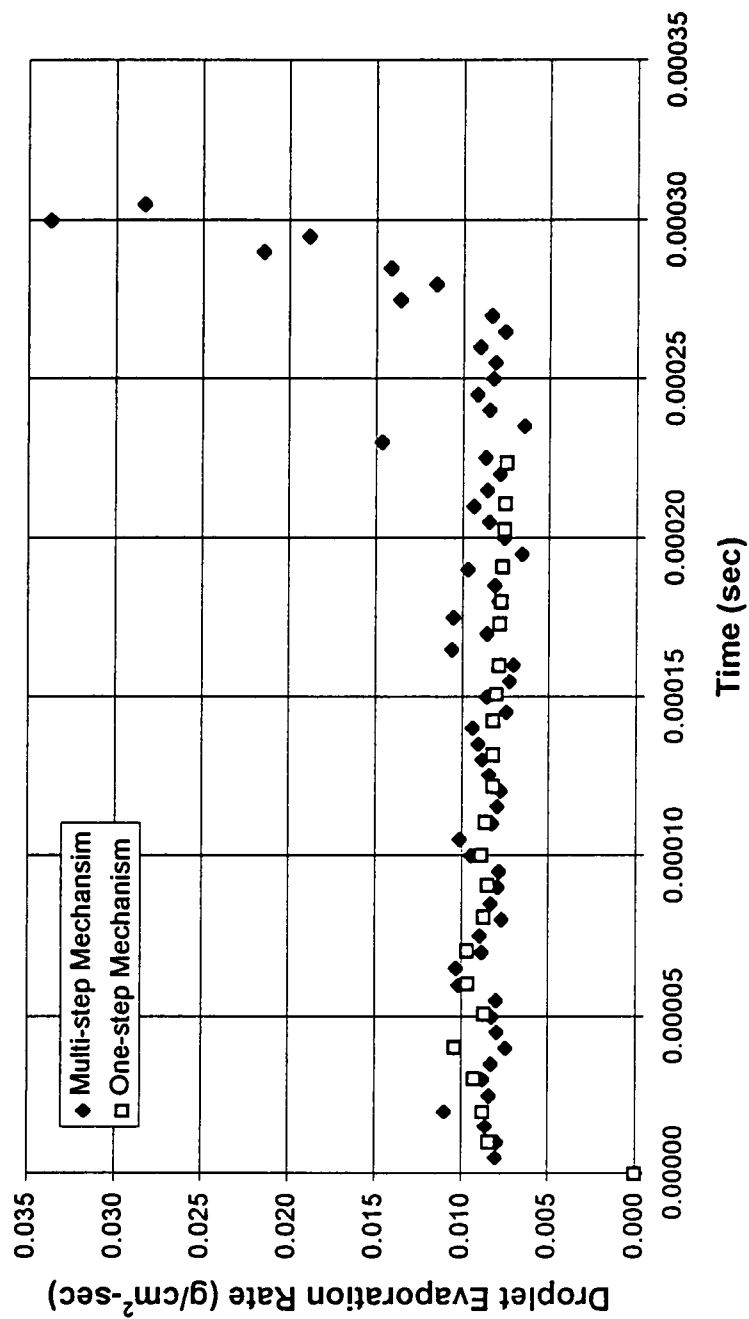


Figure 5.144. Comparison Between Evaporation Rates of a Multi-step and One-step Chemical Kinetic Mechanism for a Methanol Droplet with an Initial Radius of 0.06 cm in Air at 1080 K.

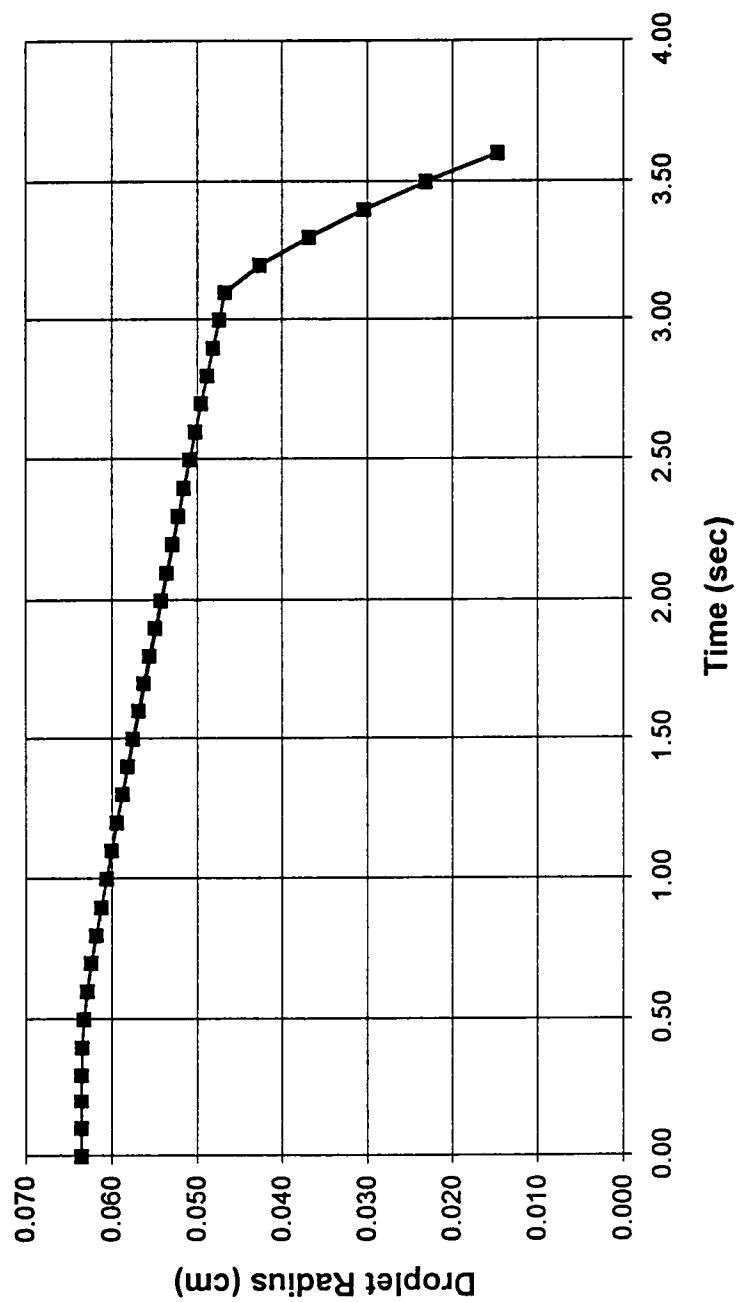


Figure 5.145. Model Results of Spark-Induced Ignition of n-Octane: Droplet Radius Variation with Time.

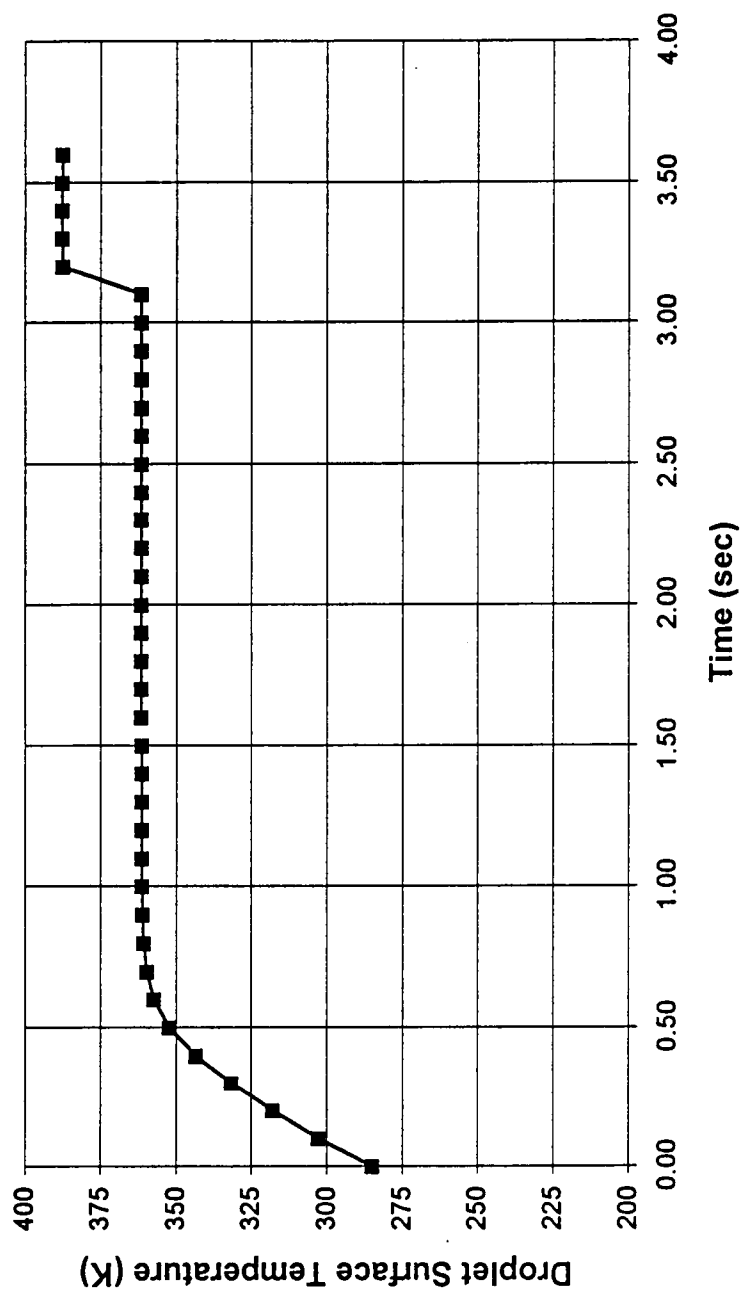


Figure 5.146. Model Results of Spark-Induced Ignition of n-Octane: Droplet Surface Temperature Variation with Time.

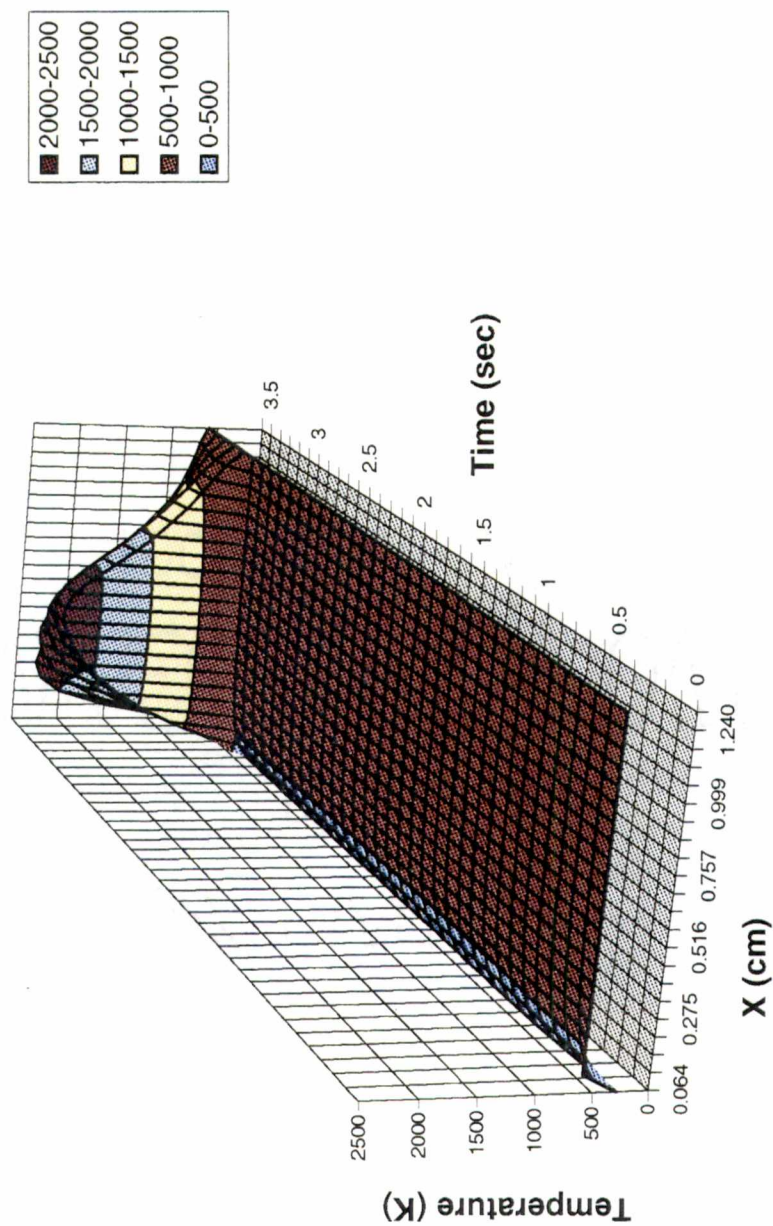


Figure 5.147. Model Results of Spark-Induced Ignition of n-Octane:
Gaseous Flow Field Static Temperature Variation with Time and Space.

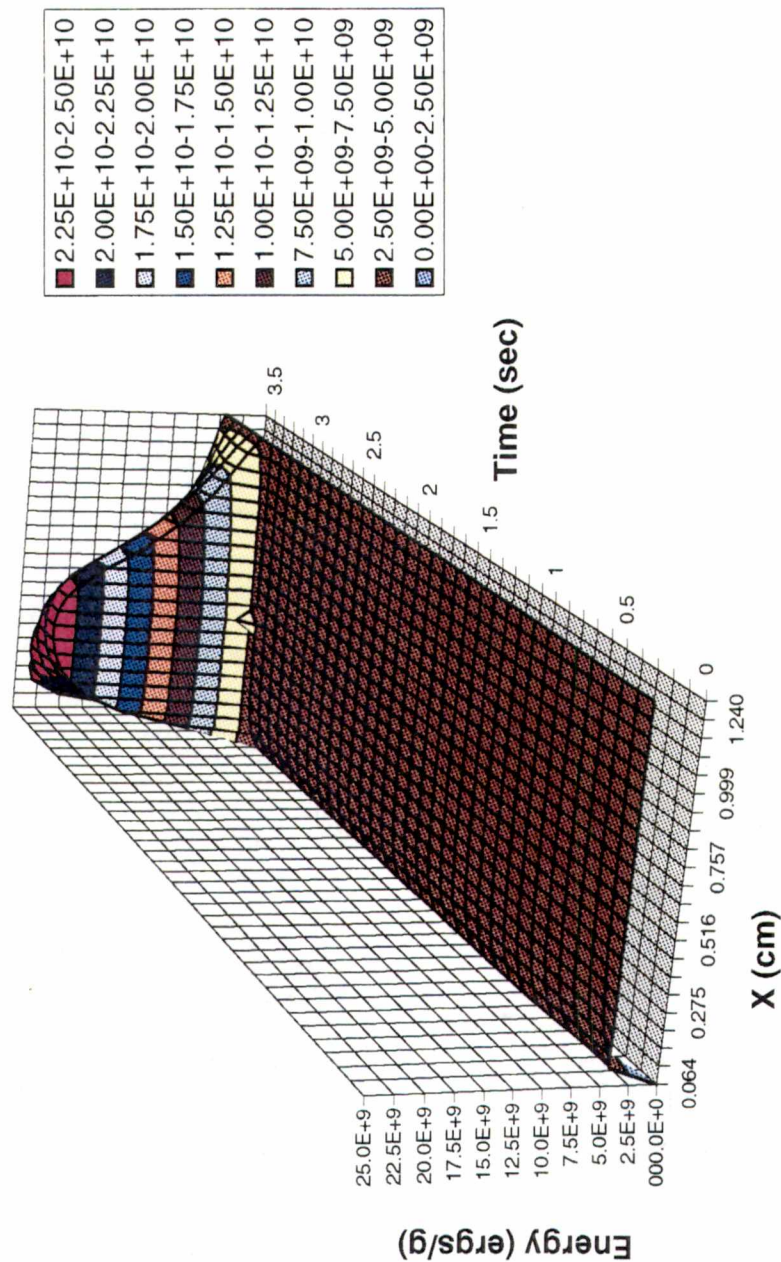


Figure 5.148. Model Results of Spark-Induced Ignition of n-Octane:
Gaseous Flow Field Energy Variation with Time and Space.

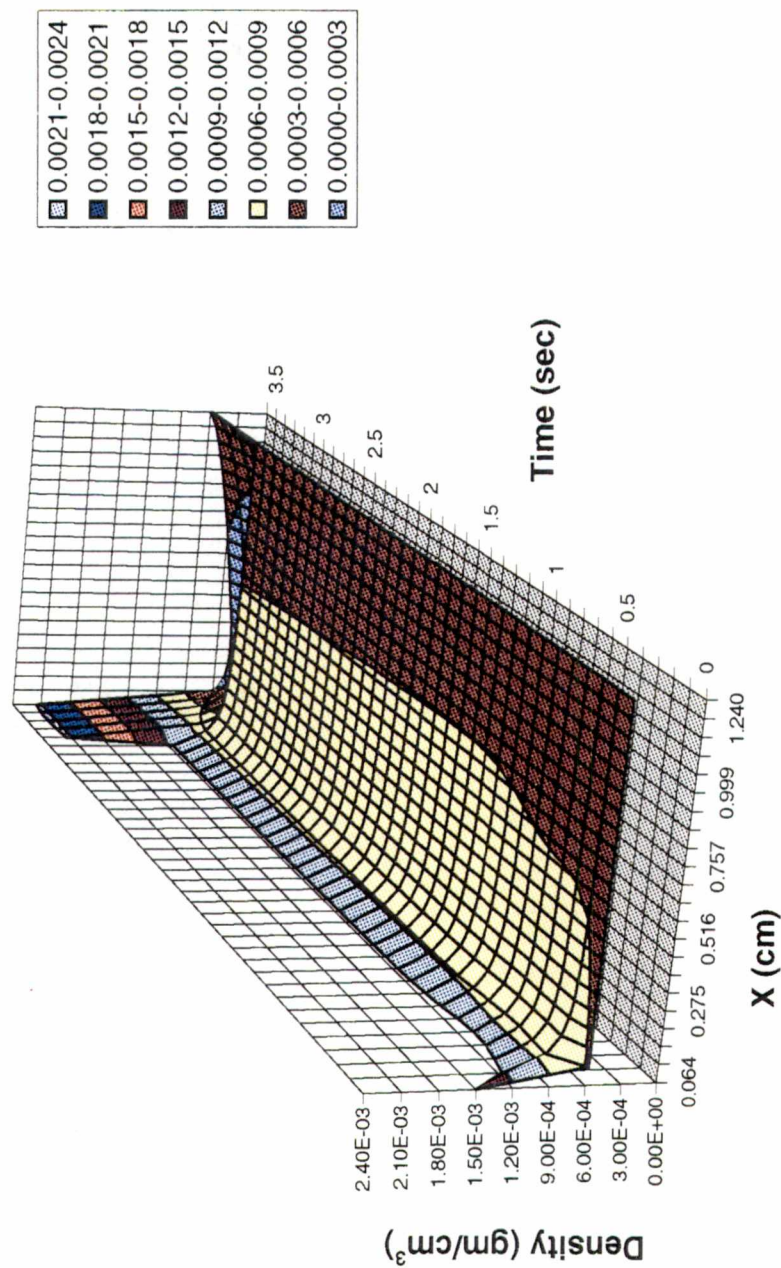


Figure 5.149. Model Results of Spark-Induced Ignition of n-Octane:
Gaseous Flow Field Density Variation with Time and Space.

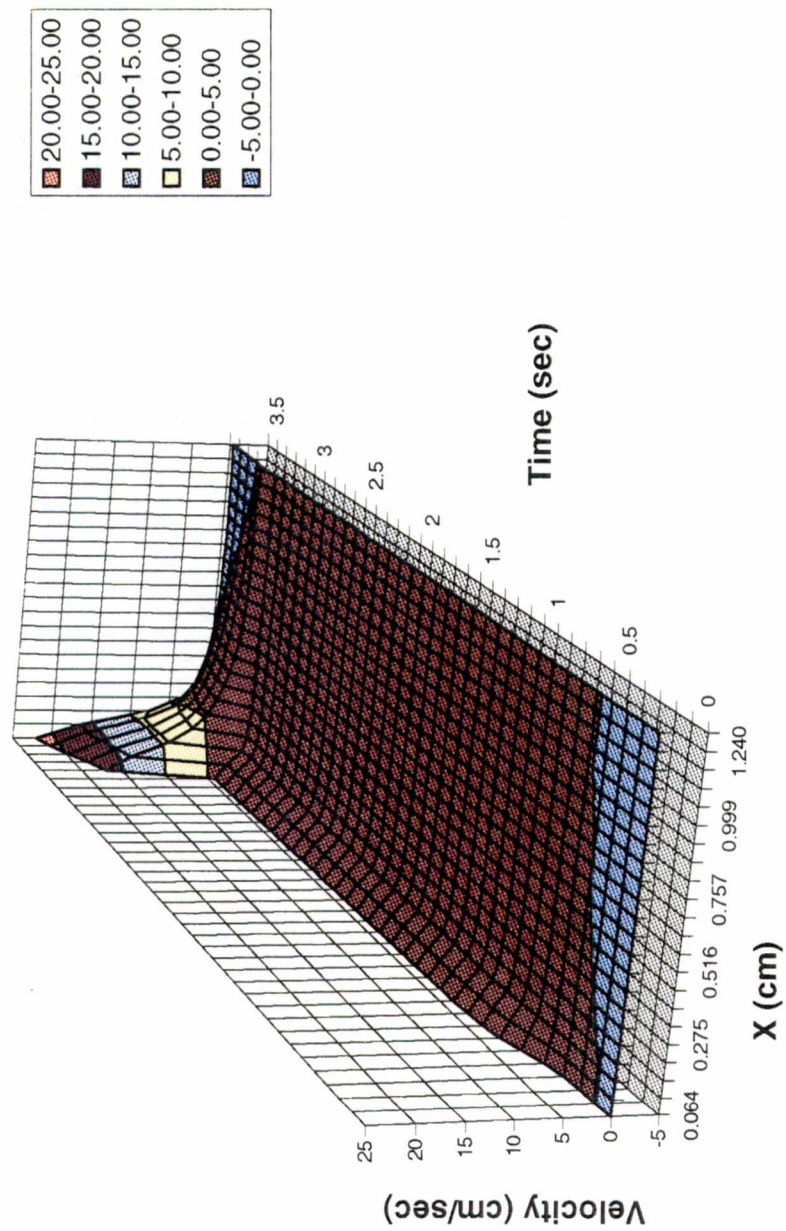


Figure 5.150. Model Results of Spark-Induced Ignition of n-Octane: Gaseous Flow Field Bulk Velocity Variation with Time and Space.

