89

0	7	3	0	1
---	---	---	---	---

U·M·I

MICROFILMED 1989

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book. These are also available as one exposure on a standard 35mm slide or as a 17" x 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

U·M·I

**University Microfilms International
A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600**

Order Number 8907301

Determination of global kinetics of coal volatiles combustion

Shaw, David William, Ph.D.

The Ohio State University, 1988

Copyright ©1988 by Shaw, David William. All rights reserved.

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

DETERMINATION OF GLOBAL KINETICS
OF COAL VOLATILES COMBUSTION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate School
of the Ohio State University.

By

David William Shaw, B.S.M.E., M.S.

* * * * *

The Ohio State University

1988

Dissertation Committee:

Robert H. Essenhight

J. William Rich

Duane R. Skidmore

Approved by

A handwritten signature in dark ink, reading "Robert H. Essenhight", is written over a horizontal line.

Advisor

Department of Mechanical Engineering

Copyright by
David William Shaw
1988

To the Glory of God

ACKNOWLEDGEMENTS

I wish to express my gratitude to Prof. R.H. Essenhigh for his advice, encouragement and constructive criticism throughout this work. The comments and corrections of Prof. D.R. Skidmore and Prof. J.W. Rich were also appreciated.

The support of U.S. DOE/PETC under project # DE-AC22-84PC-70815 as a subcontract from TRW Space and Technologies Group under Dr. N. Gat made this work possible. Thanks also to Steve Benson of University of North Dakota Energy Research Center and Bob Douglas of Consolidation Coal Co. for donation of coal samples.

Others who contributed by experimental assistance include Andrew Shillington, Jeff Janosek and George Nicololias as undergraduate research assistants and William Marek, Ned Heminger and Tom Gieseke as work toward an ME 581 project.

Thanks also to Mahendra Misra for his many useful observations, questions and answers and for the time spent in helping to clarify many new ideas.

Special thanks to my wife Val for her encouragement and prayers, and to baby Kirsten for not crying too much and for sleeping through the nights.

VITA

January 10, 1961	Born - Whittier, California
May 1983	B.S.M.E., Geneva College, Beaver Falls, Pennsylvania
June 1983-June 1985	Graduate Research Associate The Ohio State University Mechanical Engineering Columbus, Ohio
June 1984-August 1984 and June 1985-August 1985	Mechanical Engineer National Bureau of Standards Gaithersburg, Maryland
September 1985-September 1986	Graduate Trainee The Ohio State University Mechanical Engineering Columbus, Ohio
June 1986	M.S., The Ohio State University Columbus, Ohio
September 1986-present	Graduate Research Associate The Ohio State University Mechanical Engineering Columbus, Ohio
Fields of Study:	Studies in Combustion, Measurement Techniques, Heat and Mass Transfer under Prof. R.H. Essenhigh.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
VITA	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
NOMENCLATURE.....	x
CHAPTER	
I. INTRODUCTION	1
II. EXPERIMENTAL	4
2.1 Selection of Experimental System	4
2.2 The Experimental System	6
2.3 Burner Development and Design	12
2.4 Pyrolyzer and Tray Design	16
2.5 Channel and Heater Design	21
2.6 Methods of Experiment	25
III. THEORY	28
3.1 Model Basis and Kinetic Equations	28
3.2 Thermal Formulation of Equations: Method 1	29
3.3 Extinction Analysis: Method 2	30
3.4 The Uniqueness Problem: Selection of Reaction Order	33
IV. METHODS OF MEASUREMENT	36
4.1 Burner Parameters and Constituent Balances	37
4.2 Supplementary Balances from a Burn-up Section	39
4.3 Methods of Primary Measurement	41
4.3.1 Mass Flows	41
4.3.2 Heat of Volatiles Combustion	41
4.3.3 Sensible Heat in Burner Exhaust	44
4.4 Problems of Redundancy Measurements	45

4.5 Ancillary Measurements and Determinations	47
V. RESULTS	49
5.1 General Characteristics	49
5.2 Coals: Near-Stoichiometric Measurements	50
5.3 Gases: Near-Stoichiometric Measurements	54
5.4 Extinction Loop Measurements	60
5.5 Predicted Extinction Loop for Bituminous Coal VM ...	60
5.6 Predicted Extinction Loops for Reference Gases	67
5.7 Times for Burn-Out and Pyrolysis	67
VI. DISCUSSION	73
6.1 Comparison of Kinetic Constants	73
6.1.1 Comparison with Previous Work	73
6.1.2 Comparison Among VM and Reference Gases	77
6.2 Rank Sensitivity of Kinetics	77
6.3 Comparison of Experimental and Predicted Extinction Loops	79
6.4 Applicability of CO Limited Reaction	79
6.5 Relative Time Scales of Pyrolysis and Combustion ...	81
VII. CONCLUSIONS	82
REFERENCES	85
APPENDICES	
Appendix A - Computer Programs	89
Appendix B - Data	131

LIST OF TABLES

TABLE	Page
1. Coal Analyses	53
2. Kinetic Constants	55

LIST OF FIGURES

FIGURE	Page
1. Schematic of Experimental System	7
2. Counter-Vortex Burner	8
3. Method of Tray Connection	11
4. Burner Variants Used in Preliminary Studies	13
5. Batch Pyrolyser	17
6. Channel Designs: Initial and Final	22
7. Schematic of Burner with Mass and Energy Flows	38
8. Variation of VM Heating Value with Coal Heating Value for Several Values of Fixed Carbon	43
9. Arrhenius Plot for Second Order Analysis of VM Data	52
10. Arrhenius Plot for Second Order Analysis of Reference Gas Data	56
11. Arrhenius Plot for Second Order Least Squares Fits of VM and Reference Gas Data	57
12. Arrhenius Plot Showing Change in Apparent Activation Energy for Reference Gas	58
13. Temperature Map of High Air/Fuel Flame	59
14. Experimental Stability Limits for Pittsburgh #8 VM Flame	61
15. Experimental Stability Limits for Propane Flame ...	62
16. Experimental Stability Limits for Methane Flame ...	63

17. Experimental Stability Limits for CO Flame	64
18. Experimental Stability Limit Trend Lines for All Fuels on a Thermal Basis	65
19. Predicted Stability Limits for Pittsburg #8 VM with Experimental Extinction Points	66
20. Predicted Stability Limits for Methane with Experimental Extinction Points	69
21. Predicted Stability Limits for Propane with Experimental Extinction Points	70
22. Predicted Stability Loops for All Fuels Plotted on a Thermal Basis	71
23. Comparative Burning and Pyrolysis Times	72
24. Comparison of Second Order Kinetics of Data from Several Sources	74
25. Comparison of 1.5 Order Kinetics with Data from Westbrook and Dryer	76
26. Schematic Explanation of Apparent Low Activation Energies for Reactions as Proposed by Howard <u>et al.</u>	78

NOMENCLATURE

A	Area (m^2)
a,b,c	Coefficients in Polynomial Curve Fits
c	Concentration (kg/kg)
d	Diameter (m)
E	Activation Energy (kcal/mole)
F	Firing Rate (kg/s)
f	Mass Fractions (kg/kg)
H	Enthalpy (J)
h	Specific Enthalpy (J/kg)
H_f	Heat of Combustion (J)
h_f	Specific Heat of Combustion (J/kg)
J	Total Mass Flow Rate (kg/s)
k_o	Pre-exponential Constant (units vary with reaction order)
M_a	Mass Flow Rate of Air (kg/s)
n	Overall Reaction Order
Nu	Nusselt Number
Q	Heat Flux
R	Universal Gas Constant (kcal/mole K)
r	Reaction Order With Respect to Fuel

T	Temperature (K or C)
t	Time (s)
u_{∞}	Gas Velocity (m/s)
V_c	Combustor Volume (m^3)
ρ	Density in Reactor (kg/m^3)
η	Efficiency
ϕ	Equivalence Ratio
τ_s	Residence Time in Reactor (s)
ν_f	Kinematic Viscosity
λ	Thermal Conductivity
σ	Stefan-Boltzmann Constant
ϵ	Emissivity

Subscripts

b	Bead
e	Exhaust
f	Fuel
G	Generation
g	
L	Loss
ox	Oxidizer
$p.c.$	"Pure Coal" (see Ref. 30)
u	Unburned
w	Wall
$w1$	Wall Loss in Burner

w2 Wall Loss in Burn-up Section

Superscripts

o Initial

CHAPTER I

INTRODUCTION

This dissertation which presents experimental values for the global kinetics of coal volatiles combustion is believed to be the first in which such measurements and calculations are made. Comparative values of CO, CH₄ and C₃H₈ kinetics obtained in the same equipment are also reported.