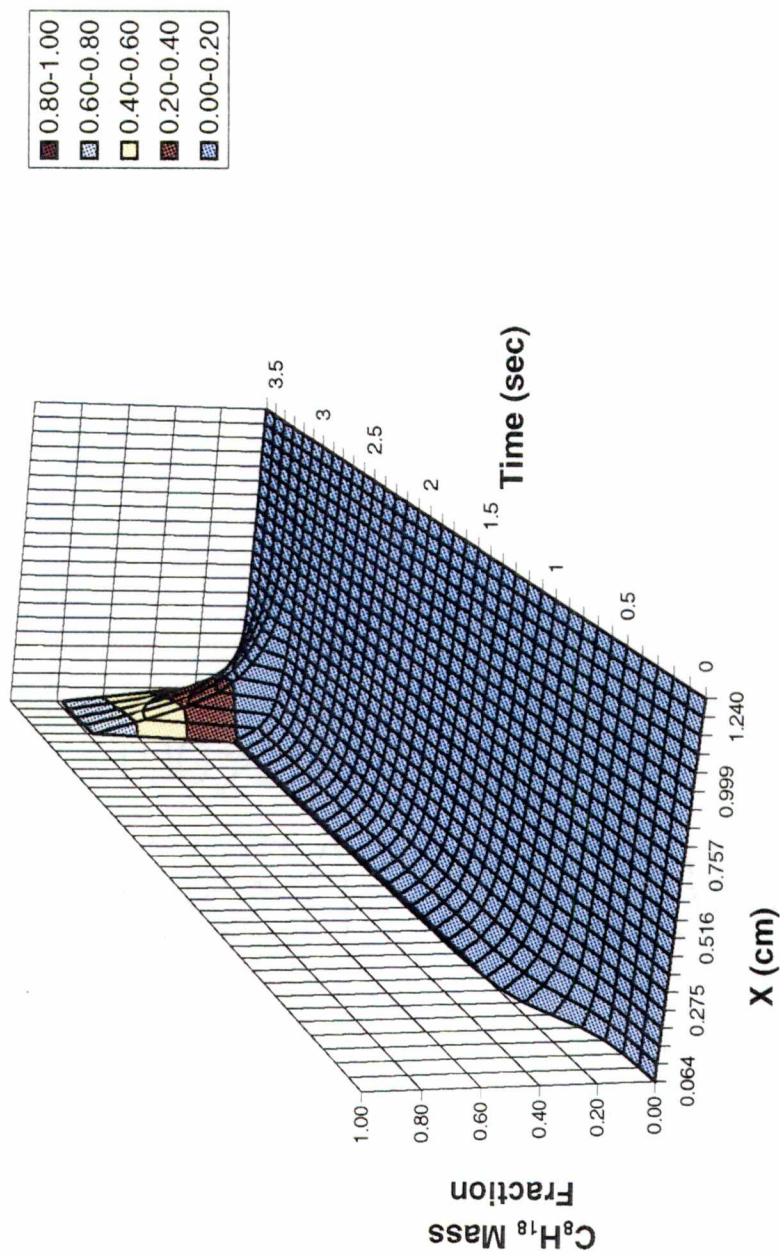


Figure 5.151. Model Results of Spark-Induced Ignition of n-Octane:
Gaseous Fuel Mass Fraction Variation with Time and Space.

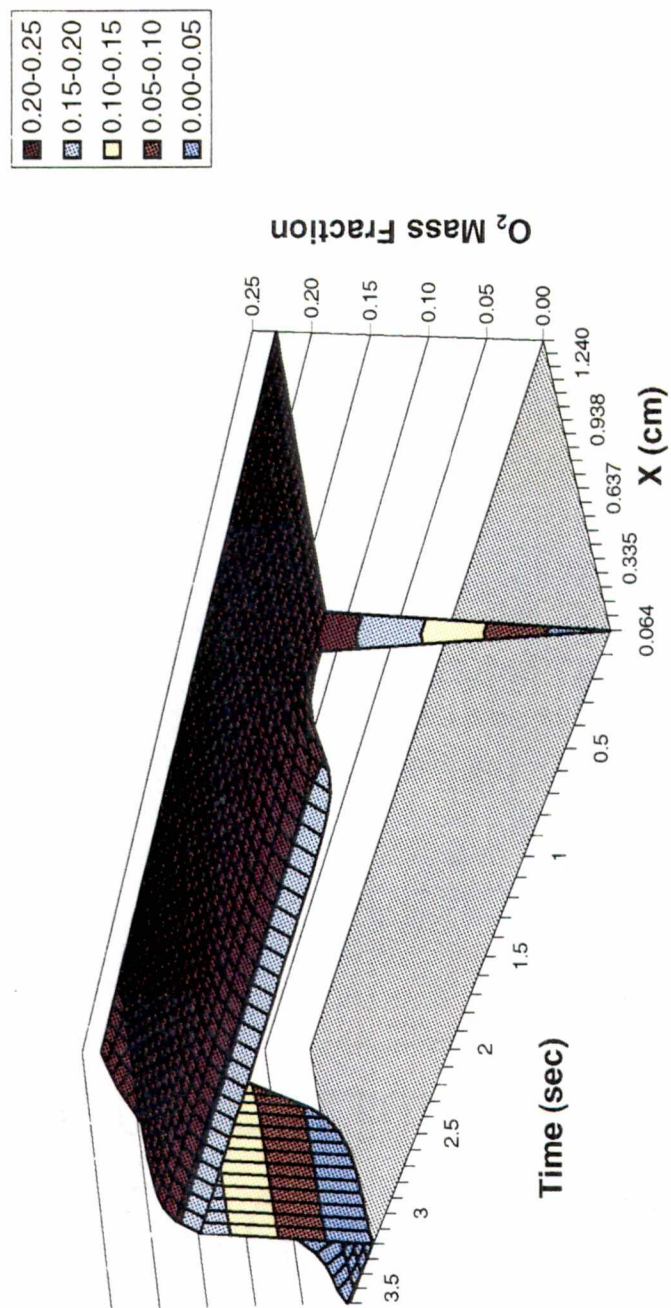


Figure 5.152. Model Results of Spark-Induced Ignition of n-Octane: Oxygen Mass Fraction Variation with Time and Space.

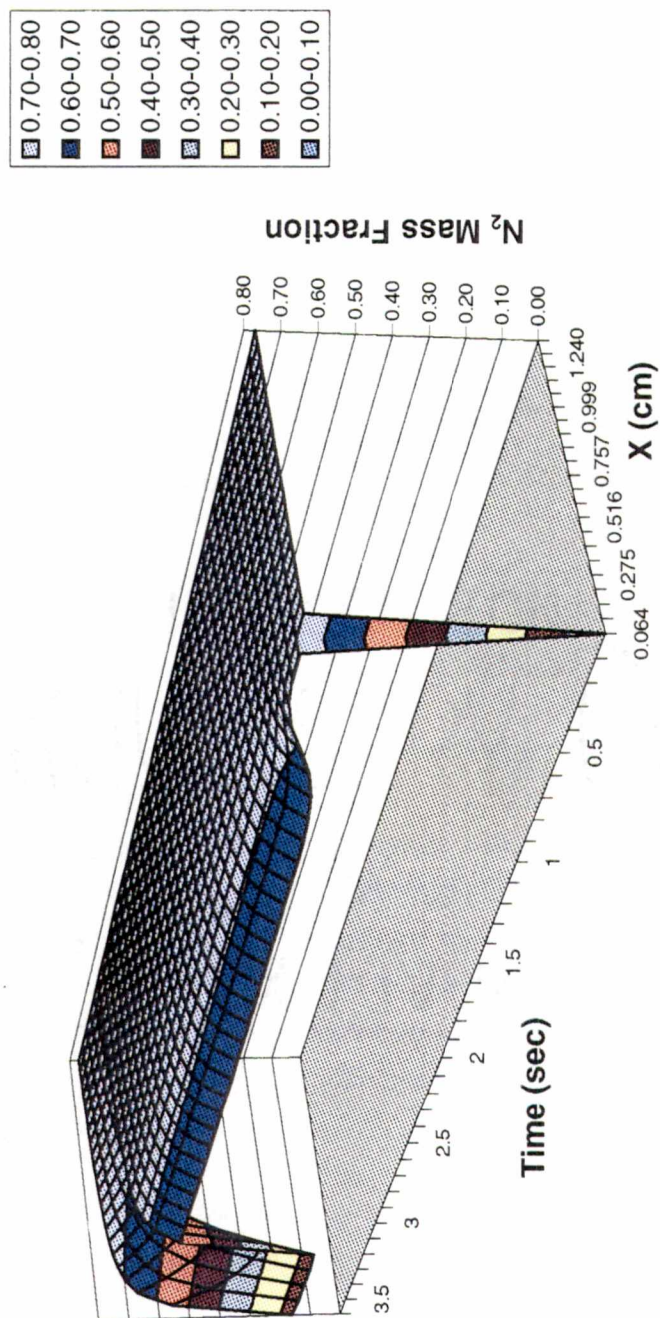


Figure 5.153. Model Results of Spark-Induced Ignition of n-Octane:
Nitrogen Mass Fraction Variation with Time and Space.

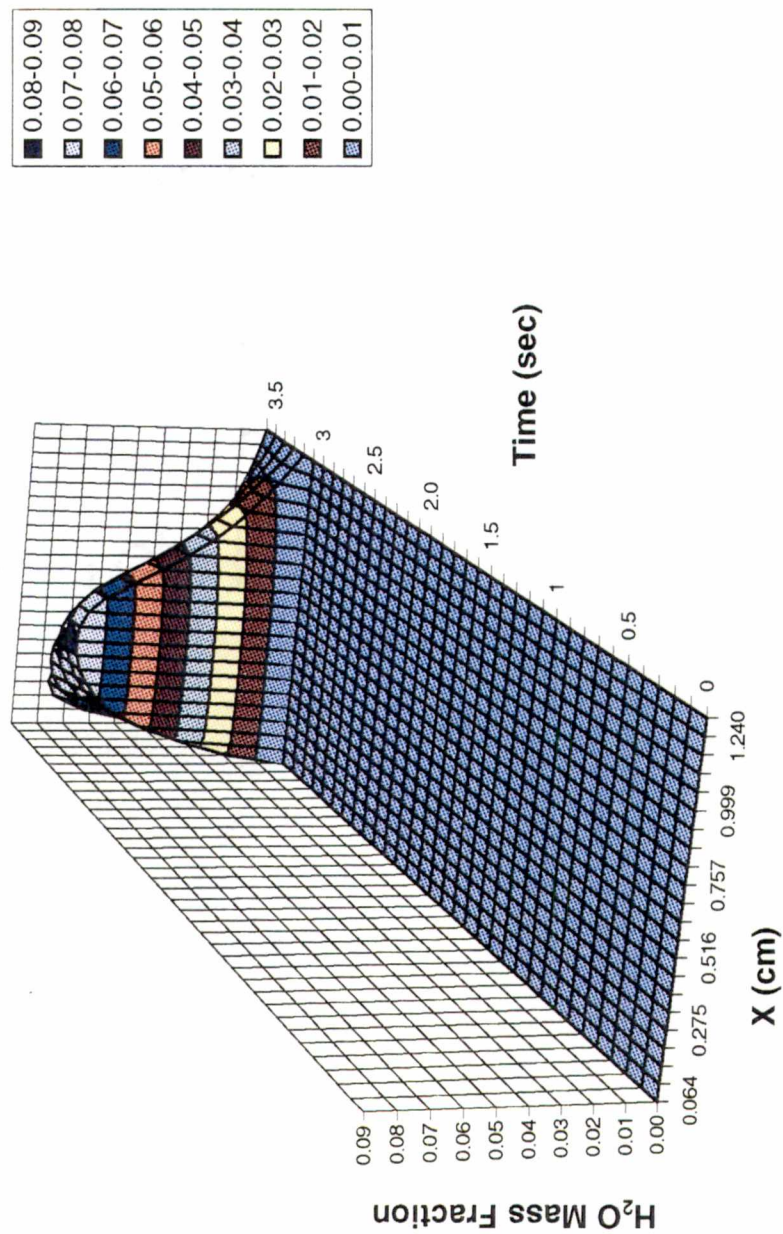


Figure 5.154. Model Results of Spark-Induced Ignition of n-Octane:
Water Vapor Mass Fraction Variation with Time and Space.

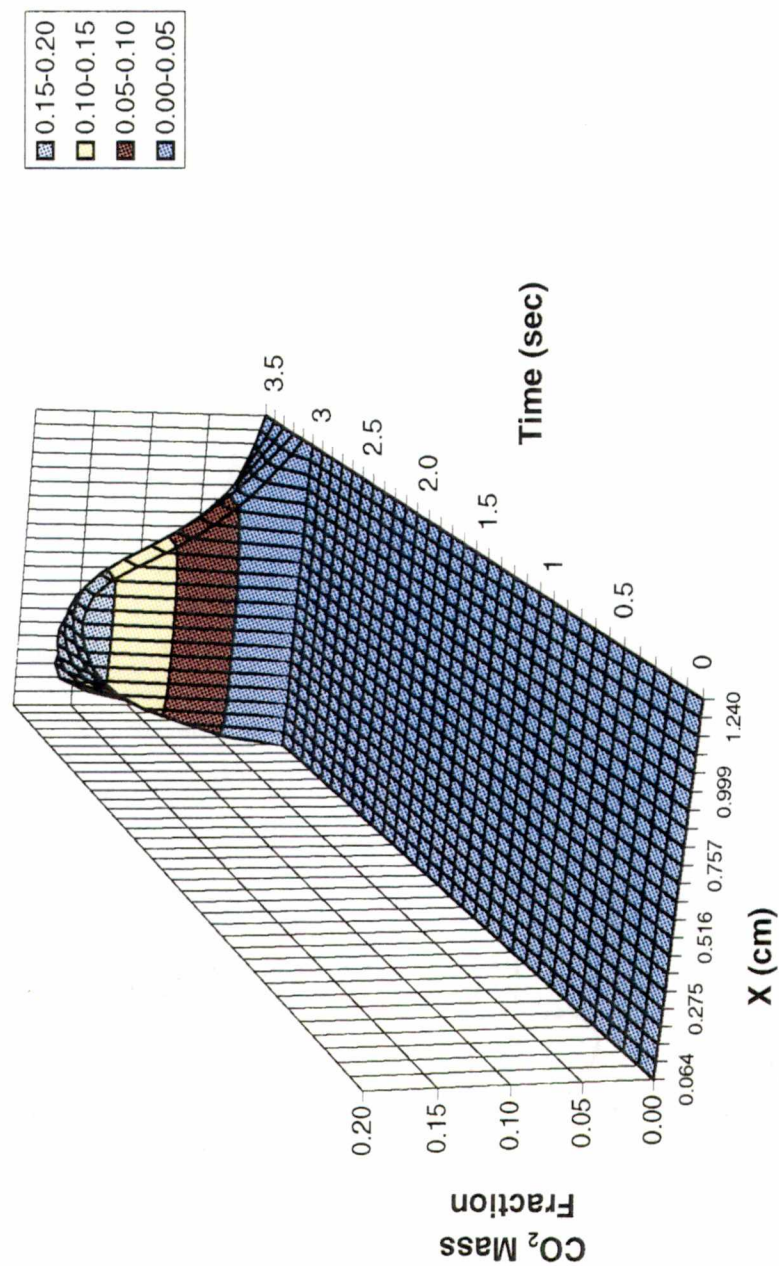


Figure 5.155. Model Results of Spark-Induced Ignition of n-Octane: Carbon Dioxide Mass Fraction Variation with Time and Space.

APPENDIX B

SOLUTION TO THE GOVERNING EQUATIONS ASSUMING QUASI-STEADY DROPLET COMBUSTION

With these assumptions defined, the time dependent conservation equations of mass, fuel species, oxidizer species, and energy can be written for a burning droplet as follows:

$$\frac{\partial p}{\partial t} + \frac{1}{r^2} \frac{d}{dr} (\rho r^2 v) = 0 \quad (\text{B-1})$$

$$r^2 \frac{\partial}{\partial t} (\rho Y_F) + r^2 \rho v \frac{dY_F}{dr} = \frac{d}{dr} \left(r^2 D \frac{dY_F}{dr} \right) + r^2 \dot{\rho}_F \quad (\text{B-2})$$

$$r^2 \frac{\partial}{\partial t} (\rho Y_o) + r^2 \rho v \frac{dY_o}{dr} = \frac{d}{dr} \left(r^2 D \frac{dY_o}{dr} \right) + r^2 \dot{\rho}_o \quad (\text{B-3})$$

$$\frac{\partial}{\partial t} (\rho C_p T) + r^2 \rho v \frac{d(C_p T)}{dr} = \frac{d}{dr} \left[r^2 \frac{\lambda}{C_p} \frac{d(C_p T)}{dr} \right] + r^2 \dot{Q} \quad (\text{B-4})$$

Because the system is assumed to be quasi-steady, the time dependent terms are eliminated from the system. The conservation of momentum equation

$$\frac{\partial(\rho v)}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho v^2) = - \frac{\partial p}{\partial r} \quad (\text{B-5})$$

is typically ignored and combustion is assumed to occur without pressure gradients in the field.

The boundary conditions may be defined at the droplet surface and infinity for these equations given the specified assumptions. Because the droplet surface boundary is assumed insoluble, the mass flux of fuel and oxidizer can be specified. A vaporizing droplet of radius r_s will lose fuel mass by convection and diffusion from its surface. Also, it is assumed that no oxidizer is leaving the surface. Therefore, the fuel and oxidizer mass flow rate at the surface are defined as follows:

$$\text{Fuel:} \quad \rho_s v_s = \rho_s Y_F v_s - \rho_s D_s' \left(\frac{dY_F}{dr} \right)_s \quad (\text{B-6})$$

$$\text{Oxidizer:} \quad 0 = \rho_s Y_o v_s - \rho_s D_s' \left(\frac{dY_o}{dr} \right)_s \quad (\text{B-7})$$

The boundary condition for the energy equation defines the temperature gradient at the droplet surface proportional to the latent heat of vaporization. Internal temperature gradients within the droplet are assumed negligible.

$$\rho_s v_s \Delta h_v = \lambda \left(\frac{dT}{dr} \right)_s = \frac{\lambda}{C_p} \left[\frac{d(C_p T)}{dr} \right]_s \quad (\text{B-8})$$

At the boundary $r = r_\infty$, the conditions are $T = T_\infty$, and $b = b_\infty$. The continuity equation can be integrated directly to yield

$$r^2 \rho v_s = \frac{\dot{m}_F}{4\pi} = \text{constant} \quad (\text{B-9})$$

A procedure similar to the Schvab-Zeldovich formulation can be applied to convert the nonhomogeneous equations into homogeneous differential equations. This is accomplished by writing them in terms of a b variable. The b variable is determined from the boundary conditions.

Glassmanⁱ defines the new b variables through reductions of the boundary equations assuming the fuel and oxidant approach each other in stoichiometric proportions at the flame front as defined by the following relations

ⁱ Glassman, I., Combustion, 2nd Edition, Academic Press, Orlando, 1987.

$$\dot{\rho}_F = \dot{\rho}_o \left(\frac{F}{O} \right)_{st} \quad (B-10)$$

$$\dot{\rho}_F \Delta h_{r,F} = \dot{\rho}_o \Delta h_{r,F} \left(\frac{F}{O} \right)_{st} = -\dot{Q} \quad (B-11)$$

With this assumption, the boundary conditions at the droplet surface can be rewritten. Multiply equation B-6 by $\Delta h_{r,f}$ and equate the result with equation B-8 using the relation, $\dot{\rho}_F \Delta h_{r,F} = -\dot{Q}$, defined in equation B-11,

$$\Delta h_{r,F} \left[\rho_s v_s (Y_{F,s} - 1) - D\rho \left(\frac{dY_F}{dr} \right)_s \right] = -\rho_s v_s \Delta h_v + \frac{\lambda}{C_p} \left(\frac{dC_p T}{dr} \right)_s \quad (B-12)$$

Rearranging, assuming Lewis Number is equal to one and therefore, $\lambda/C_p = D\rho$.

Next, invoke the relation $\dot{\rho}_o (F/O)_{st} \Delta h_{r,F} = -\dot{Q}$. Multiply equation B-7 by $(F/O)_{st} \Delta h_{r,F}$ and combine the result with the defined heat flux boundary condition, equation B-8.

$$\left(\frac{F}{O} \right)_{st} \Delta h_{r,F} \left[\rho_s Y_{o,s} v_s - D\rho \left(\frac{dY_o}{dr} \right)_s \right] = -\rho_s v_s \Delta h_v + \frac{\lambda}{C_p} \left(\frac{dC_p T}{dr} \right)_s \quad (B-13)$$

Rearranging,

$$\rho_s v_s = D\rho \frac{d}{dr} \left[\frac{Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + C_p T}{Y_{o,s} \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + \Delta h_v} \right] \quad (B-14)$$

Finally, invoke the relation $\dot{\rho}_F \Delta h_{r,F} = \dot{\rho}_o \Delta h_{r,F} (F/O)_{st}$. Multiply equation B-6 by $\Delta h_{r,F}$ and equation B-7 by $\Delta h_{r,F} (F/O)_{st}$ to obtain

$$\Delta h_{r,F} \left[\rho_s v_s (m_s - 1) - D\rho \left(\frac{dY_F}{dr} \right)_s \right] = \Delta h_{r,F} \left\{ \left(\frac{F}{O} \right)_{st} \left[\rho_s Y_{o,s} v_s - D\rho \left(\frac{dY_o}{dr} \right)_s \right] \right\} \quad (B-15)$$

Rearranging,

$$\rho_s v_s = D\rho \frac{d}{dr} \left[\frac{Y_F - Y_o \left(\frac{F}{O} \right)_{st}}{Y_{F,s} - 1 - Y_{o,s} \left(\frac{F}{O} \right)_{st}} \right] \quad (B-16)$$

The three b variables can now be defined as

$$b_{F,T} = \frac{Y_F \Delta h_{r,F} + C_p T}{\Delta h_{r,F} (Y_{F,s} - 1) + \Delta h_v} \quad (B-17)$$

$$b_{o,T} = \frac{Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + C_p T}{Y_{o,s} \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + \Delta h_v} \quad (B-18)$$

$$b_{F,o} = \frac{Y_F - Y_o \left(\frac{F}{O} \right)_{st}}{Y_{F,s} - 1 - Y_{o,s} \left(\frac{F}{O} \right)_{st}} \quad (B-19)$$

The governing equations may now be transformed into these variables using the relations defined in equations B-6 and B-7. First, multiply equation B-2 by $\Delta h_{r,F}$ and equate to the energy equation through the relation $\dot{\rho} \Delta h_{r,F} = -\dot{Q}$

$$\Delta h_{r,F} \left[r^2 \rho v \frac{dY_F}{dr} - \frac{d}{dr} \left(r^2 D\rho \frac{dY_F}{dr} \right) - r^2 \dot{\rho}_F \right] = -r^2 \rho v \frac{d(C_p T)}{dr} + \frac{d}{dr} \left(r^2 \frac{\lambda}{C_p} \frac{d(C_p T)}{dr} \right) - r^2 \dot{Q} \quad (B-20)$$

Rearranging, and dividing by $\Delta h_{r,F}(Y_{F,s}-1)$

$$r^2 \rho v \frac{d}{dr} \left[\frac{Y_F \Delta h_{r,F} + C_p T}{\Delta h_{r,F}(Y_F - 1)} \right] = \frac{d}{dr} \left[r^2 D \rho \frac{d}{dr} \left(\frac{Y_F \Delta h_{r,F} + C_p T}{\Delta h_{r,F}(Y_F - 1)} \right) \right] \quad (B-21)$$

This can be rewritten as

$$r^2 \rho v \frac{d}{dr} \left(\frac{db_{F,T}}{dr} \right) = \frac{d}{dr} \left(r^2 D \rho \frac{db_{F,T}}{dr} \right) \quad (B-22)$$

Continuing in this manner, multiply equation B-3 by $\Delta h_{r,F}(F/O)_{st}$ and equate the result to the energy equation through the relation

$$\Delta h_{r,F} \left(\frac{F}{O} \right)_{st} \left[r^2 \rho v \frac{dY_o}{dr} - \frac{d}{dr} \left(r^2 D \rho \frac{dY_o}{dr} \right) - r^2 \dot{\rho}_o \right] = -r^2 \rho v \frac{d(C_p T)}{dr} + \frac{d}{dr} \left(r^2 \frac{\lambda}{C_p} \frac{d(C_p T)}{dr} \right) - r^2 \dot{Q} \quad (B-23)$$

Rearranging and dividing by $\Delta h_{r,F} Y_{o,s}(F/O)_{st} + \Delta h_v$

$$r^2 \rho v \frac{d}{dr} \left[\frac{Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + C_p T}{Y_{o,s} \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + \Delta h_v} \right] = \frac{d}{dr} \left[r^2 \rho \frac{d}{dr} \left(\frac{Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + C_p T}{Y_{o,s} \left(\frac{F}{O} \right)_{st} \Delta h_{r,F} + \Delta h_v} \right) \right] \quad (B-24)$$

This can be rewritten as

$$r^2 \rho v \frac{d}{dr} \left(\frac{db_{o,T}}{dr} \right) = \frac{d}{dr} \left(r^2 D \rho \frac{db_{o,T}}{dr} \right) \quad (B-25)$$