The incentive for this work derives from the increasing precision expected from predictive coal flame models in which, at present, assumptions of unknown accuracy must be used for the combustion of the volatiles because of the total absence of direct data on their kinetics. The two principal assumptions commonly used at this time^{1,2} are that: either, the volatiles burn as they are evolved, so that their combustion rate equals the pyrolysis rate¹; or, that the volatiles are rapidly converted to CO (and H₂), and that global or detailed kinetics for CO combustion can be used as a stand-in for the volatiles combustion^{2,1}.

The global kinetics results reported here provide a basis for evaluating these commonly used assumptions. The volatile matter (VM) combustion rates obtained here are used to compare predicted VM burning

times with pyrolysis times at the same temperature; and the comparative CO data are used to compare CO and VM reaction rates.

The technique used is to pyrolyze coal carried in trays through a gas-heated muffle furnace, and to burn the VM products at the top of a tube in an aerodynamically stabilized flame that produces intense mixing³. The pyrolysis component of the method originated with Finch⁴ in 1956, and was used by Underwood and Thring⁵ in 1958, but in neither instance were any rate values obtained for the combustion. In 1972, Biswas and Essenhigh⁶ reported global kinetic values for cellulose smoke using a batch pyrolyzer feeding into a tube similar to that described here. Additional data on cellulose smoke were obtained by Shieh and Essenhigh⁷ in 1972 when burning computer cards in a small (2' by 2' by 10') incinerator simulator; the kinetics values obtained from a well-mixed zone above the bed were then used to predict the burn-out above the bed, with good agreement with experiment.

In 1981, Essenhigh⁸ reported in a review that there were no known values for coal volatiles kinetics per se, and that the two assumptions identified above were still the most commonly used. To our present knowledge this is still true today, so that the values given here are believed to be the first reported values for global kinetics of VM combustion obtained from direct measurements on burning volatiles from coals.

While there has been little or no work on combustion of VM, there has been much research on characterizing the pyrolysis process.

Thorough reviews of coal pyrolysis research are given by Juntgen and van Heek⁹, Howard¹⁰, and Gavalas¹¹. The kinetics of the pyrolysis process have been measured and modelled^{12,13,14,15,16} in oxidizing and non-oxidizing environments; product distributions have been measured, and the possibility of enhanced VM yield (the Q-factor effect)¹⁷ has been debated. These studies provide a framework for the study of VM combustion. The product distributions give clues to the identity of possibly important species for combustion and the expected rates, and the kinetics of pyrolysis give a basis for comparison with combustion rates. Based on pyrolysis studies some modellers have chosen VM combustion kinetics to be represented by the major pyrolysis product species. For example, Annamalai and Durbetaki¹⁸ chose methane for their modelling of the ignition process. Smoot¹⁹ gives several options in his textbook, including methane and CO-limited combustion. However, all of these models should eventually be retested with measured VM combustion kinetics and analyzed for sensitivity to the kinetic constants over the experimentally determined range.

CHAPTER II

EXPERIMENTAL

2.1 Selection of Experimental System. Design of an apparatus suitable for combustion of coal volatiles independently of the char residue, and for determination of their kinetic data, presents some unusual and somewhat formidable difficulties. The total coal volatiles can only be released by heating the coal to about 1000 C. Volatiles maintained at this temperature can crack and deposit a substantial fraction of the carbon held in the tars; at the very least, the volatiles are substantially transformed. If the volatiles are cooled, the tars condense out, separating them from the permanent gases (mainly H_2 , CH_4 and CO). Once condensed, the tars cannot be re-evaporated since the heat required to do this, again, results in cracking with loss of carbon from the mixture being investigated. Thus, the volatiles have to be burned almost immediately after release; they cannot be stored for later use.