Finally, combine equations B-2 and B-3 through the relation $\dot{\rho}_F \Delta h_{r,F} = \dot{\rho}_o \Delta h_{r,F}$

$$\begin{aligned} \Delta h_{r,F} \left[r^2 \rho v \frac{dY_F}{dr} - \frac{d}{dr} \left(r^2 D \rho \frac{dY_F}{dr} \right) - r^2 \dot{\rho}_F \right] = \\ \Delta h_{r,F} \left(\frac{F}{O} \right)_{st} \left[r^2 \rho v \frac{dY_o}{dr} - \frac{d}{dr} \left(r^2 D \rho \frac{dY_o}{dr} \right) - r^2 \dot{\rho}_o \right] \end{aligned} \quad (B-26)$$

Rearranging and dividing by $Y_{F,s} - 1 - Y_{o,s}(F/O)_{st}$

$$r^2 \rho v \frac{d}{dr} \left[\frac{Y_F \Delta h_{r,F} - Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F}}{Y_{F,s} - 1 - Y_{o,s} \left(\frac{F}{O} \right)_{st}} \right] = \frac{d}{dr} \left[r^2 D \rho \frac{d}{dr} \left(\frac{Y_F \Delta h_{r,F} - Y_o \left(\frac{F}{O} \right)_{st} \Delta h_{r,F}}{Y_{F,s} - 1 - Y_{o,s} \left(\frac{F}{O} \right)_{st}} \right) \right] \quad (B-27)$$

And this can be rewritten as

$$r^2 \rho v \frac{d}{dr} \left(\frac{db_{F,o}}{dr} \right) = \frac{d}{dr} \left(r^2 D \rho \frac{db_{F,o}}{dr} \right) \quad (B-28)$$

Now the original nonhomogeneous equations B-1 through B-4 have been rewritten in terms of the b number. In general,

$$r^2 \rho v \frac{d}{dr} \left(\frac{db}{dr} \right) = \frac{d}{dr} \left(r^2 D \rho \frac{db}{dr} \right) \quad (B-29)$$

where b is defined by equations B-17, B-18, B-19. The corresponding boundary conditions to the above equation are

$$\text{at } r = r_s \quad \rho_s v_s = D \rho \left(\frac{db}{dr} \right)_s \quad (B-30)$$

$$\text{at } r = r_\infty \qquad b = b_\infty \qquad (B-31)$$

Equation B-29 can be solved by double integration. The first integration yields

$$r^2 \rho v b = r^2 D \rho \frac{db}{dr} + \text{constant} \qquad (B-32)$$

applying the boundary condition at the surface,

$$\text{constant} = r_s^2 \rho_s v_s b_s - r^2 \rho v_s \qquad (B-33)$$

and the equation is now

$$r_s^2 \rho_s v_s (b - b_s + 1) = r^2 \rho D \frac{db}{dr} \qquad (B-34)$$

Next, separate variables

$$\frac{r_s^2 \rho_s v_s}{r^2 \rho D} dr = \frac{db}{b - b_s + 1} \qquad (B-35)$$

and integrate

$$-\frac{r_s^2 \rho_s v_s}{r \rho D} = \ln(b - b_s + 1) + \text{constant} \qquad (B-36)$$

Employing the boundary condition,

$$\text{constant} = -\ln(b_{\infty} - b_s + 1) - \frac{r_s^2 \rho_s V_s}{r_{\infty} \rho D} \quad (\text{B-37})$$

for large r_{∞}

$$\text{constant} = -\ln(b_{\infty} - b_s + 1) \quad (\text{B-38})$$

Therefore,

$$\frac{r_s^2 V_s}{r D_s} = \ln\left(\frac{b_{\infty} - b_s + 1}{b - b_s + 1}\right) \quad (\text{B-39})$$

The mass flux or droplet regression rate can be deduced at $r = r_s$

$$\frac{r_s V_s}{D_s} = \ln(b_{\infty} - b_s + 1) \quad (\text{B-40})$$

or

$$\dot{m}_f'' = \frac{\dot{m}_f}{4\pi r_s} = D_s \rho_s \frac{\ln(1+B)}{r_s} \quad (\text{B-41})$$

where the Spalding transfer number, B, is defined as

$$B = b_{\infty} - b_s \quad (\text{B-42})$$

The most convenient form of B is often $B_{o,T}$ where

$$B_{o,T} \approx \frac{Y_{o,\infty} \Delta h_{r,F}}{\Delta h_v} \left(\frac{F}{O} \right)_{st} \quad (\text{B-43})$$

Assuming that the flame exists where the reactants meet stoichiometrically, $\dot{\rho}_o(F/O)_{st} = \dot{\rho}_F$, and writing b in terms of $b_{f,o}$,

$$\frac{r_s^2 \rho_s v_s}{D_s \rho_s r_{flame}} = \ln(1 + Y_{o,\infty} \left(\frac{F}{O} \right)_{st}) \quad (B-44)$$

Combining equation B-41 leads to an equation for the flame standoff distance

$$\frac{r_{flame}}{r_s} = \frac{\ln(1 + B)}{\ln(1 + (F/O)_{st} Y_{o,\infty})} \quad (B-45)$$

Glassman notes that flame standoff distances computed using this equation are larger than experimental values because the assumption of equal diffusivities. Droplet lifetime is estimated from the d^2 law as

$$t = \frac{d_o^2 - d^2}{\beta} \quad (B-46)$$

Since the droplet rate of mass change is related to the rate of radius change by

$$\frac{dm}{dt} = 4\pi\rho_s r_s^2 \left(\frac{dr}{dt} \right)_s = 2\pi\rho_s r_s \left(\frac{dr^2}{dt} \right)_s = \frac{\pi\rho_s r_s}{2} \left(\frac{d(d^2)}{dt} \right)_s = \dot{m}_F \quad (B-47)$$

Combining this equation with equation B-41,

$$\frac{\rho_s}{8} \left[\frac{d(d^2)}{dt} \right]_s = \frac{\lambda}{C_p} \ln(1 + B) \quad (B-48)$$

and the variation of droplet surface area with time is

$$\beta = \left[\frac{d(d^2)}{dt} \right]_s = \frac{8\lambda}{\rho C_p} \ln(1+B) \quad (\text{B-49})$$

Therefore, the total droplet vaporization time is

$$\tau = \frac{d_{s,0}^2}{\beta} \quad (\text{B-50})$$

The flame temperature at r_f can be calculated using equation B-39 with $b = b_{o,T}$ and equation B-44.

$$T_{\text{flame}} = \frac{1}{C_p} \left\{ \frac{\Delta h_{r,F} \left(\frac{F}{O} \right)_{st} Y_{o,\infty} + C_p (T_{\infty} - T_s) + \Delta h_v}{1 + \left(\frac{F}{O} \right)_{st} Y_{o,\infty}} - \Delta h_v \right\} + T_s \quad (\text{B-51})$$

APPENDIX C

REACTION MECHANISM FOR METHANOL IN AIR

The proposed mechanism of Westbrook and Dryer contains 25 species and 84 forward reactions. Activation energies are in kcal/mole. The reaction rate is specified by the following relation

$$k = AT^n \exp\left(\frac{-E_a}{R_u T}\right)$$

Species: CH₃OH, CH₂OH, CH₃O, CH₂O, C₂H₆, C₂H₅, C₂H₄, C₂H₃, C₂H₂, C₂H, CH₄, CH₃, CH₂, CH, CO, CO₂, H, H₂, H₂O, H₂O₂, HO₂, HCO, O, O₂, OH, M

Reaction Set:

	Reaction	Log A	n	Ea
1	CH ₃ OH+M→CH ₃ +OH+M	18.5	0	80.0
2	CH ₃ OH+O ₂ →CH ₂ OH+HO ₂	13.6	0	50.9
3	CH ₃ OH+OH→CH ₂ OH+H ₂ O	12.6	0	2.0
4	CH ₃ OH+O→CH ₂ OH+OH	12.2	0	2.3
5	CH ₃ OH+H→CH ₂ OH+H ₂	13.5	0	7.0
6	CH ₃ OH+H→CH ₃ +H ₂ O	12.7	0	5.3
7	CH ₃ OH+CH ₃ →CH ₂ OH+CH ₄	11.3	0	9.8
8	CH ₃ OH+HO ₂ →CH ₂ OH+H ₂ O ₂	12.0	0	6.0
9	CH ₂ OH+M→CH ₂ O+H+M	13.4	0	29.0
10	CH ₂ OH+O ₂ →CH ₂ O+HO ₂	12.0	0	6.0
11	CH ₄ +M→CH ₃ +H+M	17.1	0	88.4
12	CH ₄ +H→CH ₃ +H ₂	14.1	0	11.9
13	CH ₄ +OH→CH ₃ +H ₂ O	3.5	3.08	2.0
14	CH ₄ +O→CH ₃ +OH	13.2	0	9.2

	Reaction	Log A	n	Ea
15	$\text{CH}_4 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{H}_2\text{O}_2$	13.3	0	18.0
16	$\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_3\text{O} + \text{OH}$	13.2	0	0.0
17	$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$	12.6	0	0.0
18	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	14.1	0	2.0
19	$\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O} + \text{O}$	13.4	0	29.0
20	$\text{CH}_2\text{O} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{HCO}$	10.0	0.5	6.0
21	$\text{CH}_3 + \text{HCO} \rightarrow \text{CH}_4 + \text{CO}$	11.5	0.5	0.0
22	$\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$	12.0	0	0.4
23	$\text{CH}_3\text{O} + \text{M} \rightarrow \text{CH}_2\text{O} + \text{H} + \text{M}$	13.7	0	21.0
24	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	12.0	0	6.0
25	$\text{CH}_2\text{O} + \text{M} \rightarrow \text{HCO} + \text{H} + \text{M}$	16.7	0	72.0
26	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	14.7	0	6.3
27	$\text{CH}_2\text{O} + \text{H} \rightarrow \text{HCO} + \text{H}_2$	12.6	0	3.8
28	$\text{CH}_2\text{O} + \text{O} \rightarrow \text{HCO} + \text{OH}$	13.7	0	4.6
29	$\text{CH}_2\text{O} + \text{HO}_2 \rightarrow \text{HCO} + \text{H}_2\text{O}_2$	12.0	0	8.0
30	$\text{HCO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$	14.0	0	0.0
31	$\text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M}$	14.2	0	19.0
32	$\text{HCO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	14.3	0	0.0
33	$\text{HCO} + \text{O} \rightarrow \text{CO} + \text{OH}$	14.0	0	0.0
34	$\text{HCO} + \text{HO}_2 \rightarrow \text{CH}_2\text{O} + \text{O}_2$	14.0	0	3.0
35	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	12.5	0	7.0
36	$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	7.1	1.3	-0.8
37	$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	14.0	0	23.0
38	$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M}$	15.8	0	4.1
39	$\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$	12.4	0	43.8

	Reaction	Log A	n	Ea
40	$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$	14.3	0	16.8
41	$\text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH}$	10.3	1	8.9
42	$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$	13.5	0	18.4
43	$\text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2 + \text{OH}$	14.0	0	20.3
44	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	13.0	0	1.8
45	$\text{H}_2\text{O} + \text{M} \rightarrow \text{H} + \text{OH} + \text{M}$	16.3	0	105.1
46	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	15.2	0	-1.0
47	$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	13.7	0	1.0
48	$\text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH}$	14.4	0	0.7
49	$\text{HO}_2 + \text{H} \rightarrow \text{H}_2 + \text{O}_2$	13.4	0	0.7
50	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	13.7	0	1.0
51	$\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{HO}_2$	13.6	0	42.6
52	$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M}$	17.1	0	45.5
53	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{HO}_2 + \text{H}_2$	12.2	0	3.8
54	$\text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M}$	16.0	0	0.0
55	$\text{O}_2 + \text{M} \rightarrow \text{O} + \text{O} + \text{M}$	15.7	0	115.0
56	$\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$	14.3	0	96.0
57	$\text{C}_2\text{H}_6 \rightarrow \text{CH}_3 + \text{CH}_3$	19.4	-1	88.3
58	$\text{C}_2\text{H}_6 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{CH}_4$	-0.3	4	8.3
59	$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	2.7	3.5	5.2
60	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	13.8	0	2.4
61	$\text{C}_2\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{OH}$	13.4	0	6.4
62	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	13.6	0	38.0
63	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	12.0	0	5.0
64	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4$	17.5	0	35.6

	Reaction	Log A	n	Ea
65	$C_2H_4 + O \rightarrow CH_3 + HCO$	13.0	0	1.1
66	$C_2H_4 + M \rightarrow C_2H_3 + H + M$	17.6	0	98.2
67	$C_2H_4 + H \rightarrow C_2H_3 + H_2$	13.8	0	3.5
68	$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$	14.0	0	3.5
69	$C_2H_4 + O \rightarrow CH_2O + CH_2$	13.4	0	5.0
70	$C_2H_3 + M \rightarrow C_2H_2 + H + M$	16.5	0	40.5
71	$C_2H_2 + M \rightarrow C_2H + H + M$	14.0	0	114.0
72	$C_2H_2 + O_2 \rightarrow HCO + HCO$	12.6	0	28.0
73	$C_2H_2 + H \rightarrow C_2H + H_2$	14.3	0	19.0
74	$C_2H_2 + OH \rightarrow C_2H + H_2O$	12.8	0	7.0
75	$C_2H_2 + O \rightarrow C_2H + OH$	15.5	-0.6	17.0
76	$C_2H_2 + O \rightarrow CH_2 + CO$	13.8	0	4.0
77	$C_2H + O_2 \rightarrow HCO + CO$	13.0	0	7.0
78	$C_2H + O \rightarrow CO + CH$	13.7	0	0.0
79	$CH_2 + O_2 \rightarrow HCO + OH$	14.0	0	3.7
80	$CH_2 + O \rightarrow CH + OH$	11.3	0.68	25.0
81	$CH_2 + H \rightarrow CH + H_2$	11.4	0.67	25.7
82	$CH_2 + OH \rightarrow CH + H_2O$	11.4	0.67	25.7
83	$CH + O_2 \rightarrow CO + OH$	11.1	0.67	25.7
84	$CH + O_2 \rightarrow HCO + O$	13.0	0	0.0

APPENDIX D

DISCRETIZED EQUATIONS FOR THE ENERGY DISTRIBUTION WITHIN THE DROPLET

The discretization of the governing equation can be written in terms of the center node, interior nodes and surface node for both the time and spatial derivatives.

D.1 Spatial Discretization of Internal Nodes

In general, the spatial discretization may be considered by the symbolic notation in Fig. D1:

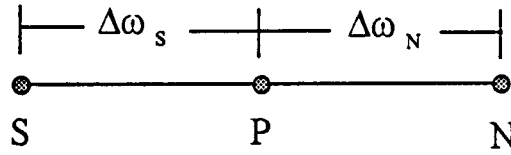


Figure D1. Notation for Spatial Discretization.

The Taylor series expansion for the north and south nodes provides:

$$T_N = T_P + \Delta\omega_n \left. \frac{\partial T}{\partial \omega} \right|_P + \frac{\Delta\omega_n^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_P + \frac{\Delta\omega_n^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_P + \dots \quad (D-1)$$

$$T_S = T_P - \Delta\omega_s \left. \frac{\partial T}{\partial \omega} \right|_P + \frac{\Delta\omega_s^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_P - \frac{\Delta\omega_s^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_P + \dots \quad (D-2)$$

Each equation is multiplied by as-yet undetermined coefficients, A, B,

$$AT_N = AT_P + A\Delta\omega_n \left. \frac{\partial T}{\partial \omega} \right|_P + A \frac{\Delta\omega_n^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_P + A \frac{\Delta\omega_n^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_P + \dots \quad (D-3)$$

$$BT_S = BT_P - B\Delta\omega_s \left. \frac{\partial T}{\partial \omega} \right|_P + B \frac{\Delta\omega_s^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_P - B \frac{\Delta\omega_s^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_P + \dots \quad (D-4)$$

The following constraints are enforced to produce finite difference expressions

$$\begin{aligned}\sum c_i \frac{\partial T}{\partial \omega} \Big|_p &= \left(\frac{2}{\omega_p \Gamma^2} + \frac{\omega_p}{\Gamma} \frac{d\Gamma}{d\tau} \right) \frac{\partial T}{\partial \omega} \Big|_p \\ \sum c_i \frac{\partial^2 T}{\partial \omega^2} \Big|_p &= \frac{1}{\Gamma^2} \frac{\partial^2 T}{\partial \omega^2} \Big|_p\end{aligned}\tag{D-5}$$

These constraints imply two simultaneous equations for A and B.

$$A \Delta \omega_n - B \Delta \omega_s = \frac{2}{\omega_p \Gamma^2} + \frac{\omega_p}{\Gamma} \frac{d\Gamma}{d\tau} \tag{D-6}$$

$$A \frac{\Delta \omega_n^2}{2} + B \frac{\Delta \omega_s^2}{2} = \frac{1}{\Gamma^2} \tag{D-7}$$

Equation D-7 may be solved for A and substituted into the equation D-6.

$$A = \frac{2}{\Delta \omega_n^2 \Gamma^2} - B \frac{\Delta \omega_s^2}{\Delta \omega_n^2} \tag{D-8}$$

$$B = \frac{2}{(\Delta \omega_s^2 + \Delta \omega_s \Delta \omega_n) \Gamma^2} - \left(\frac{\Delta \omega_n}{\Delta \omega_s^2 + \Delta \omega_s \Delta \omega_n} \right) \left(\frac{2}{\omega_p \Gamma^2} + \frac{\omega_p}{\Gamma} \frac{d\Gamma}{d\tau} \right) \tag{D-9}$$

Likewise, solving for A,

$$A = \frac{2}{(\Delta \omega_s^2 + \Delta \omega_s \Delta \omega_n) \Gamma^2} \left(\frac{\Delta \omega_s}{\Delta \omega_n} \right) + \frac{\Delta \omega_s^2}{\Delta \omega_n^2} \left(\frac{\Delta \omega_n}{\Delta \omega_s^2 + \Delta \omega_s \Delta \omega_n} \right) \left(\frac{2}{\omega_p \Gamma^2} + \frac{\omega_p}{\Gamma} \frac{d\Gamma}{d\tau} \right) \tag{D-10}$$

The finite difference form may now be written,

$$AT_N + BT_S = (A+B)T_P + (A\Delta\omega_n - B\Delta\omega_s) \frac{\partial T}{\partial \omega} \Big|_P + \left(A \frac{\Delta\omega_n^2}{2} + B \frac{\Delta\omega_s^2}{2} \right) \frac{\partial^2 T}{\partial \omega^2} \Big|_P \quad (D-11)$$

Therefore, the energy equation can be discretized as follows:

$$\frac{1}{\Gamma^2} \frac{\partial^2 T}{\partial \omega^2} \Big|_P + \left(\frac{2}{\omega_P \Gamma^2} + \frac{\omega_P}{\Gamma} \frac{d\Gamma}{d\tau} \right) \frac{\partial T}{\partial \omega} \Big|_P = AT_N + BT_S - (A+B)T_P \quad (D-12)$$

where A and B are defined as

$$A = \frac{2}{(\Delta\omega_s^2 + \Delta\omega_s \Delta\omega_n) \Gamma^2} \left(\frac{\Delta\omega_s}{\Delta\omega_n} \right) + \frac{\Delta\omega_s^2}{\Delta\omega_n^2} \left(\frac{\Delta\omega_n}{\Delta\omega_s^2 + \Delta\omega_s \Delta\omega_n} \right) \left(\frac{2}{\omega_P \Gamma^2} + \frac{\omega_P}{\Gamma} \frac{d\Gamma}{d\tau} \right) \quad (D-13)$$

$$B = \frac{2}{(\Delta\omega_s^2 + \Delta\omega_s \Delta\omega_n) \Gamma^2} - \left(\frac{\Delta\omega_n}{\Delta\omega_s^2 + \Delta\omega_s \Delta\omega_n} \right) \left(\frac{2}{\omega_P \Gamma^2} + \frac{\omega_P}{\Gamma} \frac{d\Gamma}{d\tau} \right) \quad (D-14)$$

This is further simplified by assuming that the grid spacing is uniform

$$\Delta\omega = \Delta\omega_s = \Delta\omega_n \quad (D-15)$$

$$A = \frac{1}{\Delta\omega^2 \Gamma^2} + \frac{1}{2\Delta\omega} \left(\frac{2}{\omega_P \Gamma^2} + \frac{\omega_P}{\Gamma} \frac{d\Gamma}{d\tau} \right) \quad (D-16)$$

$$B = \frac{1}{\Delta\omega^2 \Gamma^2} - \frac{1}{2\Delta\omega} \left(\frac{2}{\omega_P \Gamma^2} + \frac{\omega_P}{\Gamma} \frac{d\Gamma}{d\tau} \right) \quad (D-17)$$

D.2 Spatial Discretization of Center Node

The boundary condition for the center node simply prescribes that the node located at the droplet center is the same temperature as the adjacent node

$$\left. \frac{\partial T}{\partial \omega} \right|_{\omega=0} = 0$$

$$T_0 = T_1$$
(D-18)

D.3 Spatial Discretization of Surface Node

The surface node may be represented by the depiction in Fig. D2.

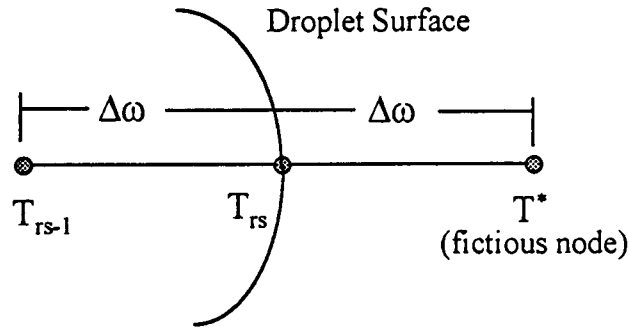


Figure D2. Surface Node Notation for Spatial Discretization.