These characteristics, thus, limit the options on possible experimental methods for the kinetic determinations. Strehlow²⁰ lists six general techniques, as follows: (1) Vessel explosion; (2) Plug-flow (heated) tube reactor; (3) Chemical shock tube; (4) Well-stirred reactor; (5) Flame structure methods (mostly burners); and (6) Radical

excitation techniques (including flash photolysis). In essentially all cases, with the partial exception of the stirred reactor, pre-mixing of the fuel and air is imperative. However, mixing of warm or hot volatiles with cold air promotes condensation. Mixing with heated air might be possible but it is estimated, from available values of spontaneous ignition temperatures and from experience with the volatiles, that there is only a small temperature window, which if it exists at all, would allow mixing without condensation on the low side, or mixing without premature ignition or explosion on the high side.

These considerations eliminated all fully-premixed systems at this time, and the only method that allowed simultaneous mixing and combustion was the stirred reactor. If mixing is perfect then, theoretically, there is no distinction between pre-mixed and non pre-mixed, and the relative locations of the points of injection of fuel and air are also irrelevant. If the reactor is only well-stirred, however, these factors can become important, and are also both difficult to quantify and to correct for in kinetic measurements. This is discussed more fully below. The principal point here is that, by elimination, the only appropriate experimental method at this time, in spite of its recognized faults, is the stirred reactor.

Even with this choice, further practical problems remain, the most important being that of rapid mixing between fuel and air. In previous stirred reactor studies (see Essenhigh's review²¹) injector pressures have been very high, sometimes generating sonic flow at small nozzle orifices. In the experiments described here on the volatiles, only the

air could be pressurized. For the volatiles flow up the vertical tube leading from the pyrolyzer into the burner at the top, the only driving force available to the volatiles is buoyancy. In principle, a pressurized pyrolyzer could be designed; however, pressurized coal units are notorious for the difficulties in solid fuel feed (and, in this case, simultaneous char extraction). They are also potentially very dangerous and require major safety precautions such as isolation and remote operation. Accordingly, only a normal-pressure pyrolyzer was used, and all mixing was driven by the air injection system as described below. Therefore, to allow for the possibility that mixing may not have adequately approached the (unattainable) ideal of perfect mixing, some of the experiments were structured so that the principal questions of concern could be answered by comparative procedures (among fuels) in spite of non-perfect but constant mixing.

2.2 The Experimental System. The experimental concept which was outlined in the Introduction is shown schematically in Fig. 1. It consists essentially of a flame tube of steel 0.3 m long and 50 mm i.d. erected vertically with a pyrolyzer at the bottom and a burner at the top.

The burner (Fig. 2) is a 150 mm length of 50 mm i.d. steel tube with air injection ports of 5 mm i.d. arranged to produce two vortex flows rotating in opposite senses. This is a system used extensively in previous work^{3,6,7,22-24} as identified below. The ports consist of a total of eight horizontal jets through the tube wall, set in two sets of four each, each set being arranged on a horizontal plane, with the

Figure 1. Schematic of Experimental System

Figure 2. Counter-Vortex Burner

two planes 25 mm apart and the top plane approximately 90 mm below the top of the smoke tube. On each plane, the four nozzles are aimed tangential to an imaginary circle of 38 mm diameter. The angle of each jet axis to a radius through the nozzle exit is about 35° (the "offset" angle -- mentioned in Refs. 3,22-24). These jets generate the vortices, and the relatively small vertical displacement of one set of jets from the other, coupled with the opposed rotation, generates such shear between the flows that intense horizontal and backmixing are produced²²⁻²⁴. The burner walls are wound with water-cooled copper tubing to measure the burner wall losses, and this is encased in a fiberglass insulation jacket approximately 3 cm thick. This design was first used by Kuwata et al³ investigating combustion of methane; it was also used for the study of cellulose smoke flames by Biswas and Essenhigh⁶, and for the mixing section above the fuel bed in the incinerator simulator by Shieh and Essenhigh⁷, with parallel cold-model studies by Rao and Essenhigh^{22,23} and by Zeinalov et al²⁴ to determine the structure of the mixing pattern.

The pyrolyzer is a stainless steel channel to carry the trays filled with crushed coal through a muffle furnace. The furnace is a firebrick enclosure heated by premixed natural gas and air. The channel is made of 2.6 mm thick 304 stainless, 0.9 m long and with a rectangular cross section 115 mm wide by 25 mm deep. The channel section leaving the furnace is cooled by two air jets impinging on the top and bottom. Finch⁴ and Underwood⁵ both used a single long tray.

In the present experiment a series of trays was used for improved accuracy in measuring the weight loss with time.

The trays are pulled through the muffle furnace by a sprocket chain driven by a gearmotor through a system of reducing gears. The motor speed is controlled using a Variac. The tray speed is determined from the rate of change of resistance in a calibrated 10 turn potentiometer connected to the sprocket drive. The trays are 206 mm long, 95 mm wide and 13 mm deep, made of 1.5 mm thick stainless steel, and are connected together using wire loops (#22 chromel) which slip over pins spot welded at both ends of each tray as shown in Fig. 3. The volatiles supply-rate to the burner is determined from the tray velocity and the mass loss from each tray (measured by weighing before and after traversing the furnace).

Air, gas and water flows are measured by rotameters. The flame temperature is measured by a .010" diameter Type S thermocouple with calculated heat loss corrections. Other temperatures are measured by Type K thermocouples in stainless steel sheaths; these include the ambient temperature, temperatures at three points within the muffle furnace, the VM temperature, and the temperatures of water entering and leaving the burner jacket. These last were individually calibrated over the range of 293 to 353 K in a water bath to minimize the error in determining heat loss to the wall.

The flame thermocouple was constructed in an L-shape by joining two alumina insulators using furnace cement and stiffened by a short truss at a 45 degree angle to prevent breakage under high flow rates. The TC is mounted on an X-Y traversing mechanism to allow measurements

Figure 3. Method of Tray Connection

in the axial and radial direction; the values recorded are corrected for radiation losses.

All thermocouples and the potentiometer are connected to a datalogger. The potentiometer reading (ohms) is taken every 20 seconds, the thermocouples in the muffle furnace are read once a minute; and the flame temperature and water temperatures are measured at any time by pushing a button to trigger a switch.

2.3 Burner Development and Design. The burner shown in Fig. 2 with dimensions given above (Sec. 2.2) is the form used in all the quantitative experiments reported here, and is the same design as that used by Biswas and Essenhigh⁶ except for a reduction in diameter from 75 mm to 50 mm. In the present experiments, however, some modified configurations were examined in preliminary tests. In all cases the double array of injection jets was used to create the double-vortex backmix-flow system. The variants mostly refer to the diameters and length of the VM supply pipe, spacing of the air-jet planes, and wall materials. Figure 4 illustrates some of the variants used.

In Fig. 4A the VM delivery tube was reduced to 25 mm before the sudden expansion into the 50 mm dia burner. This was intended to aid definition of the lower boundary of the stirred (back mix) region. In practice, this design segregated the volatiles efflux to a center core in the burner (as indicated by the dotted lines), creating a center core of flame with a cold annular cylinder, mainly of air, between the flame and the walls. In one formulation of this burner the walls were of 1/2" refractory (to reduce wall losses) but the walls never became

Figure 4. Burner Variants Used in Preliminary Studies

hot enough to radiate and immediately after flame extinction were usually only warm to the touch. Something similar to this phenomenon was reported previously by Kuwata and Essenhigh³, burning methane, where TC measurements showed reasonably uniform temperature maps over most of the flame volume, with gas temperatures as high as 1200 C, but the uncooled metal rings of the burner never overheated. There was always a thin annular cylinder of cooler and higher density gases adjacent to the burner walls that were there due to the centrifugal effects of the rotational flows.

At low fuel and air-flow rates it was also found that the flame core settled just above the fuel entry and not in the main mixing flow. As an attempt to project the fuel into the main mixing flow, an extension was added to the supply pipe as shown in Fig. 4B, but this made matters worse by allowing the formation of a turbulent diffusion flame, with the air pattern as shown by the arrows. These flames were at the opposite extreme from being even well mixed.

In a third configuration shown in Fig. 4C, a small-volume, high-velocity jet was used as shown in an injector mode, for three independent reasons. The first was to increase the momentum of the fuel supply to improve the injection of the fuel into the mixing core in the burner. The second was to utilize the injector characteristics to aid extraction of the volatiles from the pyrolyzer. The third was to use the injection design to allow turning the burner on its side, as illustrated, as flame probing was easier in this configuration than in probing through the flame gases from the top.