The Taylor Series Expansion for the surface node and imaginary external node is

$$T^* = T_{rs} + \Delta\omega \left. \frac{\partial T}{\partial \omega} \right|_{rs} + \frac{\Delta\omega^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs} + \frac{\Delta\omega^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_{rs} + \dots$$

$$T_{rs} = T_{rs} - \Delta\omega \left. \frac{\partial T}{\partial \omega} \right|_{rs} + \frac{\Delta\omega^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs} - \frac{\Delta\omega^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_{rs} + \dots$$
(D-19)

Each equation is multiplied by as-yet undetermined coefficients, E, F,

$$\begin{aligned}
ET^* &= ET_{rs} + E\Delta\omega \left. \frac{\partial T}{\partial \omega} \right|_{rs} + E \frac{\Delta\omega^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs} + E \frac{\Delta\omega^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_{rs} + \dots \\
FT_{rs} &= FT_{rs} - F\Delta\omega \left. \frac{\partial T}{\partial \omega} \right|_{rs} + F \frac{\Delta\omega^2}{2!} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs} - F \frac{\Delta\omega^3}{3!} \left. \frac{\partial^3 T}{\partial \omega^3} \right|_{rs} + \dots
\end{aligned} \tag{D-20}$$

The following constraints are enforced to produce finite difference expressions

$$\begin{aligned}
\sum C_i \left. \frac{\partial T}{\partial \omega} \right|_{rs} &= \left(\frac{2}{\omega_{rs} \Gamma^2} + \frac{\omega_{rs}}{\Gamma} \frac{d\Gamma}{d\tau} \right) \left. \frac{\partial T}{\partial \omega} \right|_{rs} \\
\sum C_i \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs} &= \frac{1}{\Gamma^2} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_{rs}
\end{aligned} \tag{D-21}$$

These constraints imply two simultaneous equations for E and F.

$$E\Delta\omega - F\Delta\omega = \frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \tag{D-22}$$

$$E \frac{\Delta\omega^2}{2} + F \frac{\Delta\omega^2}{2} = \frac{1}{\Gamma^2} \tag{D-23}$$

Equation D-22 may be solved for E and substituted into equation D-21.

$$E = \frac{2}{\Delta\omega^2 \Gamma^2} - F \tag{D-24}$$

$$F = \frac{1}{\Delta\omega^2 \Gamma^2} - \frac{1}{2\Delta\omega} \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \tag{D-25}$$

Likewise, solving for E,

$$E = \frac{1}{\Delta\omega^2 \Gamma^2} + \frac{1}{2\Delta\omega} \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \tag{D-26}$$

The finite difference form may now be written,

$$ET^* + FT_{rs-1} = (E + F)T_{rs} + (E\Delta\omega - F\Delta\omega)\left.\frac{\partial T}{\partial\omega}\right|_{rs} + \left(E\frac{\Delta\omega^2}{2} + F\frac{\Delta\omega^2}{2}\right)\left.\frac{\partial^2 T}{\partial\omega^2}\right|_{rs} \quad (D-27)$$

Therefore, the energy equation can be discretized as follows:

$$\frac{1}{\Gamma^2}\left.\frac{\partial^2 T}{\partial\omega^2}\right|_{rs} + \left(\frac{2}{\Gamma} + \frac{1}{\Gamma}\frac{d\Gamma}{d\tau}\right)\left.\frac{\partial T}{\partial\omega}\right|_{rs} = ET^* + FT_{rs-1} - (E + F)T_{rs} \quad (D-28)$$

A central difference approximation for $\partial T/\partial\omega|_{rs}$ is

$$\left.\frac{\partial T}{\partial\omega}\right|_{rs} = \frac{T^* - T_{rs-1}}{2\Delta\omega} = \left(\frac{T^* - T_{rs}}{2\Delta\omega}\right) - \left(\frac{T_{rs-1} - T_{rs}}{2\Delta\omega}\right) \quad (D-29)$$

therefore,

$$T^* - T_{rs} = 2\Delta\omega\left.\frac{\partial T}{\partial\omega}\right|_{rs} + (T_{rs-1} - T_{rs}) \quad (D-30)$$

Rearranging and substituting for $T^* - T_{rs}$,

$$\frac{1}{\Gamma^2}\left.\frac{\partial^2 T}{\partial\omega^2}\right|_{rs} + \left(\frac{2}{\Gamma} + \frac{1}{\Gamma}\frac{d\Gamma}{d\tau}\right)\left.\frac{\partial T}{\partial\omega}\right|_{rs} = E2\Delta\omega\left.\frac{\partial T}{\partial\omega}\right|_{rs} + (E + F)T_{rs-1} - (E + F)T_{rs} \quad (D-31)$$

where E and F are defined by

$$E = \frac{1}{\Delta\omega^2\Gamma^2} + \frac{1}{2\Delta\omega}\left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma}\frac{d\Gamma}{d\tau}\right) \quad (D-32)$$

$$F = \frac{1}{\Delta\omega^2\Gamma^2} - \frac{1}{2\Delta\omega} \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \quad (D-33)$$

D.4 Discretization of Time Derivative

Using the backward difference in time results in a fully implicit formulation

$$\left. \frac{\partial T}{\partial t} \right|_p^m = \frac{T_p^m - T_p^{m-1}}{\Delta\tau} + \tilde{q} \quad (D-34)$$

where the radiative source term is defined as

$$\tilde{q} = r_d \frac{3\sigma\varepsilon(T_\infty^4 - T_s^4)}{\lambda_l} \quad (D-35)$$

An internal node may then be defined as follows

$$\left. \frac{\partial T}{\partial \tau} \right|_p^m = \frac{1}{\Gamma^2} \left. \frac{\partial^2 T}{\partial \omega^2} \right|_p^m + \left(\frac{2}{\omega_p \Gamma^2} + \frac{\omega_p}{\Gamma} \frac{d\Gamma}{d\tau} \right) \left. \frac{\partial T}{\partial \omega} \right|_p^m + \tilde{q} \quad (D-36)$$

where the discretized form would appear as

$$\frac{T_p^m - T_p^{m-1}}{\Delta\tau} = AT_N^m + BT_s^m - (A+B)T_p^m + \tilde{q} \quad (D-37)$$

where q is evaluated using the droplet surface temperature from the previous time step. Solving for the temperature at point "P" and time "m" yields

$$T_p^m \left(A + B + \frac{1}{\Delta\tau} \right) = A T_N^m + B T_s^m + \frac{T_p^{m-1}}{\Delta\tau} + \tilde{q} \quad (D-38)$$

Likewise, the energy equation at the surface node may be defined as

$$\frac{\partial T}{\partial \tau} \Big|_{rs}^m = \frac{1}{\Gamma^2} \frac{\partial^2 T}{\partial \omega^2} \Big|_{rs}^m + \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \frac{\partial T}{\partial \omega} \Big|_{rs}^m + \tilde{q} \quad (D-39)$$

where the discretized form would appear as

$$\frac{T_{rs}^m - T_{rs}^{m-1}}{\Delta\tau} = A 2 \Delta\omega \frac{\partial T}{\partial \omega} \Big|_{rs} + (A + B) T_{rs-1}^m - (A + B) T_{rs}^m + \tilde{q} \quad (D-40)$$

and solving for the surface temperature yields

$$T_{rs}^m \left(A + B + \frac{1}{\Delta\tau} \right) = A 2 \Delta\omega \frac{\partial T}{\partial \omega} \Big|_{rs} + (A + B) T_{rs-1}^m + \frac{T_{rs}^{m-1}}{\Delta\tau} + \tilde{q} \quad (D-41)$$

The temperature gradient at the surface can be resolved by employing the boundary condition of heat flux at the droplet surface

$$\begin{aligned} \frac{\partial T}{\partial \omega} \Big|_{\omega=1} &= \frac{r_s \dot{q}''}{\lambda_l} \\ \dot{q}'' &= \lambda_g \frac{\partial T}{\partial r} \Big|_g - m \Delta h - m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_\pi}{\rho} \right) \end{aligned} \quad (D-42)$$

where q represents the total heat flux at the surface. The temperature gradient at the surface on the gas-side of the droplet can be discretized using existing nodal temperatures in the gas-phase region

$$\left. \frac{\partial T}{\partial r} \right|_g = \frac{T(2) - T_{rs}^m}{(x(3) - x(2)) / 2} \lambda_g \quad (D-43)$$

where the division by 2 is necessary to account for cell centered temperature values and cell edge spatial values. Substituting the above relation, the final form of the discretized surface temperature is

$$\begin{aligned} T_{rs}^m \left(A + B + \frac{1}{\Delta \tau} + \frac{2A\Delta \omega r_s}{x(3) - x(2)} \frac{\lambda_g}{\lambda_l} \right) = \\ \frac{A2\Delta \omega r_s}{\lambda_l} \left(\frac{T(2)}{x(3) - x(2)} \lambda_g - m\Delta h_v - m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{rr}}{\rho} \right) \right) + (A + B)T_{rs-1}^m + \frac{T_{rs}^{m-1}}{\Delta \tau} + \tilde{q} \end{aligned} \quad (D-44)$$

D.5 Solution of the Linear Algebraic Equations

All of the discretized equations are of the form

$$a_i T_i^m = b_i T_{i+1}^m + c_i T_{i-1}^m + d_i \quad (D-45)$$

By inspection with the derived finite difference equations, the above coefficients are as follows:

Center Node:

$$\begin{aligned} a_1 &= 1 \\ b_1 &= 1 \\ c_1 &= 0 \\ d_1 &= 0 \end{aligned} \quad (D-46)$$

Internal Node:

$$\begin{aligned}
 a_i &= \frac{2}{\Delta\omega^2\Gamma^2} + \frac{1}{\Delta\tau} \\
 b_i &= \frac{1}{\Delta\omega^2\Gamma^2} + \frac{1}{2\Delta\omega} \left(\frac{2}{\omega_i\Gamma^2} + \frac{\omega_i}{\Gamma} \frac{d\Gamma}{d\tau} \right) \\
 c_i &= \frac{1}{\Delta\omega^2\Gamma^2} - \frac{1}{2\Delta\omega} \left(\frac{2}{\omega_i\Gamma^2} + \frac{\omega_i}{\Gamma} \frac{d\Gamma}{d\tau} \right) \\
 d_i &= \frac{T_i^{m-1}}{\Delta\tau}
 \end{aligned} \tag{D-47}$$

Surface Node:

$$\begin{aligned}
 a_n &= \frac{2}{\Delta\omega^2\Gamma^2} + \frac{1}{\Delta\tau} + \frac{2\Delta\omega r_s}{x(3) - x(2)} \frac{k_g}{k_l} \left[\frac{1}{\Delta\omega^2\Gamma^2} + \frac{1}{2\Delta\omega} \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \right] \\
 b_n &= 0 \\
 c_n &= \frac{2}{\Delta\omega^2\Gamma^2} \\
 d_n &= \frac{2\Delta\omega r_s}{k_l} \left[\frac{T(2)}{x(3) - x(2)} k_g - m\Delta h - m \left(\frac{u^2}{2} - u \frac{dr_s}{dt} - \frac{\Sigma_{rr}}{\rho} \right) \right] * \\
 &\quad \left[\frac{1}{\Delta\omega^2\Gamma^2} + \frac{1}{2\Delta\omega} \left(\frac{2}{\Gamma^2} + \frac{1}{\Gamma} \frac{d\Gamma}{d\tau} \right) \right] + \frac{T_{rs}^{m-1}}{\Delta\tau}
 \end{aligned} \tag{D-48}$$

D.6 Outline of the Tridiagonal Solution Methodology

First, calculate P_1 and Q_1 using the following relations

$$\begin{aligned} P_1 &= \frac{b_1}{a_1} \\ Q_1 &= \frac{d_1}{a_1} \end{aligned} \quad (D-49)$$

Second, calculate P_i and Q_i for $i=2,3,4,\dots,N$

$$\begin{aligned} P_i &= \frac{b_i}{a_i - c_i P_{i-1}} \\ Q_i &= \frac{d_i + c_i Q_{i-1}}{a_i - c_i P_{i-1}} \end{aligned} \quad (D-50)$$

Third, set

$$T_N = Q_N \quad (D-51)$$

Fourth, calculate T_i for $i=N-1, N-2, N-3, \dots, T_3, T_2, T_1$

$$T_i = P_i T_{i+1} + Q_i \quad (D-52)$$

APPENDIX E

HYDROCARBON THERMODYNAMIC PROPERTIES

Thermodynamic liquid properties density, specific heat capacity, heat of vaporization, vapor pressure and thermal conductivity are defined as a function of temperature for n-heptane, iso-octane, n-octane, n-hexadecane, and methanol.

Gaseous enthalpy is defined as a function of temperature for n-heptane, iso-octane, n-octane, n-hexadecane, and methanol. Enthalpy data were extracted from the Thermodynamic Research Center (TRC) Tables and extrapolated to 5000 K using a linear fit of all the data, a linear fit of only the last three data points, and a polynomial fit. In addition, enthalpy were calculated using the curve fits available from NASA SP273. No curve fit parameters were available for n-hexadecane.

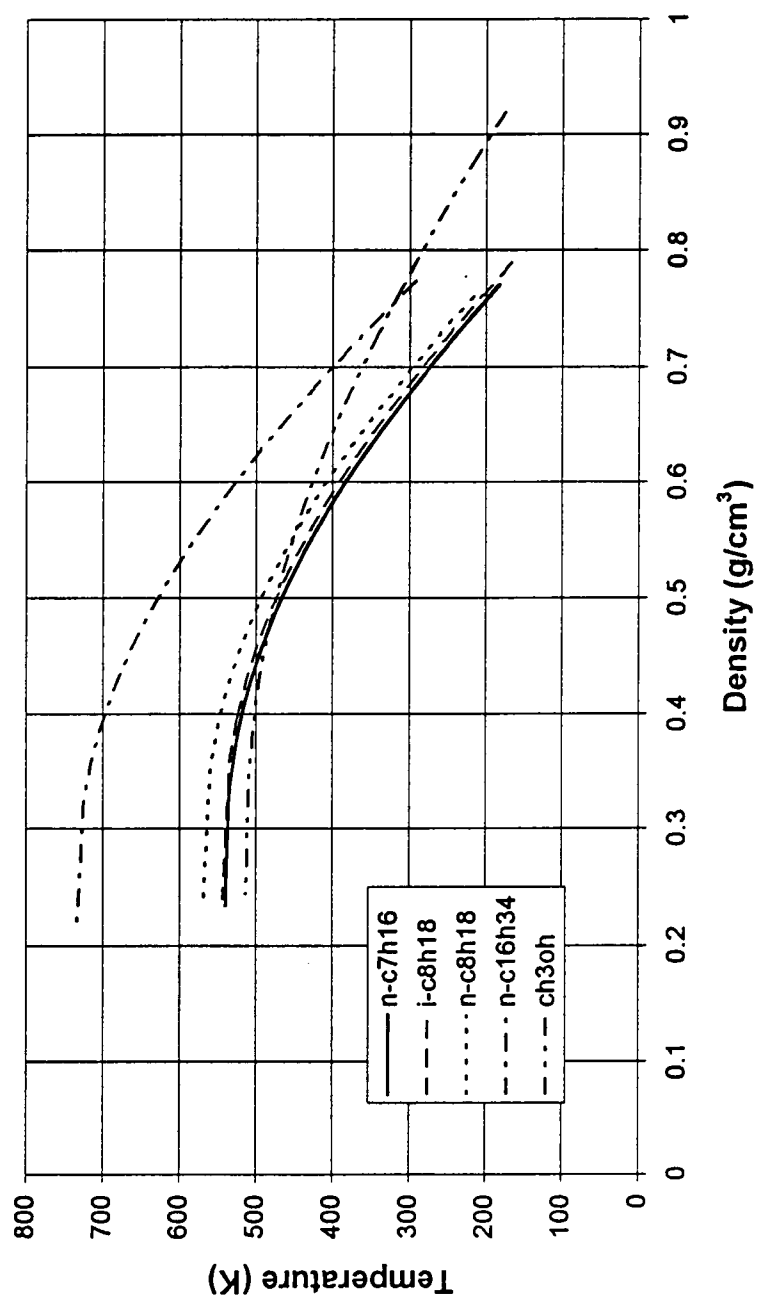


Figure E1. Liquid Density of Selected Hydrocarbons as a Function of Temperature.

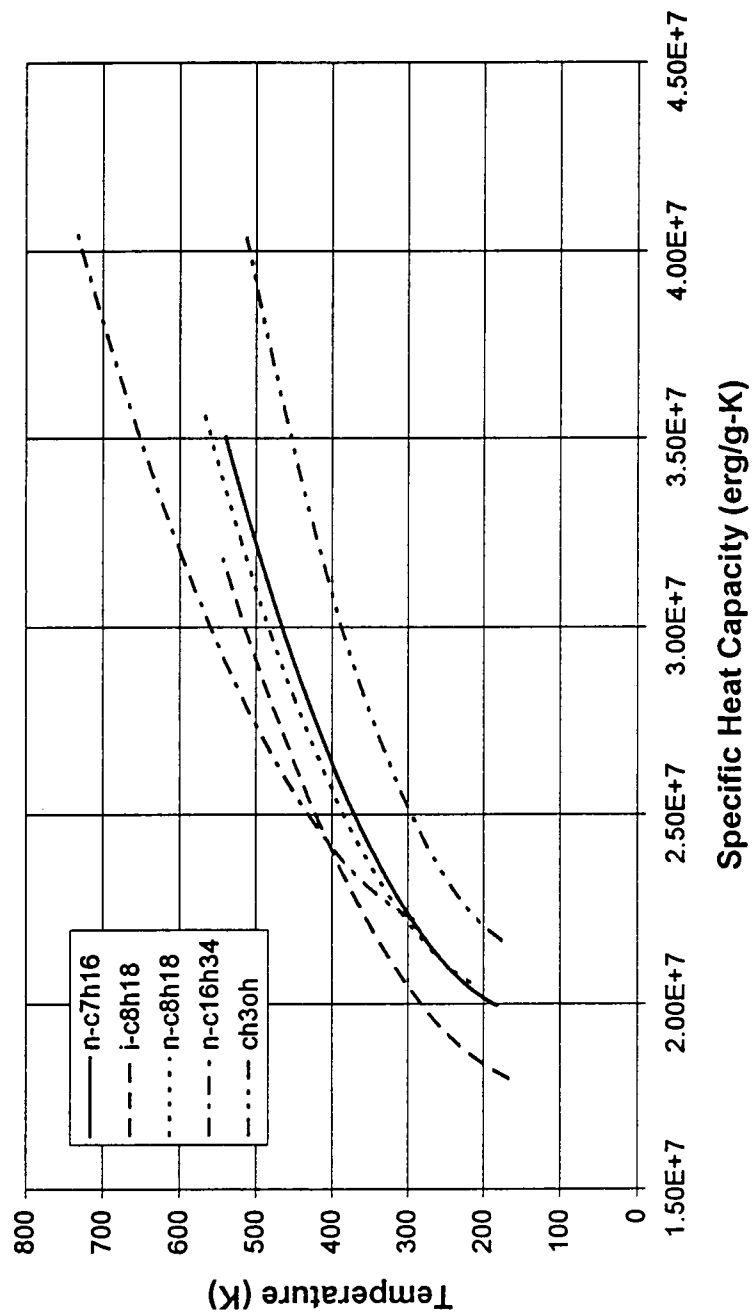


Figure E2. Liquid Specific Heat Capacity of Selected Hydrocarbons as a Function of Temperature.

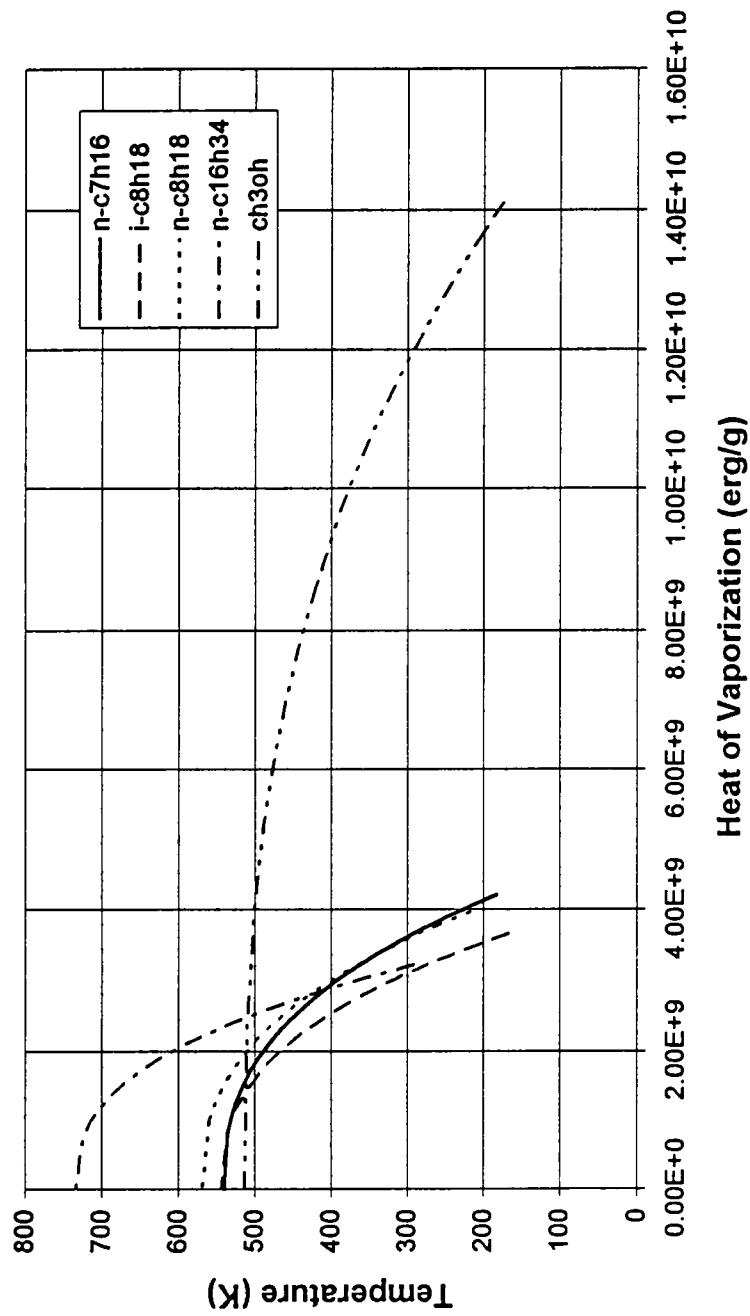


Figure E3. Liquid Heat of Vaporization of Selected Hydrocarbons as a Function of Temperature.

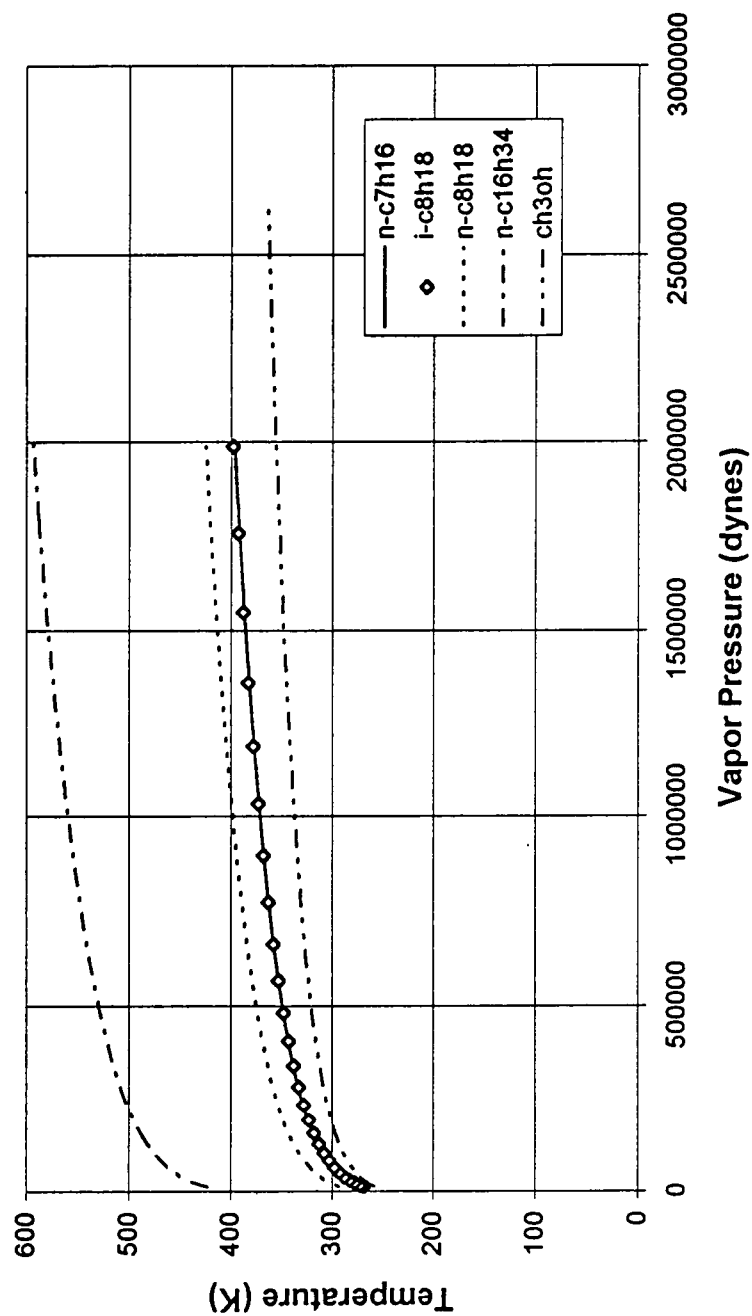


Figure E4. Vapor Pressure of Selected Hydrocarbons as a Function of Temperature.