This burner was also designed to permit attachment of a burn-out section for redundancy measurements as described below, and difficulty with this attachment had been experienced in the vertical configuration because of increased buoyancy. This is elaborated below. This injector system also caused problems. The principal one was that the injector was too effective and pulled air into the pyrolyzer, causing some gasification simultaneously with the pyrolysis.

There was also an additional problem that was not entirely unexpected. In the cold model studies²²⁻²⁴ an intense backmixing flow was identified located on the geometric axis between the two injector planes. This backmix flow was found to be the core for flame stabilization. In experiments with a large burner (1000 MJ/hr) using the same double-vortex design, and burning gas (as thermal support for incinerating tear gas in water), it was found that for good flame stability the gas ports and atomized tear gas had to be directed towards the walls away from the geometric axis. (With this design the burner was also found to have zero by-pass as judged by the total destruction of the tear gas; this is also a good partial measure of the uniformity of cross-mixing.) If the gas jet was directed down the burner axis it evidently disrupted the flame-stabilizing backmix core. The injector configuration of Fig. 4C appeared to have some of these characteristics although the jet momentum was initially judged to be too low to exhibit a strong disruptive effect.

On the basis of these results a return to the original burner design was deemed necessary, using the full pipe diameter of 50 mm

running without restriction from the pyrolyzer to the burner section. Under these conditions the flame filled the burner quite uniformly from wall to wall as shown by radial TC profiles.

In a final modification, the refractory lining of the burner walls was removed. The refractory was originally installed to reduce wall losses and to aid creation of uniform temperature fields across the burner diameter. One of the techniques used for data quantification, however, as described in the section following, is to determine blow-off loops, and it appeared that the blow-off conditions were not so easily determined with the refractory present. The hot refractory piloted some degree of continued reaction and flame holding beyond the extinction limit for a short period of time and increased the uncertainty in determining the blow-off boundary.

2.4 Pyrolyzer and Tray Design. The initial experiments were carried out using a batch pyrolyzer (Fig. 5) similar to that used by Biswas and Essenhigh⁶ which, in turn, was an independent development from the tray system used previously by Finch,⁴ and by Underwood and Thring⁵. The batch pyrolyzer was developed for use with computer card clippings to generate cellulose volatiles as the tray method did not work with these materials; there was sufficient inleakage of air from each end of the channel containing the trays that combustion of the computer card clippings could not be prevented. With the batch pyrolyzer, a controlled, metered air feed was used to burn and gasify the char chips formed from pyrolysis of the card clippings, and the heat of partial reaction provided the heat for pyrolysis. Under these conditions, 90%

Figure 5. Batch Pyrolyzer

of the solid mass was pyrolyzed/gasified, and the mass balance on the pyrolyzer required only a minor correction on this account. The residue at the end of an experiment was weighed and averaged over the duration of the experiment. The mass flow of volatiles was then the sum of the mass feed rate of the card clippings plus that of the metered air, minus the correction for the mass not gasified.

With coal in the batch pyrolyzer the conditions were quite different. The pyrolyzer had to be run much hotter to obtain significant pyrolysis, but even with appreciable combustion/gasification of the resultant char, only 25 to 40% of the coal was pyrolyzed/gasified. This meant that the pyrolyzer filled up with char rather quickly, thus limiting the duration of an experiment to 10 or 15 minutes, and it was much more difficult to maintain reasonably uniform or steady-state conditions through the duration of an experiment. The determination of the mass flux of pyrolyzed/gasified products then depended much more critically on the weight of char formed, and on its uniform rate of production for accurate averaging through the complete experiment. It was eventually determined that the accuracy of the system was too low (depending on a relatively small difference of two fairly large numbers) and the batch pyrolyzer was abandoned.

Reversion to the tray system introduced new though relatively minor problems, but largely eliminated the major ones. The most important consequences were: elimination of the char gasification products (N_2 , CO, and CO_2) that diluted the volatiles; establishment of

acceptable accuracy in the measurement of weight loss by the coal in transit through the pyrolyzer to give the volatiles mass flux; maintenance of much better control in changing the volatiles mass flux (fuel feed rate to the burner) by adjusting the tray speed; and establishment of substantially independent control over the peak pyrolysis temperature (generally held as constant as possible at about 1020° C). In principle, it was also possible to run indefinitely by periodically adding sets of new trays upstream of the pyrolyzer. In practice, a single experiment was usually completed using only six to eight trays.

The trays were also redesigned several times. The first trays were deliberately constructed of light steel sheet for speed in demonstrating proof-of-concept. They proved to be surprisingly durable but did eventually buckle and jam in the muffle tube, on which account they were replaced by stainless steel. These also buckled at first and, accordingly, they were reinforced by welded-in diagonals to form a cross inside the tray. This design prevented buckling but produced uneven heating of the coal. The final solution was to use a heavier gage stainless without any internal reinforcing. The heavier gage was not used initially from concern over adverse thermal-response properties of the trays and consequent reduction in heat transfer to the coal.

Another problem identified when using the original light sheet trays involved the method of attachment of one tray to the next. In the first design this was provided by an overlap at the leading edge of

each tray that hooked over the trailing edge of the tray in front. This acted as a crude hinge allowing some up and down motion, but longitudinally the sets of trays were rigid. When the muffle tube was cold the trays traveled through without any problem, but with any small distortations in trays or channel when hot, the tray set would periodically jam on account of the longitudinal rigidity. Several other different fastening systems were tried; the solution was to allow about a 1 mm gap between the trays to eliminate the longitudinal rigidity, and use of the wire loop over a post. The original concerns were that any gap between the trays might introduce an unwanted perturbation in the uniform flow of volatiles, and that thermally fractured particles might be ejected out of a tray and fall between two trays which could be a cause of jamming. This occasionally does happen but it is so infrequent that it is not a problem of any account; and no significant perturbation in the volatiles flow was observed due to the gap between the trays.

In the early experiments coal swelling became a more serious source of jamming. The trays were designed to fit quite snugly into the channel to provide blockage to air infiltration from the ends of the channel, an objective that was essentially achieved. However, if the coal in the loaded trays was level with the tray top then, on swelling, it would solidly jam that tray and terminate the experiment. The procedure of loading the trays and leveling the top of the load with the tray top was initially adopted as the most efficient means of obtaining a sufficiently reproducible weight loading in each tray. Prior weighing of a preset quantity of coal is time consuming, and

liable to error from spillage when loading and leveling the trays (leaving sufficient free board to allow for swelling). The procedure now used utilizes a shaped key that levels a pre-filled tray with about 1 mm freeboard. The trays are then placed on a tared (triple beam) balance and the final net weight adjusted to 80 g (usually by a small addition). This leaves a small space above each tray that allows the coal to swell without jamming the feed train.

2.5 Channel and Heater Design. In expectation of periodic jamming, the channel was made of two overlapping pieces of 304 stainless as illustrated in Fig. 6A. The figure also shows the relative dimensions of the riser for the volatiles. When the trays jam, the channel is easily dismantled for cleaning. The two pieces are held together by two large C-clamps, one at each end outside the heated zone. The original design of the channel is shown in Fig. 6B and did not include the complete top overlap. The original design was again adopted for speed in proof-of-concept, as the channel was easily made by cutting a piece of standard mild steel channel in two and overlapping the two pieces as shown. However, this design was not always tight, and volatiles would occasionally leak from one side. This showed that escape along the channel to each end was more difficult than leakage through the overlap, and that resistance to flow of the volatiles due to blockage by the trays was generally sufficient to prevent such escape. The problem of volatiles escape along the overlap only developed when the channel had warped and when, as shown, the volatiles riser diameter was reduced from 50 mm to 25 mm. With the modified design of Fig. 6A no further leakage occurred.