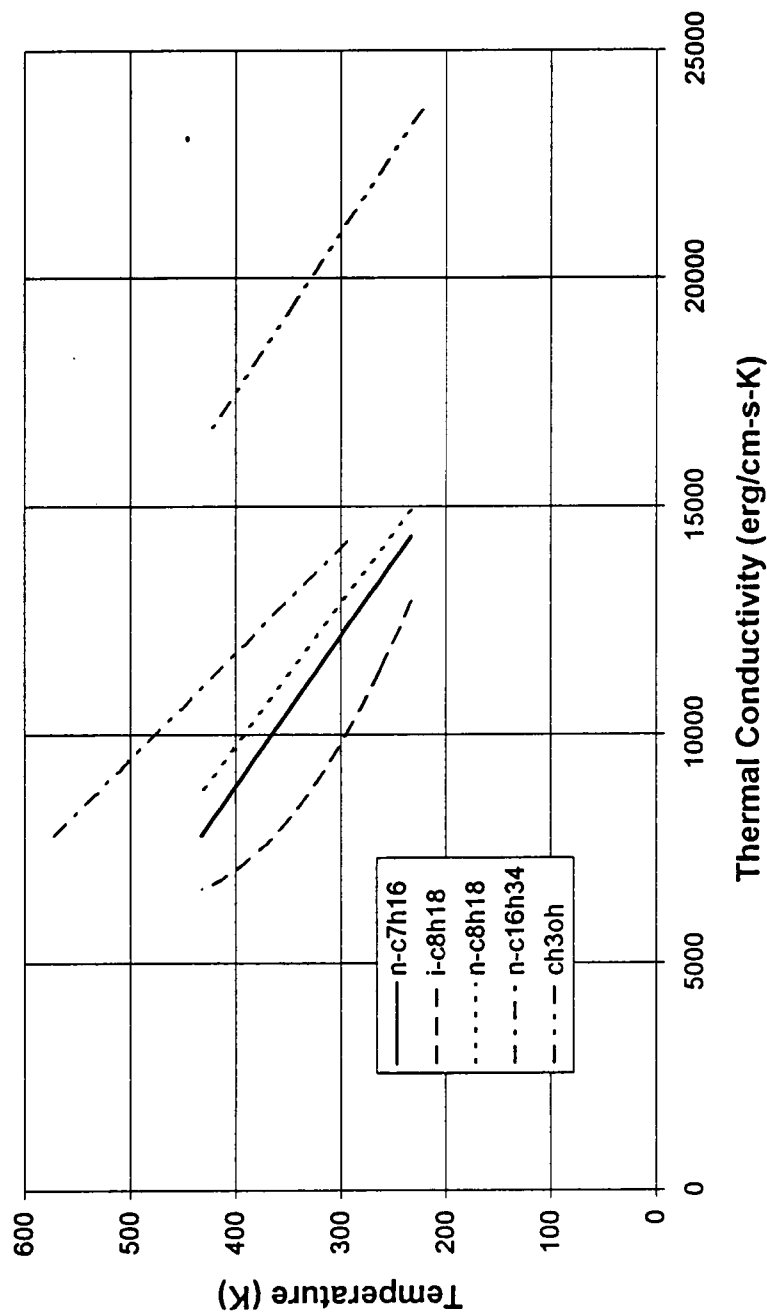


Figure E5. Liquid Thermal Conductivity of Selected Hydrocarbons as a Function of Temperature.

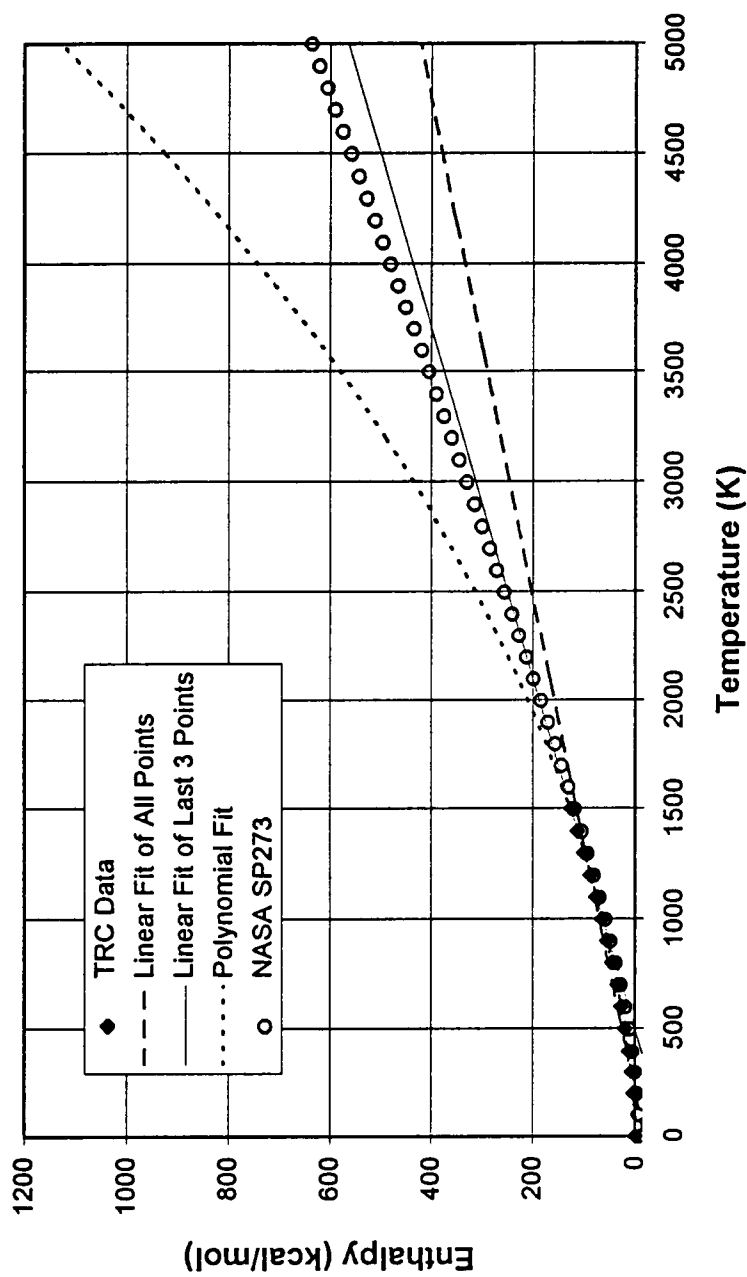


Figure E6. Iso-Octane Enthalpy as a Function of Temperature.

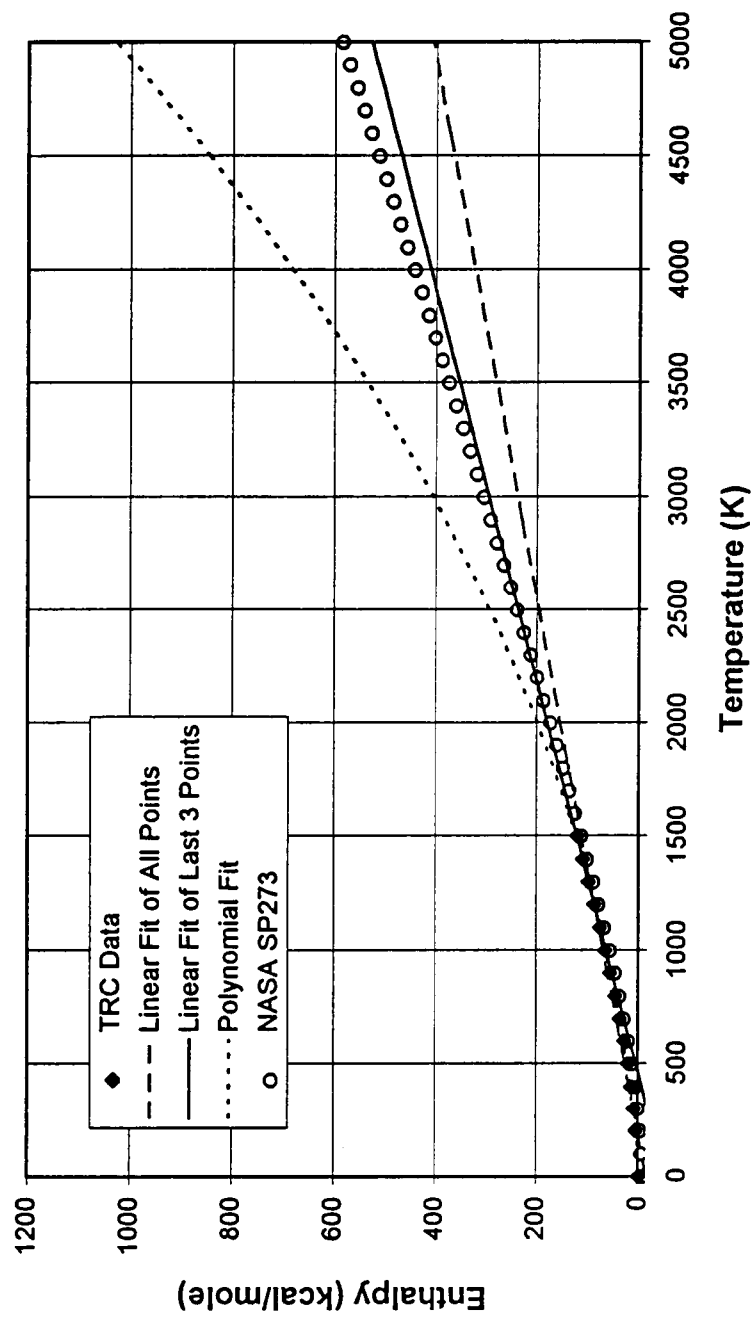


Figure E7. N-Octane Enthalpy as a Function of Temperature.

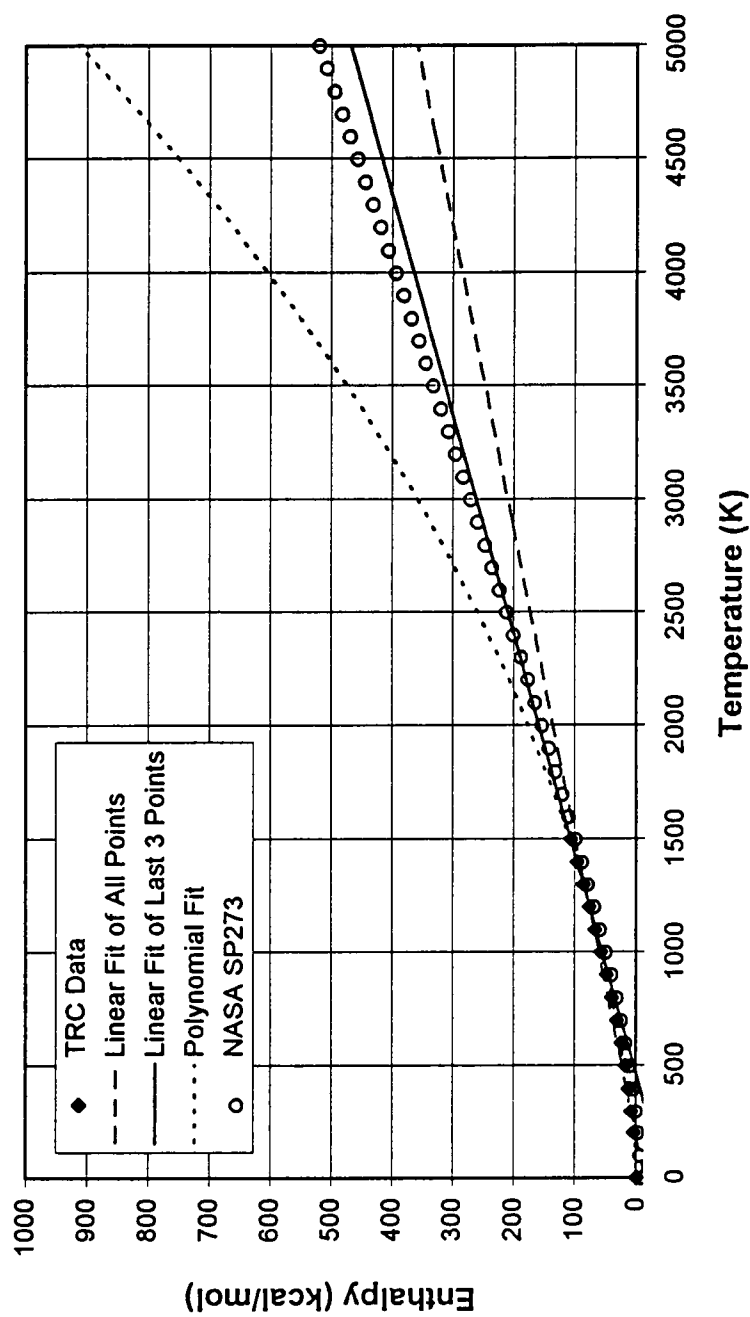


Figure E8. N-Heptane Enthalpy as a Function of Temperature.

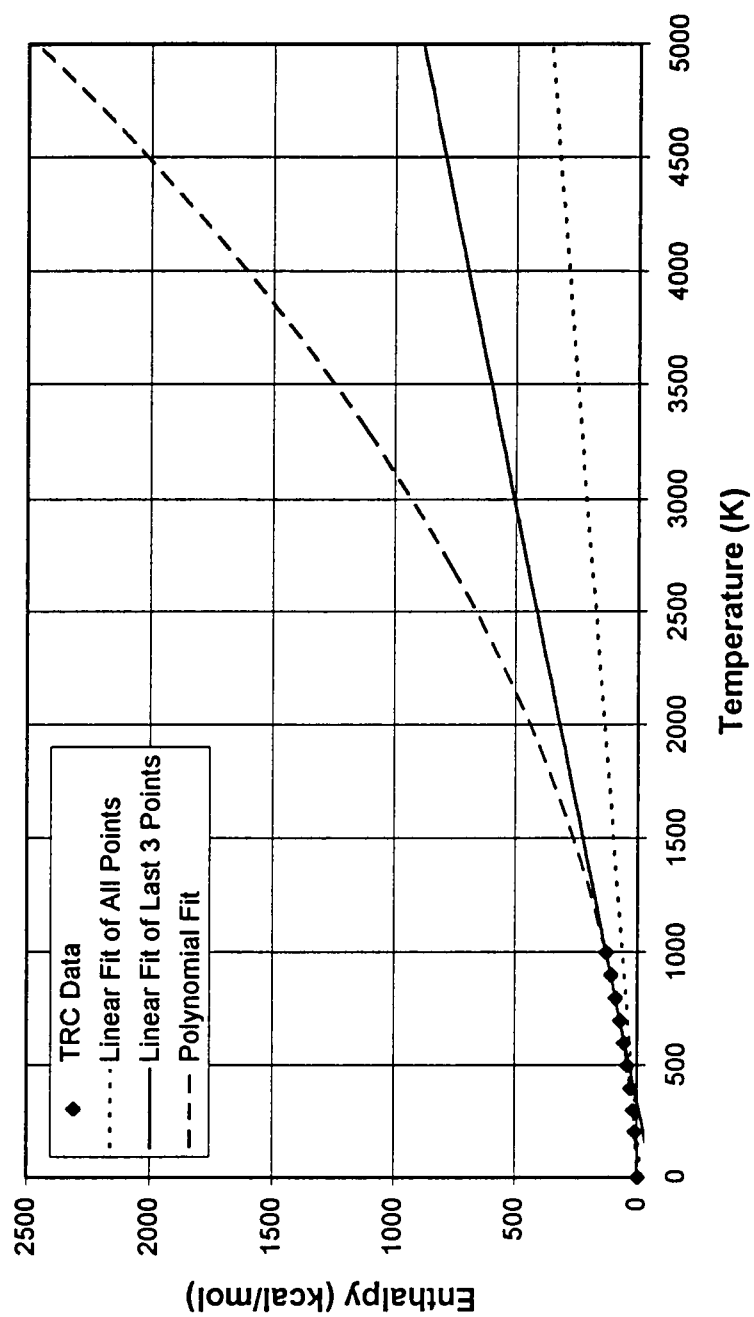


Figure E9. N-Hexadecane Enthalpy as a Function of Temperature.

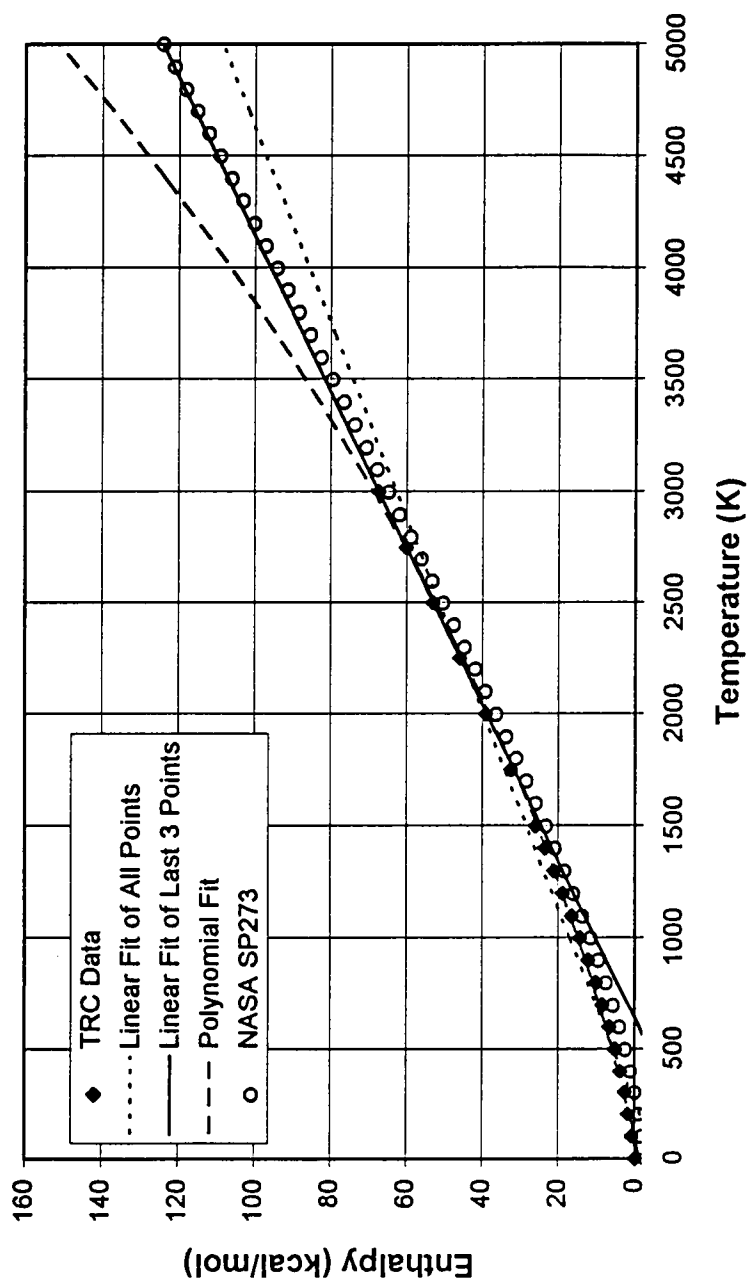


Figure E10. Methanol Enthalpy as a Function of Temperature.

APPENDIX F

ENTHALPY, SPECIFIC HEAT, ENTROPY, AND GIBBS FREE ENERGY OF SELECTED SPECIES

Thermodynamic properties have been defined in a temperature range of 0 K to 5000 K using data and curve fits from JANAF, TRC, and NASA SP273. Values are defined in 100 K temperature increments and are documented in a Fortran data statement format to facilitate use. Specifically, this means that each line in a data block is continued using a continuation number in column six. This number is equivalent to the number one would assign to the continuation lines. For example, CH has an enthalpy value of 2.835 at the end of the first line. The next line (i.e., the first continuation line) is numbered 1 and the numerals .835 are the first entry in that line to conclude the value 2.835. NASA SP273 curve fits are defined as follows:

specific heat: $C_p/R_u = A_1 + A_2 * T + A_3 * T^2 + A_4 * T^3 + A_5 * T^4$

enthalpy: $h/R_u T = 1.0/T * (A_1 * T + A_2 * T^2 + A_3 * T^3 + A_4 * T^4 + A_5 * T^5 + A_6)$

entropy $s/R_u = A_1 * \ln T + A_2 * T + A_3 * T^2/2 + A_4 * T^3/3 + A_5 * T^4/4 + A_7$

Specific notes using the defined coefficients in NASA SP273 are (1) the coefficients, A_i , exist in three rows of five each with two sets of seven, (2) the 15th coefficient is not used, (3) the first seven coefficients are for the temperature range 1000 to the maximum temperature value listed, and (4) The second seven coefficients are for the temperature range beginning with the minimum value ranging to 1000 K.

F.1 Enthalpy

Units of Enthalpy, $(h-h(T_o))$, are kcal/mole.

c CH (methylidyne, Ref: JANAF)

data (hk(n,7),n=1,51) /-2.086,-1.382,-.684,.013,.711,1.411,2.117,2
1 .835,3.566,4.315,5.084,5.872,6.681,7.509,8.357,9.222,10.103,11.00
2 0,11.910,12.832,13.765,14.708,15.660,16.618,17.583,18.554,19.529,
3 20.508,21.491,22.477,23.465,24.456,25.448,26.442,27.438,28.435,29
4 .433,30.432,31.432,32.433,33.435,34.437,35.441,36.445,37.451,38.4
5 57,39.465,40.473,41.482,42.493,43.505/

c CH₂ (methylene, Ref: JANAF)

data (hk(n,6),n=1,51) /-2.096,-1.408,-.710,.014,.797,1.647,2.559,3
1 .527,4.547,5.616,6.730,7.885,9.076,10.301,11.554,12.834,14.136,15
2 .458,16.798,18.153,19.522,20.903,22.296,23.698,25.109,26.529,27.9
3 95,29.389,30.828,32.273,33.723,35.178,36.637,38.100,39.566,41.036
4 ,42.509,43.985,45.464,46.945,48.429,49.914,51.402,52.892,54.383,5
5 5.876,57.730,58.866,60.363,61.861,63.361/

c CH₂O (formaldehyde, Ref: JANAF)

data (hk(n,7),n=1,51) /-2.395,-1.600,-.804,.016,.906,1.898,2.998,4
1 .200,5.495,6.872,8.322,9.833,11.398,16.009,14.660,16.346,18.602,1
2 9.803,21.567,23.351,25.153,26.970,28.800,30.643,32.497,34.360,36.
3 232,38.112,39.998,41.892,43.791,45.695,47.605,49.518,51.436,53.35
4 8,55.283,57.212,59.143,61.077,63.014,64.953,66.894,68.837,70.782,
5 72.729,74.678,76.628,78.580,80.534,82.488/

c CH₂OH (Ref. NASA SP273)

data (hk(n,2),n=1,51) /-2.840,-2.021,-1.067,0.023,1.247,2.599,4.06

1 8,5.640,7.302,9.043,10.856,12.734,14.667,16.650,18.678,20.748,22.
 2 855,24.996,27.168,29.367,31.591,33.836,36.101,38.384,40.681,42.99
 3 3,45.316,47.650,49.993,52.344,54.702,57.067,59.437,61.813,64.193,
 4 66.578,68.966,71.358,73.754,76.153,78.555,80.961,83.370,85.783,88
 5 .199,90.618,93.041,95.468,97.898,100.331,102.767/

c CH_3 (methyl, Ref: JANAF)

data (hk(n,4),n=1,51) /-2.487,-1.692,-.871,.017,.983,2.026,3.144,4
 1 .333,5.589,6.910,8.290,9.726,11.213,12.746,14.321,15.933,17.578,1
 2 9.252,20.953,22.677,24.422,26.186,27.966,29.762,31.571,33.393,35.
 3 226,37.069,38.921,40.781,42.649,44.524,46.405,48.293,50.185,52.08
 4 3,53.986,55.892,57.803,59.717,61.635,63.556,65.480,67.406,69.336,
 5 71.266,73.202,75.138,77.076,79.017,80.959/

c CH_3O (methoxyl, Ref: NASA SP273)

data (hk(n,5),n=1,51) /-2.435,-1.750,-0.940,0.021,1.146,2.436,3.87
 1 8,5.456,7.151,8.946,10.832,12.794,14.819,16.900,19.032,21.209,23.
 2 428,25.684,27.972,30.290,32.633,34.998,37.384,39.786,42.204,44.63
 3 4,47.076,49.527,51.986,54.453,56.925,59.402,61.884,64.370,66.860,
 4 69.352,71.848,74.347,76.849,79.354,81.861,84.373,86.887,89.405,91
 5 .927,94.453,96.983,99.516,102.054,104.596,107.142/

c CH_3OH (methanol, Ref: TRC to 3000K, then extrapolated using a

c linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.0,0.8,1.8,2.8,3.9,5.2,6.7,8.4,10.3,12.2,1
 1 4.3,16.5,18.8,21.1,23.6,26.1,28.0,30.4,32.9,35.5,38.2,40.9,43.7,4
 2 6.6,49.5,52.5,55.6,58.8,62.0,65.3,68.7,70.19,73.04,75.89,78.75,81
 3 .60,84.45,87.30,90.15,93.0,95.86,98.71,101.56,104.41,107.26,110.1
 4 1,112.97,115.82,118.67,121.52,124.37/

c CH₃OH (methanol, Ref. NASA SP273)

data (hk(n,1),n=1,51) /-2.917,-1.905,-0.971,0.021,1.159,2.483,4.00
1 0,5.692,7.532,9.498,11.578,13.764,16.034,18.380,20.796,23.274,25.
2 809,28.395,31.026,33.699,36.408,39.149,41.919,44.714,47.532,50.36
3 9,53.223,56.092,58.974,61.867,64.770,67.682,70.602,73.529,76.462,
4 79.400,82.344,85.293,88.247,91.206,94.169,97.138,100.111,103.089,
5 106.073,109.061,112.055,115.054,118.058,121.067,124.081/

c CH₄ (methane, Ref: JANAF)

data (hk(n,3),n=1,51) /-2.396,-1.601,-.805,.016,.923,1.960,3.138,4
1 .454,5.897,7.458,9.125,10.887,12.732,14.652,16.637,18.679,20.772,
2 22.910,25.086,27.298,29.540,31.809,34.103,36.418,38.753,41.106,43
3 .474,45.857,48.253,50.660,53.079,55.507,57.944,60.389,62.842,65.3
4 02,67.768,70.241,72.719,75.202,77.690,80.182,82.678,85.179,87.683
5 ,90.190,92.701,95.214,97.730,100.249,102.771/

c CO (carbon monoxide, Ref: JANAF)

data (hk(n,9),n=1,51) /-2.072,-1.379,-.683,.013,.711,1.417,2.137,2
1 .873,3.627,4.397,5.183,5.983,6.794,7.616,8.446,9.285,10.130,10.98
2 0,11.836,12.697,13.561,14.430,15.301,16.175,17.052,17.931,18.813,
3 19.696,20.582,21.469,22.357,23.248,24.139,25.032,25.927,26.822,27
4 .719,28.617,29.516,30.416,31.316,32.218,33.121,34.025,34.930,35.8
5 35,36.741,37.649,38.557,39.465,40.375/

c CO₂ (carbon dioxide, Ref: JANAF)

data (hk(n,10),n=1,51)/-2.238,-1.543,-.816,.016,.958,1.987,3.087,4
1 .245,5.453,6.702,7.984,9.296,10.632,11.988,13.362,14.750,16.157,1
2 7.565,18.987,20.418,21.857,23.303,24.755,26.217,27.674,29.141,30.
3 613,32.088,33.567,35.049,36.535,38.024,39.515,41.010,42.507,44.00

4 6,45.508,47.012,48.518,50.027,51.538,53.051,54.566,56.082,57.601,
5 59.122,60.644,62.169,63.695,65.223,66.753/

c C_2H (CCH radical, Ref: JANAF)

data (hk(n,16),n=1,51)/-2.248,-1.553,-.821,.016,.946,1.941,2.989,4
1 .082,5.216,6.386,7.588,8.820,10.078,11.359,12.662,13.985,15.325,1
2 6.683,18.054,19.445,20.849,22.267,23.689,25.144,26.602,28.073,29.
3 557,31.052,32.558,34.075,35.603,37.140,38.686,40.241,41.804,43.37
4 4,44.951,46.534,48.123,49.715,51.315,52.918,54.524,56.134,57.745,
5 59.361,60.978,62.596,64.216,65.837,67.458/

c C_2H_2 (acetylene, Ref: JANAF)

data (hk(n,15),n=1,51)/-2.393,-1.698,-.938,.020,1.155,2.418,3.771,
1 5.199,6.693,8.245,9.852,11.507,13.208,14.950,16.729,18.543,20.387
2 ,22.258,24.155,26.074,28.015,29.974,31.951,33.944,35.952,37.974,4
3 0.008,42.055,44.112,46.179,48.257,50.343,52.439,54.542,56.654,58.
4 773,60.899,63.032,65.172,67.319,69.471,71.630,73.794,75.964,78.13
5 9,80.320,82.506,84.697,86.893,89.094,91.300/

c C_2H_3 (Ref: NASA SP273)

data (hk(n,14),n=1,51)/-2.356,-1.694,-0.916,0.020,1.133,2.421,3.86
1 6,5.445,7.131,8.907,10.768,12.706,14.706,16.761,18.866,21.017,23.
2 210,25.439,27.701,29.993,32.312,34.653,37.016,39.396,41.793,44.20
3 4,46.627,49.060,51.503,53.954,56.412,58.876,61.345,63.820,66.298,
4 68.781,71.268,73.758,76.251,78.748,81.248,83.752,86.259,88.770,91
5 .285,93.803,96.325,98.850,101.380,103.913,106.449/

c C_2H_4 (ethylene, Ref: JANAF)

data (hk(n,13),n=1,51)/-2.514,-1.719,-.909,.019,1.167,2.550,4.143,
1 5.918,7.851,9.920,12.100,14.404,16.791,19.258,21.797,24.397,27.05

2 1,29.753,32.408,35.279,38.094,40.937,43.807,46.700,49.614,52.546,
 3 55.496,58.461,61.440,64.431,67.434,70.447,73.470,76.502,79.542,82
 4 .590,85.664,88.705,91.722,94.844,97.921,101.003,104.090,107.180,1
 5 10.275,113.373,116.475,119.579,122.687,125.798,128.911/

c C_2H_5 (ethyl, Ref: TRC to 3000K, then extrapolated using a

c linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.0,0.0,1.84,2.96,4.33,5.96,7.81,9.87,12.10

1 ,14.49,17.01,19.66,22.41,25.26,28.19,31.19,33.51,36.45,39.48,42.6

2 0,45.80,49.08,52.45,55.91,59.45,63.07,66.78,70.58,74.46,78.42,82.

3 47,84.33,87.77,91.21,94.65,98.06,101.54,104.98,108.42,111.86,115.

4 30,118.74,122.18,125.62,129.06,132.50,135.94,139.38,142.82,146.26

5 ,149.70/

c C_2H_5 (ethyl, Ref: NASA SP273)

data (hk(n,12),n=1,51)/-2.829,-1.994,-1.074,0.024,1.357,2.940,4.76

1 3,6.797,9.010,11.374,13.877,16.507,19.237,22.059,24.964,27.943,30

2 .990,34.097,37.259,40.469,43.722,47.013,50.337,53.691,57.071,60.4

3 73,63.895,67.334,70.787,74.253,77.731,81.218,84.713,88.217,91.727

4 ,95.243,98.765,102.293,105.826,109.364,112.908,116.457,120.012,12

5 3.572,127.139,130.712,134.290,137.875,141.466,145.063,148.666/

c C_2H_6 (ethane, Ref: TRC to 1500K, then extrapolated using a

c linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.0,0.57,1.73,2.86,4.27,5.98,7.98,10.23,12.

1 71,15.39,18.24,21.23,24.37,27.62,30.98,34.43,37.81,41.22,44.62,48

2 .02,51.42,54.83,58.23,61.63,65.03,68.44,71.84,75.24,78.64,82.05,8

3 5.45,88.85,92.25,95.66,99.06,102.46,109.27,112.67,116.07,119.47,1

4 22.88,126.28,129.68,133.08,136.49,139.89,143.29,146.69,150.10,153

5 .50/

- c C_2H_6 (ethane, Ref: NASA SP273)

data (hk(n,11),n=1,51)/-2.844,-2.018,-1.102,0.025,1.431,3.138,5.13
1 7,7.395,9.876,12.544,15.386,18.382,21.502,24.734,28.068,31.494,35
2 .003,38.585,42.235,45.943,49.703,53.510,57.358,61.242,65.157,69.0
3 99,73.065,77.051,81.056,85.075,89.108,93.153,97.207,101.271,105.3
4 43,109.422,113.508,117.601,121.700,125.806,129.918,134.037,138.16
5 3,142.295,146.435,150.582,154.737,158.899,163.069,167.246,171.430
6 /

- c C_7H_{16} (n-heptane, Ref: TRC to 1500K, then extrapolated using a

- c linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.0,2.25,4.53,8.02,12.51,18.05,24.50,31.73,
1 39.57,48.07,56.96,66.25,75.95,85.84,96.04,106.52,116.81,127.16,13
2 7.50,147.84,158.18,168.52,178.86,189.20,199.55,209.89,220.23,230.
3 57,240.91,251.25,261.60,271.94,282.28,292.62,302.96,313.30,323.64
4 ,333.99,344.33,354.67,365.01,375.35,385.69,396.04,406.38,416.72,4
5 27.06,437.40,447.74,458.08,468.43/

- c C_7H_{16} (n-heptane, Ref: NASA SP273)

data (hk(n,7),n=1,51) /-8.281,-6.065,-3.401,0.079,4.560,10.070,16.
1 528,23.790,31.696,40.117,49.001,58.299,67.919,77.830,88.006,98.42
2 3,109.058,119.889,130.896,142.061,153.367,164.800,176.345,187.990
3 ,199.723,211.535,223.416,235.358,247.355,259.400,271.488,283.616,
4 295.779,307.974,320.200,332.454,344.735,357.042,369.376,381.735,3
5 94.120,406.531,418.968,431.432,443.922,456.441,468.986,481.559,49
6 4.159,506.785,519.437/

- c C_8H_{18} (iso-octane, {2,2,4 trimethylpentane}, Ref: TRC to 1500K,

c then extrapolated using a linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.,2.8960,5.7936,8.6904,13.827,20.130,27.41

1 9,35.58,44.51,54.079,64.177,74.768,85.796,97.157,108.84,120.75,13

2 2.65,144.56,156.47,168.38,180.29,192.2,204.11,216.02,227.93,239.8

3 4,251.74,263.65,275.56,287.47,299.38,311.29,323.2,335.11,347.02,3

4 58.95,370.83,382.74,394.65,406.56,418.47,430.38,442.29,454.20,466

5 .11,478.02,489.92,501.83,516.74,525.65,537.56/

c C₈H₁₈ (iso-octane Ref: NASA SP273)

data (hk(n,7),n=1,51) /-7.012,-6.116,-3.737,0.090,5.278,11.705,19.

1 227,27.694,36.965,46.924,57.496,68.601,80.157,92.123,104.462,117.

2 137,130.115,143.367,156.864,170.579,184.489,198.572,212.808,227.1

3 78,241.667,256.260,270.943,285.706,300.537,315.429,330.374,345.36

4 4,360.396,375.464,390.565,405.697,420.857,436.044,451.258,466.497

5 ,481.763,497.054,512.373,527.718,543.091,558.493,573.923,589.381,

6 604.868,620.382,635.923/

c C₈H₁₈ (n-octane, Ref: TRC to 1500K, then extrapolated using a

c linear fit of the last three data points)

data (hk(n,7),n=1,51) /0.0,2.5,5.15,9.10,14.23,20.53,27.86,36.08,4

1 5.07,54.56,64.65,75.14,86.03,97.33,108.81,120.61,132.20,143.85,15

2 5.49,167.13,178.78,190.42,202.06,213.71,225.35,236.99,248.63,260.

3 28,271.92,283.56,295.21,306.85,318.49,330.14,341.78,353.42,365.07

4 ,376.71,388.35,400.00,411.64,423.28,434.93,446.57,458.21,469.86,4

5 81.50,493.14,504.78,516.43,528.07/

c C₈H₁₈ (n-octane, Ref: NASA SP273)

data (hk(n,7),n=1,51) /-9.375,-6.879,-3.863,0.090,5.186,11.454,18.

1 797,27.047,36.019,45.561,55.612,66.117,76.971,88.143,99.605,111.3

- 2 30,123.292,135.470,147.841,160.385,173.086,185.925,198.889,211.96
 3 3,225.136,238.396,251.734,265.142,278.610,292.134,305.708,319.326
 4 ,332.986,346.683,360.416,374.182,387.980,401.809,415.669,429.559,
 5 443.479,457.430,471.412,485.425,499.469,513.546,527.654,541.794,5
 6 55.966,570.168,584.399/
- c C_8H_{18} (octane, data from the conchas spray report)
 data (hk(n,1),n=1,51) /0.,2.8960,5.7936,8.6904,13.827,20.130,27.41
 1 9,35.58,44.51,54.079,64.177,74.768,85.796,97.157,108.84,120.75,13
 2 2.65,144.56,156.47,168.38,180.29,192.2,204.11,216.02,227.93,239.8
 3 4,251.74,263.65,275.56,287.47,299.38,311.29,323.2,335.11,347.02,3
 4 58.95,370.83,382.74,394.65,406.56,418.47,430.38,442.29,454.20,466
 5 .11,478.02,489.92,501.83,516.74,525.65,537.56/
- c $C_{16}H_{34}$ (n-hexadecane, Ref: TRC to 1000K, then extrapolated using a
 c linear fit of the last three data points)
 data (hk(n,7),n=1,51) /0.0,2.2,4.53,8.02,12.51,18.05,24.50,31.73,3
 1 9.57,48.07,56.96,66.25,75.95,85.84,96.04,106.52,116.81,127.16,137
 2 .50,147.84,158.18,168.52,178.86,189.20,199.55,209.89,220.23,230.5
 3 7,240.91,251.25,261.60,271.94,282.28,292.62,302.96,313.30,323.64,
 4 333.99,344.99,354.67,365.01,375.35,385.69,369.04,406.38,416.72,42
 5 7.06,437.40,447.74,458.08,468.43/
- c H (monatomic hydrogen, Ref: JANAF)
 data (hk(n,17),n=1,51)/-1.481,-.948,-.488,.009,.506,1.003,1.500,1.
 1 996,2.493,2.990,3.487,3.984,4.481,4.977,5.474,5.971,6.468,6.965,7
 2 .461,7.958,8.455,8.952,9.449,9.945,10.442,10.939,11.436,11.933,12
 3 .430,12.926,13.423,13.920,14.417,14.914,15.410,15.907,16.404,16.9
 4 01,17.398,17.895,18.391,18.888,19.385,19.882,20.379,20.875,21.372

5 ,21.869,22.366,22.863,23.359/

c H₂ (hydrogen, Ref: JANAF)

data (hk(n,20),n=1,51)/-2.024,-1.265,-.662,.013,.707,1.406,2.106,2

1 .808,3.514,4.226,4.944,5.67,6.404,7.148,7.902,8.668,9.446,10.233,

2 11.03,11.836,12.651,13.475,14.307,15.146,15.993,16.848,17.708,18.

3 575,19.448,20.326,21.21,22.098,22.992,23.891,24.794,25.703,26.616

4 ,27.535,28.457,29.385,30.317,31.253,32.194,33.139,34.088,35.042,3

5 5.999,36.961,37.926,38.895,39.868/

c H₂O (water, Ref: JANAF)

data (hk(n,21),n=1,51)/-2.367,-1.581,-.784,.015,.825,1.654,2.509,3

1 .39,4.3,5.24,6.209,7.21,8.24,9.298,10.384,11.495,12.63,13.787,14.

2 964,16.16,17.373,18.602,19.846,21.103,22.372,23.653,24.945,26.246

3 ,27.556,28.875,30.201,31.535,32.876,34.223,35.577,36.936,38.3,39.

4 669,41.043,42.422,43.805,45.192,46.583,47.977,49.375,50.777,52.18

5 1,53.589,55.,56.413,57.829/

c H₂O₂ (hydrogen peroxide, Ref: TRC)

data (hk(n,22),n=1,51)/0.0,0.82,1.71,2.68,3.74,4.90,6.14,7.45,8.82

1 ,10.24,11.71,13.23,14.78,16.36,17.99,19.63,21.05,22.69,24.37,26.0

2 8,27.83,29.61,31.42,33.27,35.15,37.07,39.02,41.00,43.02,45.07,47.

3 16,48.47,50.34,52.21,54.08,55.94,57.81,59.68,61.55,63.41,67.15,69

4 .02,70.88,72.75,74.62,76.49,78.35,80.22,82.09,83.96/

c HCO (formyl{cho}, Ref: JANAF)

data (hk(n,18),n=1,51)/-2.387,-1.593,-.796,.015,.863,1.758,2.700,3

1 .689,4.720,5.791,6.896,8.033,9.196,10.383,11.591,12.817,14.059,15

2 .314,16.582,17.860,19.148,20.444,21.747,23.058,24.374,25.695,27.0

3 22,28.353,29.687,31.025,32.367,33.711,35.058,36.408,37.760,39.114

4 ,40.470,41.828,43.187,44.548,45.911,47.275,48.640,50.006,51.373,5
5 2.741,54.111,55.481,56.852,58.224,59.596/

c HO₂ (hydroperoxyl, Ref: JANAF)

data (hk(n,19),n=1,51)/-2.390,-1.596,-.799,.015,.877,1.797,2.771,3
1 .791,4.850,5.943,7.066,8.215,9.387,10.580,11.791,13.019,14.261,15
2 .515,16.782,18.058,19.343,20.637,21.937,23.245,24.558,25.876,27.2
3 00,28.528,29.859,31.195,32.534,33.875,35.220,36.567,37.917,39.268
4 ,40.622,41.978,43.335,44.694,46.055,47.417,48.780,50.144,51.510,5
5 2.876,54.244,55.613,56.982,58.353,59.724/

c O (monatomic oxygen, Ref: JANAF)

data (hk(n,23),n=1,51)/-1.608,-1.080,-.523,.010,.528,1.038,10544,2
1 .048,2.550,3.052,3.552,4.051,4.551,5.049,5.548,6.046,6.544,7.042,
2 7.540,8.038,8.536,9.034,9.532,10.029,10.527,11.026,11.524,12.023,
3 12.522,13.022,13.522,14.023,14.524,15.026,15.529,16.023,16.537,17
4 .043,17.459,18.057,18.565,19.075,19.586,20.098,20.611,21.126,21.6
5 41,22.158,22.676,23.195,23.715/

c O₂ (oxygen, Ref: JANAF)

data (hk(n,25),n=1,51)/-2.075,-1.381,-.685,.013,.724,1.455,2.21,2.
1 988,3.786,4.6,5.427,6.266,7.114,7.971,8.835,9.706,10.583,11.465,1
2 2.354,13.249,14.149,15.054,15.966,16.882,17.804,18.732,19.664,20.
3 602,21.545,22.493,23.446,24.403,25.365,26.331,27.302,28.276,29.25
4 4,30.236,31.221,32.209,33.201,34.196,35.193,36.193,37.196,38.201,
5 39.208,40.218,41.229,42.242,43.257/

c OH (hydroxyl, Ref: JANAF)

data (hk(n,24),n=1,51)/-2.192,-1.467,-.711,.013,.725,1.432,2.137,
1 2.845,3.556,4.275,5.003,5.742,6.491,7.252,8.023,8.805,9.596,10.39

2 7,11.207,12.024,12.849,13.681,14.52,15.364,16.214,17.069,17.929,1
 3 8.794,19.662,20.535,21.411,22.291,23.174,24.06,24.949,25.841,26.7
 4 35,27.632,28.532,29.434,30.338,31.245,32.153,33.064,33.976,34.89,
 5 35.807,36.725,37.644,38.566,39.489/

c N₂ (nitrogen, Ref: JANAF)

data (hk(n,2),n=1,51) /-2.072,-1.379,-.683,.013,.71,1.413,2.125,2.
 1 853,3.596,4.355,5.129,5.917,6.718,7.529,8.35,9.179,10.015,10.858,
 2 11.707,12.56,13.418,14.28,15.146,16.015,16.886,17.761,18.638,19.5
 3 17,20.398,21.28,22.165,23.051,23.939,24.829,25.719,26.611,27.505,
 4 28.399,29.295,30.191,31.089,31.988,32.888,33.788,34.690,35.593,36
 5 .496,37.4,38.306,39.212,40.119/

F.2 Specific Heat Capacity

Units of specific heat are cal/mole-K.

c CH (methylidyne, Ref: NASA SP273)

data (hk(n,7),n=1,51) /6.931,6.967,6.971,6.968,6.981,7.024,7.103,7
 1 .220,7.370,7.538,7.707,7.901,8.083,8.255,8.416,8.567,8.708,8.841,
 2 8.964,9.080,9.188,9.288,9.381,9.468,9.549,9.623,9.692,9.755,9.814
 3 ,9.867,9.916,9.961,10.002,10.038,10.071,10.101,10.127,10.150,10.1
 4 70,10.186,10.200,10.211,10.219,10.225,10.228,10.228,10.225,10.220
 5 ,10.212,10.201,10.187/

c CH₂ (methylene, Ref: NASA SP273)

data (hk(n,6),n=1,51) /7.439,7.705,8.023,8.370,8.728,9.085,9.437,9
 1 .783,10.126,10.477,10.852,11.179,11.477,11.748,11.992,12.213,12.4
 2 11,12.588,12.747,12.887,13.011,13.121,13.217,13.300,13.372,13.435

3 ,13.488,13.534,13.572,13.605,13.633,13.656,13.675,13.691,13.705,1
4 3.718,13.729,13.738,13.748,13.757,13.766,13.776,13.786,13.796,13.
5 807,13.818,13.829,13.841,13.853,13.864,13.875/

c CH₂O (formaldehyde, Ref: NASA SP273)

data (hk(n,7),n=1,51) /9.500,8.221,7.988,8.466,9.357,10.431,11.518
1 ,12.511,13.367,14.105,14.807,15.319,15.782,16.202,16.579,16.918,1
2 7.221,17.492,17.731,17.943,18.130,18.293,18.435,18.558,18.665,18.
3 756,18.835,18.902,18.959,19.007,19.049,19.085,19.116,19.143,19.16
4 8,19.191,19.214,19.235,19.257,19.279,19.303,19.327,19.353,19.379,
5 19.407,19.436,19.465,19.495,19.524,19.552,19.579/

c CH₂OH (Ref. NASA SP273)

data (hk(n,2),n=1,51) /7.684,8.883,10.215,11.578,12.898,14.123,15.
1 224,16.190,17.031,17.780,18.488,19.062,19.586,20.063,20.498,20.89
2 2,21.248,21.569,21.859,22.118,22.350,22.557,22.740,22.904,23.048,
3 23.175,23.287,23.386,23.473,23.549,23.617,23.677,23.731,23.779,23
4 .823,23.864,23.902,23.938,23.973,24.008,24.041,24.075,24.109,24.1
5 43,24.178,24.213,24.247,24.282,24.316,24.348,24.379/

c CH₃ (methyl, Ref: NASA SP273)

data (hk(n,4),n=1,51) /7.299,7.795,8.448,9.190,9.969,10.747,11.495
1 ,12.199,12.856,13.474,14.075,14.589,15.059,15.489,15.881,16.236,1
2 6.559,16.851,17.114,17.351,17.563,17.753,17.922,18.073,18.207,18.
3 326,18.431,18.524,18.606,18.678,18.743,18.800,18.851,18.897,18.93
4 9,18.978,19.014,19.048,19.081,19.113,19.144,19.175,19.205,19.236,
5 19.267,19.298,19.328,19.359,19.389,19.417,19.445/

c CH₃O (methoxyl, Ref: NASA SP273)

data (hk(n,5),n=1,51) /6.491,7.436,8.818,10.423,12.087,13.684,15.1

1 34,16.397,17.474,18.410,19.292,19.945,20.538,21.073,21.557,21.991
 2 ,22.380,22.727,23.035,23.308,23.549,23.760,23.944,24.104,24.243,2
 3 4.363,24.466,24.554,24.629,24.694,24.750,24.798,24.840,24.877,24.
 4 911,24.943,24.973,25.003,25.033,25.063,25.095,25.128,25.163,25.20
 5 0,25.238,25.277,25.317,25.358,25.399,25.439,25.477/

c CH₃OH (methanol, Ref. NASA SP273)

data (hk(n,7),n=1,51) /11.320,9.485,9.437,10.546,12.277,14.218,16.

1 083,17.710,19.062,20.226,21.414,22.292,23.092,23.820,24.479,25.07
 2 5,25.613,26.095,26.528,26.914,27.257,27.562,27.831,28.068,28.277,
 3 28.459,28.619,28.758,28.879,28.986,29.079,29.161,29.234,29.299,29
 4 .358,29.413,29.465,29.515,29.563,29.611,29.659,29.708,29.757,29.8
 5 08,29.859,29.911,29.963,30.016,30.067,30.116,30.163/

c CH₄ (methane, Ref: NASA SP273)

data (hk(n,3),n=1,51) /10.200,8.396,7.987,8.541,9.681,11.105,12.59

1 4,14.009,15.286,16.445,17.583,18.503,19.351,20.130,20.845,21.501,
 2 22.102,22.652,23.155,23.614,24.034,24.417,24.767,25.086,25.379,25
 3 .648,25.895,26.124,26.335,26.533,26.718,26.893,27.060,27.219,27.3
 4 74,27.524,27.671,27.817,27.962,28.106,28.251,28.397,28.544,28.692
 5 ,28.842,28.992,29.143,29.295,29.446,29.596,29.744/

c CO (carbon monoxide, Ref: NASA SP273)

data (hk(n,9),n=1,51) /7.107,7.009,6.958,6.961,7.016,7.120,7.264,7

1 .436,7.618,7.788,7.921,8.034,8.137,8.231,8.315,8.391,8.459,8.521,
 2 8.575,8.624,8.667,8.705,8.739,8.769,8.795,8.818,8.838,8.855,8.871
 3 ,8.885,8.897,8.908,8.918,8.928,8.937,8.945,8.954,8.962,8.971,8.98
 4 0,8.989,8.999,9.009,9.020,9.030,9.042,9.053,9.065,9.077,9.089,9.1
 5 01/

c CO₂ (carbon dioxide, Ref: NASA SP273)

data (hk(n,10),n=1,51)/4.698,6.328,7.721,8.889,9.859,10.657,11.311
1 ,11.845,12.284,12.653,12.974,13.200,13.405,13.590,13.757,13.907,1
2 4.041,14.160,14.266,14.359,14.442,14.514,14.578,14.633,14.681,14.
3 723,14.760,14.792,14.819,14.844,14.867,14.887,14.906,14.924,14.94
4 3,14.961,14.980,14.999,15.020,15.043,15.067,15.094,15.122,15.153,
5 15.185,15.221,15.258,15.297,15.339,15.382,15.427/

c C₂H (CCH radical, Ref: NASA SP273)

data (hk(n,16),n=1,51)/5.765,7.892,9.236,10.043,10.533,10.877,11.1
1 89,11.536,11.930,12.331,12.647,12.997,13.313,13.595,13.847,14.071
2 ,14.269,14.442,14.593,14.723,14.834,14.928,15.007,15.072,15.124,1
3 5.165,15.196,15.219,15.234,15.243,15.247,15.246,15.242,15.235,15.
4 227,15.217,15.206,15.196,15.186,15.176,15.167,15.160,15.154,15.14
5 9,15.146,15.145,15.144,15.145,15.146,15.148,15.149/

c C₂H₂ (acetylene, Ref: NASA SP273)

data (hk(n,15),n=1,51)/1.652,5.594,8.481,10.541,12.006,13.069,13.8
1 79,14.550,15.150,15.710,16.220,16.669,17.082,17.462,17.810,18.130
2 ,18.422,18.690,18.933,19.155,19.358,19.542,19.709,19.861,20.000,2
3 0.126,20.241,20.347,20.444,20.533,20.617,20.695,20.768,20.839,20.
4 906,20.971,21.035,21.099,21.162,21.225,21.289,21.354,21.420,21.48
5 7,21.557,21.627,21.700,21.774,21.850,21.926,22.004/

c C₂H₃ (Ref: NASA SP273)

data (hk(n,14),n=1,51)/6.383,7.127,8.519,10.234,12.021,13.701,15.1
1 61,16.363,17.335,18.177,19.059,19.699,20.282,20.811,21.291,21.724
2 ,22.114,22.464,22.778,23.057,23.305,23.525,23.719,23.890,24.040,2
3 4.170,24.284,24.384,24.470,24.546,24.611,24.669,24.721,24.766,24.

4 808,24.847,24.883,24.918,24.952,24.986,25.020,25.054,25.090,25.12

5 6,25.163,25.200,25.238,25.275,25.312,25.348,25.382/

c C_2H_4 (ethylene, Ref: NASA SP273)

data (hk(n,13),n=1,51)/7.848,7.361,8.378,10.283,12.574,14.875,16.9

1 43,18.661,20.040,21.222,22.475,23.365,24.175,24.910,25.575,26.176

2 ,26.716,27.200,27.633,28.018,28.360,28.662,28.929,29.162,29.367,2

3 9.545,29.700,29.834,29.951,30.053,30.141,30.218,30.287,30.348,30.

4 404,30.455,30.504,30.550,30.596,30.642,30.688,30.735,30.784,30.83

5 3,30.884,30.936,30.988,31.040,31.092,31.142,31.188/

c C_2H_5 (ethyl, Ref: NASA SP273)

data (hk(n,7),n=1,51) /8.544,8.594,9.960,12.102,14.580,17.065,19.3

1 38,21.289,22.918,24.336,25.762,26.816,27.775,28.646,29.433,30.144

2 ,30.783,31.356,31.868,32.323,32.727,33.084,33.398,33.673,33.914,3

3 4.124,34.307,34.465,34.602,34.721,34.825,34.915,34.995,35.067,35.

4 132,35.192,35.249,35.303,35.357,35.411,35.465,35.520,35.577,35.63

5 5,35.695,35.756,35.818,35.879,35.940,35.999,36.054/

c C_2H_6 (ethane, Ref: NASA SP273)

data (hk(n,11),n=1,51)/8.511,8.485,10.059,12.592,15.560,18.568,21.

1 347,23.758,25.789,27.556,29.303,30.600,31.779,32.848,33.815,34.68

2 7,35.471,36.172,36.798,37.355,37.848,38.283,38.665,39.000,39.292,

3 39.546,39.767,39.958,40.123,40.266,40.390,40.498,40.593,40.679,40

4 .756,40.828,40.895,40.960,41.025,41.089,41.155,41.222,41.291,41.3

5 62,41.435,41.510,41.585,41.661,41.735,41.807,41.875/

c H (monatomic hydrogen, Ref: NASA SP273)

data (hk(n,17),n=1,51)/4.965,4.965,4.965,4.965,4.965,4.965,4.965,4

1 .965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,

2 4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965
 3 ,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.96
 4 5,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.965,4.9
 5 65/

c H₂ (hydrogen, Ref: NASA SP273)

data (hk(n,20),n=1,51)/4.671,5.892,6.575,6.891,6.993,6.998,6.987,7
 1 .009,7.074,7.158,7.204,7.317,7.426,7.530,7.631,7.729,7.823,7.914,
 2 8.001,8.086,8.167,8.246,8.322,8.396,8.467,8.536,8.602,8.667,8.729
 3 ,8.789,8.848,8.904,8.959,9.013,9.065,9.115,9.164,9.212,9.258,9.30
 4 3,9.347,9.390,9.432,9.473,9.513,9.552,9.590,9.627,9.663,9.699,9.7
 5 34/

c H₂O (water, Ref: NASA SP273)

data (hk(n,21),n=1,51)/8.334,8.053,7.966,8.024,8.185,8.411,8.675,8
 1 .959,9.251,9.551,9.863,10.189,10.495,10.783,11.053,11.305,11.542,
 2 11.763,11.970,12.163,12.343,12.511,12.667,12.812,12.947,13.072,13
 3 .189,13.297,13.397,13.490,13.577,13.657,13.732,13.801,13.866,13.9
 4 26,13.983,14.037,14.087,14.135,14.180,14.223,14.265,14.305,14.344
 5 ,14.382,14.420,14.457,14.493,14.530,14.566/

c H₂O₂ (hydrogen peroxide, Ref: NASA SP273)

data (hk(n,22),n=1,51)/8.491,8.675,9.290,10.141,11.074,11.975,12.7
 1 72,13.435,13.974,14.439,14.923,15.306,15.661,15.988,16.290,16.569
 2 ,16.825,17.060,17.276,17.474,17.656,17.822,17.975,18.114,18.242,1
 3 8.359,18.467,18.567,18.658,18.743,18.822,18.895,18.964,19.029,19.
 4 091,19.150,19.207,19.262,19.316,19.368,19.420,19.471,19.521,19.57
 5 1,19.621,19.670,19.719,19.768,19.816,19.863,19.909/

c HCO (formyl {CHO}, Ref: NASA SP273)

data (hk(n,18),n=1,51)/8.376,7.987,7.991,8.269,8.713,9.236,9.774,1
 1 0.281,10.734,11.127,11.479,11.734,11.966,12.175,12.364,12.534,12.
 2 687,12.824,12.946,13.054,13.150,13.235,13.310,13.376,13.434,13.48
 3 5,13.530,13.569,13.604,13.635,13.663,13.689,13.713,13.735,13.756,
 4 13.777,13.797,13.818,13.839,13.860,13.882,13.905,13.928,13.952,13
 5 .977,14.002,14.027,14.052,14.077,14.101,14.125/

c HO₂ (hydroperoxyl, Ref: NASA SP273)

data (hk(n,19),n=1,51)/8.533,7.974,7.981,8.343,8.880,9.459,9.989,1
 1 0.424,10.764,11.051,11.373,11.615,11.846,12.066,12.275,12.474,12.
 2 663,12.842,13.011,13.171,13.321,13.463,13.596,13.720,13.837,13.94
 3 5,14.046,14.139,14.225,14.304,14.376,14.442,14.502,14.556,14.604,
 4 14.647,14.685,14.718,14.746,14.770,14.790,14.806,14.818,14.828,14
 5 .834,14.838,14.839,14.838,14.835,14.830,14.824/

c O (monatomic oxygen, Ref: NASA SP273)

data (hk(n,23),n=1,51)/6.285,5.761,5.426,5.231,5.126,5.075,5.049,5
 1 .031,5.013,4.998,4.998,4.993,4.989,4.986,4.982,4.980,4.977,4.975,
 2 4.974,4.973,4.973,4.973,4.974,4.976,4.978,4.980,4.983,4.987,4.992
 3 ,4.997,5.002,5.008,5.015,5.022,5.030,5.039,5.047,5.057,5.066,5.07
 4 7,5.087,5.098,5.109,5.121,5.133,5.145,5.157,5.169,5.182,5.194,5.2
 5 07/

c O₂ (oxygen, Ref: NASA SP273)

data (hk(n,25),n=1,51)/7.506,7.093,6.960,7.019,7.194,7.424,7.663,7
 1 .880,8.061,8.206,8.332,8.415,8.496,8.573,8.648,8.720,8.789,8.855,
 2 8.920,8.982,9.042,9.100,9.156,9.210,9.263,9.315,9.365,9.413,9.461
 3 ,9.507,9.552,9.596,9.640,9.682,9.723,9.764,9.803,9.842,9.880,9.91
 4 8,9.954,9.990,10.025,10.060,10.093,10.126,10.158,10.189,10.219,10

5 .248,10.276/

c OH (hydroxyl, Ref: NASA SP273)

data (hk(n,24),n=1,51)/7.923,7.535,7.283,7.136,7.064,7.042,7.054,7

1 .090,7.145,7.223,7.331,7.454,7.570,7.679,7.782,7.880,7.972,8.059,

2 8.141,8.218,8.291,8.361,8.426,8.488,8.547,8.603,8.657,8.707,8.756

3 ,8.802,8.846,8.888,8.929,8.968,9.006,9.042,9.077,9.111,9.144,9.17

4 6,9.207,9.238,9.267,9.296,9.324,9.351,9.377,9.402,9.427,9.450,9.4

5 73/

F.3 Entropy

Units of entropy are cal/mole-K.

c CH (methyldiyne, Ref: NASA SP273)

data (hk(n,7),n=1,51) /0.000,36.104,40.935,43.761,45.767,47.328,48

1 .615,49.719,50.692,51.570,52.373,53.117,53.812,54.466,55.084,55.6

2 69,56.227,56.759,57.268,57.755,58.224,58.675,59.109,59.528,59.933

3 ,60.324,60.703,61.070,61.426,61.771,62.106,62.432,62.749,63.057,6

4 3.358,63.650,63.935,64.213,64.484,64.748,65.006,65.258,65.504,65.

5 745,65.980,66.210,66.434,66.654,66.869,67.080,67.286/

c CH₂ (methylene, Ref: NASA SP273)

data (hk(n,6),n=1,51) /0.000,37.734,43.170,46.488,48.945,50.931,52

1 .618,54.099,55.428,56.641,57.764,58.813,59.799,60.729,61.608,62.4

2 43,63.238,63.996,64.720,65.413,66.077,66.715,67.327,67.917,68.484

3 ,69.032,69.560,70.070,70.562,71.039,71.501,71.948,72.382,72.803,7

4 3.212,73.610,73.996,74.373,74.739,75.096,75.445,75.785,76.117,76.

5 441,76.759,77.069,77.373,77.670,77.962,78.248,78.528/

c CH₂O (formaldehyde, Ref: NASA SP273)

data (hk(n,7),n=1,51) /0.000,43.416,48.992,52.303,54.854,57.055,59
1 .054,60.906,62.634,64.252,65.774,67.210,68.563,69.843,71.058,72.2
2 13,73.315,74.367,75.374,76.338,77.264,78.152,79.007,79.829,80.621
3 ,81.385,82.122,82.834,83.523,84.189,84.834,85.459,86.066,86.654,8
4 7.226,87.782,88.323,88.850,89.363,89.863,90.352,90.829,91.295,91.
5 751,92.196,92.633,93.060,93.479,93.890,94.293,94.688/

c CH₂OH (Ref. NASA SP273)

data (hk(n,2),n=1,51) /00.000,47.369,53.931,58.330,61.844,64.855,6
1 7.530,69.951,72.169,74.219,76.129,77.918,79.599,81.186,82.689,84.
2 117,85.477,86.775,88.016,89.205,90.346,91.441,92.495,93.509,94.48
3 7,95.431,96.342,97.223,98.075,98.900,99.699,100.475,101.227,101.9
4 58,102.669,103.360,104.033,104.688,105.327,105.950,106.558,107.15
5 2,107.733,108.301,108.856,109.400,109.932,110.454,110.966,111.468
6 ,111.960/

c CH₃ (methyl, Ref: NASA SP273)

data (hk(n,4),n=1,51) /0.000,37.234,42.831,46.395,49.145,51.454,53
1 .480,55.305,56.978,58.528,59.978,61.344,62.634,63.857,65.019,66.1
2 27,67.186,68.198,69.169,70.101,70.996,71.858,72.688,73.488,74.260
3 ,75.006,75.727,76.424,77.099,77.753,78.388,79.003,79.601,80.182,8
4 0.746,81.296,81.831,82.353,82.861,83.357,83.841,84.314,84.777,85.
5 229,85.672,86.105,86.529,86.945,87.353,87.753,88.146/

c CH₃O (methoxyl, Ref: NASA SP273)

data (hk(n,5),n=1,51) /00.000,45.419,50.979,54.853,58.080,60.951,6
1 3.576,66.006,68.268,70.381,72.367,74.237,75.998,77.663,79.243,80.
2 745,82.177,83.545,84.853,86.106,87.307,88.461,89.571,90.639,91.66

3 8.92.660,93.618,94.543,95.437,96.303,97.141,97.953,98.741,99.506,
 4 100.249,100.972,101.675,102.359,103.027,103.677,104.312,104.932,1
 5 05.538,106.131,106.710,107.278,107.834,108.379,108.913,109.437,10
 6 9.952/

c CH₃OH (methanol, Ref: NASA SP273)

data (hk(n,7),n=1,51) /00.000,46.860,53.336,57.343,60.604,63.551,6
 1 6.311,68.916,71.372,73.685,75.876,77.959,79.934,81.811,83.601,85.
 2 310,86.946,88.514,90.018,91.463,92.852,94.189,95.478,96.720,97.92
 3 0,99.078,100.197,101.280,102.328,103.343,104.327,105.282,106.209,
 4 107.110,107.985,108.837,109.667,110.475,111.262,112.031,112.781,1
 5 13.514,114.231,114.931,115.617,116.289,116.947,117.592,118.224,11
 6 8.845,119.454/

c CH₄ (methane, Ref: NASA SP273)

data (hk(n,3),n=1,51) /00.000,35.622,41.249,44.567,47.170,49.480,5
 1 1.637,53.686,55.641,57.509,59.301,61.020,62.667,64.247,65.765,67.
 2 226,68.633,69.990,71.299,72.564,73.786,74.968,76.112,77.220,78.29
 3 4,79.335,80.346,81.328,82.282,83.209,84.112,84.991,85.848,86.683,
 4 87.498,88.293,89.071,89.831,90.575,91.303,92.016,92.716,93.402,94
 5 .075,94.736,95.386,96.025,96.653,97.272,97.880,98.480/

c CO (carbon monoxide, Ref: NASA SP273)

data (hk(n,9),n=1,51) /0.000,39.593,44.433,47.253,49.261,50.837,52
 1 .148,53.280,54.285,55.192,56.020,56.780,57.484,58.139,58.752,59.3
 2 29,59.872,60.387,60.876,61.341,61.784,62.208,62.614,63.003,63.377
 3 ,63.736,64.082,64.416,64.739,65.050,65.351,65.643,65.926,66.201,6
 4 6.468,66.727,66.979,67.224,67.463,67.697,67.924,68.146,68.363,68.
 5 575,68.783,68.986,69.185,69.379,69.570,69.758,69.941/

c CO₂ (carbon dioxide, Ref: NASA SP273)

data (hk(n,10),n=1,51)/00.000,42.931,47.758,51.117,53.812,56.100,5
1 8.103,59.888,61.499,62.968,64.318,65.565,66.723,67.803,68.817,69.
2 771,70.673,71.528,72.340,73.114,73.853,74.559,75.236,75.885,76.50
3 9,77.109,77.687,78.245,78.783,79.304,79.808,80.295,80.768,81.227,
4 81.673,82.107,82.528,82.939,83.339,83.730,84.111,84.483,84.847,85
5 .203,85.552,85.894,86.229,86.557,86.880,87.197,87.508/

c C₂H (CCH radical, Ref: NASA SP273)

data (hk(n,16),n=1,51)/00.000,41.184,47.105,51.017,53.978,56.367,5
1 8.377,60.128,61.694,63.122,64.439,65.661,66.806,67.883,68.900,69.
2 863,70.777,71.648,72.478,73.270,74.028,74.754,75.451,76.119,76.76
3 2,77.380,77.976,78.550,79.103,79.638,80.155,80.655,81.139,81.608,
4 82.062,82.504,82.932,83.349,83.754,84.148,84.532,84.907,85.272,85
5 .628,85.977,86.317,86.650,86.976,87.294,87.607,87.913/

c C₂H₂ (acetylene, Ref: NASA SP273)

data (hk(n,15),n=1,51)/00.000,39.383,44.201,48.053,51.298,54.097,5
1 6.554,58.746,60.728,62.545,64.227,65.795,67.263,68.646,69.953,71.
2 192,72.372,73.497,74.572,75.602,76.590,77.539,78.452,79.331,80.17
3 9,80.998,81.790,82.556,83.298,84.017,84.714,85.392,86.050,86.690,
4 87.313,87.920,88.512,89.089,89.652,90.203,90.741,91.268,91.783,92
5 .288,92.782,93.268,93.744,94.211,94.671,95.122,95.566/

c C₂H₃ (Ref: NASA SP273)

data (hk(n,14),n=1,51)/00.000,46.815,52.155,55.927,59.117,61.983,6
1 4.614,67.045,69.295,71.386,73.346,75.193,76.932,78.577,80.137,81.
2 621,83.036,84.387,85.680,86.919,88.108,89.251,90.350,91.408,92.42
3 8,93.412,94.362,95.281,96.169,97.029,97.862,98.670,99.454,100.216

4 ,100.956,101.675,102.376,103.058,103.723,104.372,105.005,105.623,
 5 106.227,106.818,107.396,107.962,108.516,109.059,109.592,110.114,1
 6 10.627/

c C_2H_4 (ethylene, Ref: NASA SP273)

data (hk(n,13),n=1,51)/0.000,43.364,48.711,52.448,55.715,58.771,61
 1 .671,64.416,67.001,69.431,71.729,73.914,75.982,77.947,79.817,81.6
 2 03,83.310,84.944,86.511,88.016,89.462,90.853,92.193,93.484,94.730
 3 ,95.932,97.094,98.217,99.305,100.357,101.378,102.367,103.328,104.
 4 261,105.168,106.050,106.908,107.745,108.560,109.355,110.132,110.8
 5 90,111.631,112.356,113.066,113.760,114.441,115.108,115.762,116.40
 6 3,117.033/

c C_2H_5 (ethyl, Ref: NASA SP273)

data (hk(n,7),n=1,51) /0.000,48.356,54.673,59.098,62.915,66.438,69
 1 .754,72.886,75.839,78.621,81.257,83.763,86.138,88.396,90.548,92.6
 2 04,94.570,96.454,98.261,99.996,101.665,103.270,104.817,106.307,10
 3 7.746,109.135,110.477,111.774,113.030,114.247,115.426,116.569,117
 4 .679,118.757,119.805,120.824,121.816,122.783,123.725,124.644,125.
 5 541,126.417,127.274,128.112,128.932,129.735,130.521,131.292,132.0
 6 48,132.790,133.518/

c C_2H_6 (ethane, Ref: NASA SP273)

data (hk(n,11),n=1,51)/0.000,44.000,50.292,54.826,58.850,62.647,66
 1 .283,69.760,73.069,76.210,79.203,82.057,84.771,87.358,89.828,92.1
 2 91,94.456,96.627,98.713,100.718,102.647,104.504,106.294,108.020,1
 3 09.686,111.296,112.851,114.355,115.812,117.222,118.589,119.916,12
 4 1.203,122.453,123.669,124.851,126.002,127.124,128.217,129.283,130
 5 .325,131.342,132.336,133.308,134.260,135.192,136.105,137.000,137.

6 878,138.739,139.585/

c H (monatomic hydrogen, Ref: NASA SP273)

data (hk(n,17),n=1,51)/00.000,21.976,25.417,27.431,28.859,29.967,3

1 0.872,31.637,32.300,32.885,33.408,33.881,34.313,34.710,35.078,35.

2 421,35.741,36.042,36.326,36.594,36.849,37.091,37.322,37.543,37.75

3 4,37.957,38.152,38.339,38.520,38.694,38.862,39.025,39.183,39.335,

4 39.484,39.627,39.767,39.903,40.036,40.165,40.290,40.413,40.533,40

5 .649,40.764,40.875,40.984,41.091,41.196,41.298,41.398/

c H₂ (hydrogen, Ref: NASA SP273)

data (hk(n,20),n=1,51)/0.000,24.200,28.520,31.255,33.255,34.817,36

1 .092,37.170,38.109,38.948,39.705,40.397,41.038,41.637,42.198,42.7

2 28,43.230,43.707,44.162,44.597,45.014,45.414,45.799,46.171,46.530

3 ,46.877,47.213,47.539,47.855,48.163,48.461,48.753,49.036,49.313,4

4 9.582,49.846,50.103,50.355,50.601,50.842,51.079,51.310,51.537,51.

5 759,51.977,52.192,52.402,52.609,52.812,53.011,53.208/

c H₂O (water, Ref: NASA SP273)

data (hk(n,21),n=1,51)/00.000,36.369,41.914,45.151,47.479,49.329,5

1 0.885,52.244,53.459,54.566,55.588,56.543,57.443,58.295,59.104,59.

2 875,60.612,61.319,61.997,62.650,63.278,63.884,64.470,65.036,65.58

3 5,66.116,66.631,67.131,67.616,68.088,68.547,68.993,69.428,69.851,

4 70.264,70.667,71.060,71.444,71.819,72.186,72.544,72.895,73.238,73

5 .574,73.904,74.226,74.543,74.853,75.158,75.457,75.751/

c H₂O₂ (hydrogen peroxide, Ref: NASA SP273)

data (hk(n,22),n=1,51)/0.000,45.972,52.156,56.078,59.123,61.692,63

1 .948,65.968,67.799,69.472,71.017,72.458,73.805,75.072,76.268,77.4

2 01,78.479,79.506,80.487,81.427,82.328,83.193,84.026,84.828,85.602

3 ,86.349,87.071,87.770,88.447,89.103,89.740,90.358,90.959,91.544,9
4 2.113,92.667,93.207,93.734,94.249,94.751,95.242,95.722,96.192,96.
5 652,97.102,97.544,97.977,98.401,98.818,99.227,99.629/

c HCO (formyl {CHO}, Ref: NASA SP273)

data (hk(n,18),n=1,51)/0.000,44.829,50.347,53.633,56.069,58.069,59
1 .801,61.346,62.749,64.037,65.227,66.334,67.365,68.331,69.240,70.0
2 99,70.913,71.687,72.423,73.126,73.798,74.442,75.059,75.652,76.223
3 ,76.772,77.302,77.813,78.307,78.785,79.248,79.697,80.132,80.554,8
4 0.964,81.363,81.752,82.130,82.499,82.859,83.210,83.553,83.888,84.
5 216,84.537,84.852,85.160,85.461,85.758,86.048,86.333/

c HO₂ (hydroperoxyl, Ref: NASA SP273)

data (hk(n,19),n=1,51)/0.000,45.974,51.477,54.772,57.244,59.288,61
1 .060,62.634,64.049,65.334,66.514,67.609,68.630,69.587,70.489,71.3
2 42,72.154,72.927,73.666,74.373,75.053,75.706,76.336,76.943,77.529
3 ,78.096,78.645,79.177,79.693,80.193,80.680,81.152,81.611,82.059,8
4 2.494,82.918,83.331,83.734,84.127,84.510,84.884,85.250,85.607,85.
5 955,86.296,86.630,86.956,87.275,87.587,87.893,88.193/

c O (monatomic oxygen, Ref: NASA SP273)

data (hk(n,23),n=1,51)/0.000,32.460,36.341,38.501,39.990,41.127,42
1 .050,42.827,43.497,44.087,44.613,45.089,45.524,45.923,46.292,46.6
2 36,46.957,47.259,47.543,47.812,48.067,48.310,48.541,48.762,48.974
3 ,49.177,49.373,49.561,49.742,49.918,50.087,50.251,50.410,50.565,5
4 0.715,50.861,51.003,51.141,51.276,51.408,51.537,51.662,51.785,51.
5 906,52.024,52.139,52.252,52.363,52.472,52.579,52.684/

c O₂ (oxygen, Ref: NASA SP273)

data (hk(n,25),n=1,51)/0.000,41.352,46.214,49.042,51.084,52.713,54

1 .088,55.286,56.350,57.309,58.180,58.978,59.714,60.397,61.035,61.6
 2 34,62.199,62.734,63.242,63.726,64.188,64.630,65.055,65.463,65.856
 3 ,66.235,66.602,66.956,67.299,67.632,67.955,68.269,68.575,68.872,6
 4 9.161,69.444,69.719,69.989,70.252,70.509,70.760,71.007,71.248,71.
 5 484,71.716,71.943,72.166,72.385,72.599,72.810,73.018/

c OH (hydroxyl, Ref: NASA SP273)

data (hk(n,24),n=1,51)/00.000,35.868,41.007,43.929,45.971,47.544,4
 1 8.829,49.918,50.869,51.714,52.481,53.185,53.839,54.449,55.022,55.
 2 562,56.074,56.560,57.023,57.465,57.888,58.295,58.685,59.061,59.42
 3 3,59.774,60.112,60.440,60.757,61.065,61.364,61.655,61.938,62.213,
 4 62.482,62.743,62.998,63.248,63.491,63.729,63.962,64.189,64.412,64
 5 .631,64.845,65.055,65.260,65.462,65.661,65.855,66.046/

F.4 Gibbs Free Energy

Units of Gibbs function are kcal/mole.

c CH (methyldyne)

data (gk(n,7),n=1,51) /140.598,137.680,133.800,129.556,125.075,120
 1 .417,115.618,110.700,105.679,100.565,95.367,90.092,84.746,79.331,
 2 73.854,68.316,62.721,57.071,51.370,45.618,39.819,33.974,28.085,22
 3 .153,16.180,10.167,4.115,-1.973,-8.098,-14.258,-20.452,-26.679,-3
 4 2.938,-39.229,-45.549,-51.900,-58.279,-64.687,-71.122,-77.583,-84
 5 .071,-90.584,-97.122,-103.685,-110.271,-116.881,-123.513,-130.167
 6 , -136.844,-143.541,-150.259/

c CH₂ (methylene)

data (gk(n,7),n=1,51) /90.521,87.499,83.425,78.932,74.155,69.159,6
 1 3.979,58.642,53.164,47.560,41.839,36.010,30.079,24.052,17.935,11.

2 732,5.447,-0.915,-7.351,-13.858,-20.432,-27.072,-33.775,-40.537,-
 3 47.357,-54.233,-61.163,-68.144,-75.176,-82.256,-89.384,-96.556,-1
 4 03.773,-111.032,-118.333,-125.674,-133.055,-140.473,-147.929,-155.
 5 421,-162.948,-170.509,-178.104,-185.732,-193.393,-201.084,-208.80
 6 6,-216.558,-224.340,-232.151,-239.989/

c CH₂O (formaldehyde)

data (gk(n,7),n=1,51) /-28.408,-31.881,-36.535,-41.609,-46.971,-52
 1 .568,-58.375,-64.374,-70.552,-76.897,-83.399,-90.049,-96.839,-103
 2 .760,-110.805,-117.969,-125.246,-132.630,-140.118,-147.704,-155.3
 3 84,-163.155,-171.014,-178.956,-186.978,-195.079,-203.254,-211.502
 4 ,-219.820,-228.206,-236.657,-245.172,-253.749,-262.385,-271.079,-
 5 279.829,-288.635,-297.494,-306.404,-315.366,-324.377,-333.436,-34
 6 2.542,-351.694,-360.892,-370.133,-379.418,-388.745,-398.114,-407.
 7 523,-416.972/

c CH₂OH

data (gk(n,2),n=1,51) /-4.978,-8.885,-13.980,-19.603,-25.617,-31.9
 1 56,-38.577,-45.453,-52.561,-59.881,-67.400,-75.103,-82.980,-91.02
 2 0,-99.214,-107.555,-116.035,-124.648,-133.388,-142.250,-151.228,-
 3 160.317,-169.515,-178.815,-188.215,-197.711,-207.300,-216.979,-22
 4 6.744,-236.593,-246.523,-256.532,-266.617,-276.777,-287.008,-297.
 5 310,-307.679,-318.116,-328.616,-339.180,-349.806,-360.492,-371.23
 6 6,-382.038,-392.896,-403.809,-414.775,-425.795,-436.866,-447.988,
 7 -459.159/

c CH₃ (methyl)

data (gk(n,4),n=1,51) /32.662,29.687,25.656,21.185,16.403,11.370,6
 1 .122,0.681,-4.934,-10.710,-16.636,-22.703,-28.903,-35.228,-41.672

2 , -48.230, -54.896, -61.665, -68.534, -75.498, -82.553, -89.696, -96.924,
 3 -104.233, -111.620, -119.084, -126.621, -134.228, -141.905, -149.647, -1
 4 57.455, -165.324, -173.255, -181.244, -189.290, -197.393, -205.549, -213.
 5 758, -222.019, -230.330, -238.690, -247.098, -255.553, -264.053, -272.59
 6 8, -281.187, -289.819, -298.493, -307.208, -315.963, -324.758/

c CH₃O (methoxyl)

data (gk(n,7),n=1,51) /0.654, -3.189, -8.032, -13.332, -18.982, -24.936
 1 , -31.164, -37.645, -44.360, -51.293, -58.432, -65.763, -73.275, -80.959,
 2 -88.805, -96.805, -104.952, -113.239, -121.659, -130.207, -138.878, -147
 3 .667, -156.569, -165.580, -174.696, -183.912, -193.227, -202.635, -212.1
 4 34, -221.721, -231.394, -241.149, -250.983, -260.896, -270.884, -280.945
 5 , -291.078, -301.279, -311.549, -321.884, -332.284, -342.746, -353.270, -
 6 363.853, -374.496, -385.195, -395.951, -406.761, -417.626, -428.544, -43
 7 9.513/

c CH₃OH (methanol)

data (gk(n,1),n=1,51) /-50.909, -54.586, -59.633, -65.177, -71.078, -77
 1 .287, -83.782, -90.545, -97.560, -104.814, -112.293, -119.986, -127.881,
 2 -135.969, -144.241, -152.687, -161.300, -170.074, -179.001, -188.075, -1
 3 97.292, -206.644, -216.128, -225.738, -235.470, -245.321, -255.285, -265
 4 .359, -275.539, -285.823, -296.207, -306.688, -317.263, -327.929, -338.6
 5 84, -349.525, -360.450, -371.458, -382.545, -393.709, -404.950, -416.265
 6 , -427.652, -439.111, -450.638, -462.234, -473.896, -485.623, -497.413, -
 7 509.267, -521.182/

c CH₄ (methane)

data (gk(n,7),n=1,51) /-20.329, -22.994, -26.872, -31.172, -35.762, -40
 1 .597, -45.653, -50.920, -56.387, -62.046, -67.887, -73.903, -80.088, -86.

2 435,-92.936,-99.586,-106.379,-113.311,-120.376,-127.569,-134.887,
 3 -142.325,-149.879,-157.546,-165.322,-173.204,-181.188,-189.272,-1
 4 97.453,-205.727,-214.094,-222.549,-231.091,-239.718,-248.427,-257
 5 .217,-266.085,-275.030,-284.051,-293.145,-302.311,-311.547,-320.8
 6 53,-330.227,-339.668,-349.174,-358.745,-368.379,-378.075,-387.833
 7 ,-397.651/

c CO (carbon monoxide)

data (gk(n,7),n=1,51) /-28.485,-31.739,-35.969,-40.562,-45.393,-50
 1 .400,-55.552,-60.824,-66.203,-71.678,-77.239,-82.880,-88.593,-94.
 2 375,-100.220,-106.124,-112.084,-118.098,-124.161,-130.272,-136.42
 3 8,-142.628,-148.869,-155.150,-161.469,-167.825,-174.216,-180.641,
 4 -187.099,-193.588,-200.109,-206.658,-213.237,-219.843,-226.477,-2
 5 33.137,-239.822,-246.532,-253.267,-260.025,-266.806,-273.609,-280
 6 .435,-287.282,-294.150,-301.038,-307.947,-314.875,-321.823,-328.7
 7 89,-335.774/

c CO₂ (carbon dioxide)

data (gk(n,6),n=1,51) /-96.076,-99.801,-104.355,-109.307,-114.557,
 1 -120.056,-125.768,-131.669,-137.740,-143.964,-150.329,-156.824,-1
 2 63.439,-170.166,-176.998,-183.928,-190.950,-198.061,-205.254,-212
 3 .527,-219.876,-227.297,-234.787,-242.343,-249.963,-257.644,-265.3
 4 84,-273.181,-281.033,-288.937,-296.893,-304.898,-312.951,-321.051
 5 ,-329.196,-337.385,-345.617,-353.891,-362.205,-370.558,-378.950,-
 6 387.380,-395.847,-404.349,-412.887,-421.460,-430.066,-438.705,-44
 7 7.377,-456.081,-464.816/

c C₂H (CCH radical)

data (gk(n,16),n=1,51)/132.728,129.306,124.866,119.949,114.693,109

1 .172,103.432,97.505,91.413,85.171,78.792,72.287,65.663,58.928,52.
 2 088,45.150,38.117,30.996,23.789,16.501,9.136,1.697,-5.814,-13.392
 3 ,-21.037,-28.744,-36.512,-44.338,-52.221,-60.158,-68.148,-76.189,
 4 -84.279,-92.416,-100.600,-108.828,-117.100,-125.414,-133.769,-142
 5 .165,-150.599,-159.071,-167.580,-176.125,-184.705,-193.320,-201.9
 6 68,-210.650,-219.363,-228.108,-236.884/

c C_2H_2 (acetylene)

data (gk(n,15),n=1,51)/52.459,48.917,44.727,40.108,35.136,29.863,2
 1 4.328,18.561,12.586,6.421,0.081,-6.421,-13.074,-19.870,-26.801,-3
 2 3.859,-41.037,-48.331,-55.735,-63.244,-70.854,-78.561,-86.361,-94
 3 .250,-102.226,-110.285,-118.425,-126.642,-134.935,-143.301,-151.7
 4 38,-160.243,-168.815,-177.452,-186.153,-194.914,-203.736,-212.616
 5 ,-221.554,-230.546,-239.594,-248.694,-257.847,-267.050,-276.304,-
 6 285.607,-294.957,-304.355,-313.799,-323.289,-332.823/

c C_2H_3

data (hk(n,14),n=1,51)/69.217,65.214,60.243,54.832,49.077,43.019,3
 1 6.688,30.103,23.285,16.249,9.012,1.584,-6.023,-13.799,-21.736,-29
 2 .824,-38.057,-46.429,-54.933,-63.563,-72.315,-81.183,-90.164,-99.
 3 252,-108.444,-117.736,-127.125,-136.608,-146.180,-155.841,-165.58
 4 5,-175.412,-185.319,-195.302,-205.361,-215.493,-225.695,-235.967,
 5 -246.307,-256.711,-267.180,-277.712,-288.304,-298.957,-309.668,-3
 6 20.436,-331.260,-342.138,-353.071,-364.056,-375.094/

c C_2H_4 (ethylene)

data (gk(n,7),n=1,51) /10.107,6.517,1.888,-3.176,-8.586,-14.312,-2
 1 0.335,-26.641,-33.213,-40.036,-47.095,-54.378,-61.874,-69.571,-77
 2 .460,-85.532,-93.778,-102.191,-110.765,-119.492,-128.366,-137.382

3 , -146.535, -155.819, -165.230, -174.764, -184.415, -194.181, -204.057, -
 4 214.041, -224.128, -234.315, -244.600, -254.980, -265.452, -276.013, -28
 5 6.661, -297.394, -308.209, -319.105, -330.079, -341.131, -352.257, -363.
 6 456, -374.728, -386.069, -397.479, -408.957, -420.500, -432.109, -443.78
 7 1/

c C₂H₅ (ethyl)

data (gk(n,12),n=1,51)/25.501,21.510,16.330,10.634,4.530,-1.939,-8
 1 .751,-15.884,-23.322,-31.046,-39.041,-47.293,-55.789,-64.517,-73.
 2 465,-82.624,-91.983,-101.535,-111.271,-121.185,-131.268,-141.515,
 3 -151.920,-162.477,-173.180,-184.024,-195.005,-206.118,-217.359,-2
 4 28.723,-240.207,-251.807,-263.520,-275.342,-287.270,-299.302,-311
 5 .434,-323.664,-335.989,-348.408,-360.918,-373.516,-386.200,-398.9
 6 70,-411.822,-424.756,-437.769,-450.859,-464.027,-477.269,-490.584
 7 /

c C₂H₆ (ethane)

data (gk(n,11),n=1,51)/-22.878,-26.448,-31.189,-36.452,-42.138,-48
 1 .215,-54.663,-61.466,-68.609,-76.074,-83.846,-91.910,-100.253,-10
 2 8.860,-117.721,-126.822,-136.156,-145.710,-155.478,-165.450,-175.
 3 619,-185.977,-196.518,-207.234,-218.120,-229.169,-240.377,-251.73
 4 8,-263.247,-274.899,-286.689,-298.615,-310.671,-322.854,-335.161,
 5 -347.587,-360.130,-372.787,-385.554,-398.429,-411.410,-424.493,-4
 6 37.677,-450.960,-464.338,-477.811,-491.376,-505.031,-518.775,-532
 7 .607,-546.523/

c H (monatomic hydrogen)

data (hk(n,18),n=1,51)/50.593,48.886,46.497,43.848,41.030,38.087,3
 1 5.043,31.917,28.719,25.460,22.144,18.780,15.370,11.918,8.429,4.90

2 3,1.345,-2.244,-5.863,-9.509,-13.181,-16.878,-20.599,-24.342,-28.
 3 107,-31.893,-35.699,-39.523,-43.366,-47.227,-51.105,-54.999,-58.9
 4 10,-62.835,-66.776,-70.732,-74.702,-78.685,-82.682,-86.692,-90.71
 5 5,-94.750,-98.798,-102.857,-106.928,-111.009,-115.102,-119.206,-1
 6 23.321,-127.445,-131.580/

c H₂ (hydrogen)

data (gk(n,21),n=1,51)/-1.820,-3.710,-6.367,-9.364,-12.594,-16.000
 1 ,-19.548,-23.212,-26.977,-30.831,-34.764,-38.769,-42.842,-46.976,
 2 -51.168,-55.414,-59.712,-64.059,-68.453,-72.891,-77.372,-81.893,-
 3 86.454,-91.053,-95.688,-100.358,-105.063,-109.801,-114.570,-119.3
 4 71,-124.203,-129.063,-133.953,-138.870,-143.815,-148.787,-153.784
 5 ,-158.807,-163.855,-168.927,-174.023,-179.143,-184.285,-189.450,-
 6 194.637,-199.845,-205.075,-210.326,-215.597,-220.888,-226.199/

c H₂O (water)

data (gk(n,22),n=1,51)/-60.150,-62.979,-66.925,-71.289,-75.926,-80
 1 .769,-85.782,-90.940,-96.226,-101.628,-107.136,-112.743,-118.443,
 2 -124.230,-130.101,-136.050,-142.075,-148.171,-154.337,-160.570,-1
 3 66.867,-173.225,-179.643,-186.118,-192.649,-199.235,-205.872,-212
 4 .560,-219.298,-226.083,-232.915,-239.792,-246.713,-253.677,-260.6
 5 83,-267.730,-274.816,-281.941,-289.105,-296.305,-303.541,-310.813
 6 ,-318.120,-325.461,-332.835,-340.241,-347.680,-355.150,-362.650,-
 7 370.181,-377.742/

c H₂O₂ (hydrogen peroxide)

data (gk(n,23),n=1,51)/-35.256,-39.001,-43.940,-49.362,-55.127,-61
 1 .171,-67.455,-73.952,-80.642,-87.507,-94.532,-101.707,-109.021,-1
 2 16.465,-124.033,-131.717,-139.511,-147.411,-155.411,-163.507,-171

3 .695,-179.971,-188.332,-196.775,-205.297,-213.895,-222.566,-231.3
 4 08,-240.119,-248.997,-257.939,-266.944,-276.010,-285.136,-294.319
 5 , -303.558,-312.851,-322.199,-331.598,-341.048,-350.548,-360.096,-
 6 369.692,-379.334,-389.022,-398.754,-408.530,-418.349,-428.210,-43
 7 8.113,-448.056/

c HCO (formyl)

data (gk(n,19),n=1,51)/7.627,3.957,-0.834,-6.043,-11.533,-17.243,-
 1 23.138,-29.196,-35.402,-41.742,-48.206,-54.785,-61.471,-68.256,-7
 2 5.135,-82.102,-89.153,-96.284,-103.489,-110.767,-118.114,-125.526
 3 , -133.001,-140.537,-148.131,-155.781,-163.484,-171.240,-179.047,-
 4 186.901,-194.803,-202.750,-210.742,-218.776,-226.852,-234.969,-24
 5 3.125,-251.319,-259.550,-267.818,-276.122,-284.460,-292.832,-301.
 6 237,-309.675,-318.145,-326.645,-335.176,-343.737,-352.328,-360.94
 7 7/

c HO₂ (hydroperoxyl)

data (gk(n,20),n=1,51)/0.587,-3.192,-8.096,-13.418,-19.024,-24.853
 1 , -30.872,-37.058,-43.394,-49.864,-56.457,-63.164,-69.976,-76.888,
 2 -83.892,-90.984,-98.159,-105.413,-112.743,-120.145,-127.617,-135.
 3 155,-142.757,-150.421,-158.145,-165.927,-173.764,-181.655,-189.59
 4 9,-197.593,-205.637,-213.729,-221.867,-230.051,-238.278,-246.549,
 5 -254.861,-263.215,-271.608,-280.040,-288.510,-297.016,-305.559,-3
 6 14.137,-322.750,-331.396,-340.076,-348.787,-357.530,-366.305,-375
 7 .109/

c O (monatomic hydrogen)

data (gk(n,24),n=1,51)/57.836,55.188,51.724,47.974,44.045,39.987,3
 1 5.827,31.582,27.265,22.885,18.450,13.964,9.433,4.861,0.250,-4.397

2 , -9.077, -13.788, -18.528, -23.296, -28.090, -32.909, -37.751, -42.617, -
 3 47.504, -52.411, -57.339, -62.286, -67.251, -72.234, -77.234, -82.251, -8
 4 7.284, -92.333, -97.397, -102.476, -107.569, -112.676, -117.797, -122.93
 5 2, -128.079, -133.239, -138.411, -143.596, -148.792, -154.000, -159.220,
 6 -164.451, -169.693, -174.945, -180.208/

c O₂ (oxygen)

data (gk(n,24),n=1,51)/-2.113, -5.521, -9.928, -14.700, -19.710, -24.90
 1 3, -30.245, -35.715, -41.297, -46.981, -52.756, -58.615, -64.550, -70.556
 2 , -76.628, -82.761, -88.953, -95.200, -101.499, -107.848, -114.243, -120.
 3 685, -127.169, -133.695, -140.261, -146.866, -153.508, -160.186, -166.89
 4 9, -173.645, -180.425, -187.236, -194.078, -200.951, -207.852, -214.783,
 5 -221.741, -228.726, -235.738, -242.776, -249.840, -256.928, -264.041, -2
 6 71.178, -278.338, -285.521, -292.726, -299.954, -307.203, -314.473, -321
 7 .765/

c OH (hydroxyl)

data (gk(n,5),n=1,51) /7.187, 4.364, 0.489, -3.768, -8.268, -12.947, -17
 1 .767, -22.706, -27.746, -32.876, -38.086, -43.370, -48.722, -54.137, -59.
 2 610, -65.140, -70.722, -76.354, -82.033, -87.758, -93.525, -99.335, -105.
 3 184, -111.071, -116.995, -122.955, -128.950, -134.977, -141.037, -147.12
 4 9, -153.250, -159.401, -165.581, -171.789, -178.023, -184.285, -190.572,
 5 -196.884, -203.221, -209.582, -215.967, -222.374, -228.804, -235.257, -2
 6 41.730, -248.225, -254.741, -261.277, -267.834, -274.409, -281.004/

APPENDIX G

STANDARD UNITS OF THE CGS SYSTEM AND COMMONLY USED CONVERSIONS

Table G1. Standard Units of the CGS System.	
Measurand	Unit
Length	cm
Weight	g
Time	s
Temperature	K
Pressure	dyne
Density	g/cm ³
Enthalpy	erg/g
Specific Heat	erg/g-K
Dynamic Viscosity	g/cm-s
Kinematic Viscosity	cm ² /s
Thermal Conductivity	erg/s-K-cm
Universal Gas Constant	8.314 x 10 ⁷ erg/mol-K
Stefan-Boltzman Constant	5.669 x 10 ⁻⁵ erg/s-cm ² -K

Table G2. Commonly Used Conversions.
1 erg/g = 1 cm ² /s ²
1 dyne = 1 g-cm/s ²
1 Joule = 1 x 10 ⁷ erg
1 calorie = 4.184 Joules = 4.184 x 10 ⁷ erg
1 kcal/g = 4.184 x 10 ¹⁰ erg/g
1 Btu/lbm-R = 1.2910 x 10 ⁷ erg/g-K
1 atm = 1.0130 x 10 ⁶ g/cm-s ²

VITA

Robert Wood McAmis was born in Knoxville, Tennessee, on February 24, 1962, to Charles and Betty Jo McAmis. He has one brother, Steve, and three sisters, Priscilla, Cathy, and Julie. He attended Chilhowee Elementary School for eight years. After starting high school at Holston, he moved to Dandridge, Tennessee, as a freshman and graduated from Jefferson County High School in June 1980. He attended Tennessee Technological University and graduated in June 1984 with the degree of Bachelor of Science in Mechanical Engineering. He joined Sverdrup Technology, Incorporated at the Arnold Engineering Development Center on June 18, 1984. He was married to Mary Kathryn Lee on September 8, 1984. He received the degree of Master of Science from the University of Tennessee on June 12, 1987. He was blessed with three sons, Charles Michael born March 6, 1990, William Stephen born June 2, 1993, and John Robert born February 10, 1995.

He was selected by Sverdrup Technology, Incorporated and the United States Air Force to participate in the Advanced Continuing Education Program from August, 1994, to August, 1995, thus allowing full time graduate study.