**Present Channel Design Showing
Cross Section. Dashed Line is Tray
Cross Section.**

**Original Channel Design Showing
Cross Section.**

Figure 6. Channel Designs: Initial and Final

Since the pressure balance in the system is quite delicate, with driving potentials of a few thou. w.c., there was at all times greater concern with air in-leakage from the ends of the channel into the pyrolyzer. The driving force for such inleakage would be the chimney effect of the volatiles riser. For that reason, to keep buoyancy as low as possible the burner was initially set about 3" above the top of the channel, about 1" above the top of the contraction shown in Fig. 4B. When the contraction was eliminated because of the adverse effects on the burner described above, and replaced by a straight riser tube as shown in Fig. 6A, there appeared to be some sort of coupling between the flame and the pyrolysis behavior in the trays below. This was eliminated by lengthening the riser to 305 mm and, fortunately, without adverse effects on air leakage in spite of the increased chimney effect of the riser.

The addition of a burn-up section on top of the burner, however, did increase the chimney effect to the point that significant air was drawn into the pyrolyzer; this was also the case of the injector shown in Fig. 4C, as already described. The chimney effect of the added burn-up section was also sufficient to affect the structure of the flame in the burner, probably as the result of increased mass flow up the riser. On this account, the burn-up section is currently omitted.

From these results it can be seen that the pressure balance in the pyrolyzer and burner is indeed delicate but sufficiently robust to prevent either air in-leakage or volatiles ex-leakage under most conditions, and that departure from balance results in obviously adverse effects on the flame. This point is amplified below.

Adequate heating of the channel to produce sufficient efflux of volatiles also presented a number of problems. The present heating system is a refractory enclosure of FR28 hot face insulation brick of roughly 400 x 100 x 100 mm fired with natural gas at about 50,000 Btu/hr, with the underside of the channel forming the roof of the enclosure so that it is heated mainly by radiation from the brick. At the upstream end the exhaust gas is tracked over the top of the channel. The coal in the trays is heated by conduction through the bottom of the channel, and by some radiation from the top of the channel. With this arrangement the maximum volatiles efflux rate is about 1 g/sec. In the original arrangement, a single Meker burner was used and the volatiles efflux rate was then about 0.1 g/sec, and this low rate possibly contributed to some of the initial burner problems described above. The Meker burner was replaced in succession by a larger, partially contained burner that was then boosted with electric heating coils (which burned out too frequently), and finally by the enclosure and burner described. The concern at first was to limit the heated region as closely as possible to the region of the riser tube so that the chances of cracking or condensation of the volatiles inside the channel or even on the coal/char particles would be reduced. In the event, it would appear that these concerns were over-estimated. The transit time of the volatiles to the bottom of the riser tube is quite short, and the volatiles cool quite quickly to a temperature of about 300°C in the riser. The need for the required pyrolysis rate (of 1 g/s) forced extension of the heated zone upstream by about 30 cm, and

periodic inspection of the channel has not shown any significant deposits. There also appeared to be sufficient chimney draft and clearance above the trays for the volatiles to flow to the riser tube and not upstream to the channel entry. During channel development a nipple was added on the top of the channel to provide a nitrogen barrier if there was upstream escape of the volatiles, but this was only occasionally used and was eventually abandoned as it was inconvenient and evidently unnecessary.

With increased thermal input and longer heating times, the char temperature leaving the pyrolysis zone was very high, and the char started to burn (affecting the weight loss data) as it neared the channel exit. Two actions were taken to prevent char combustion. The first was a downstream nitrogen purge; however, without the upstream purge at the same time for pressure balancing, the delicate pressure balance was upset and nitrogen could flow upstream into the riser tube. The second action, found to be effective, was addition of air-cooling jets on the top and bottom of the channel. Even so, the cooling air spilling off the end of the channel acted as an ejector that drew volatiles from the pyrolysis zone down to the channel exit. This problem was eliminated by the addition of baffles on the top and bottom of the channel to deflect the air streams. These results confirmed that the system was normally in a natural balance though the balance was quite delicate and could be easily upset.

Under these conditions, the particles heated at roughly 25 deg/sec to generate a VM efflux rate of up to 1 g/sec.

2.6 Methods of Experiment. To make a run the trays are loaded with about 80 g of crushed coal per tray determined by tare measurements of each tray. Typically 6 trays are run at a time, and the drive system is started when the muffle furnace reaches steady state at 1050°C (this takes about 1 hour heating from cold). The tray speed is set by a predetermined setting of the Variac, and the data-logging system is used to set the time zero when the first tray enters the channel. As the smoke starts to emerge from the burner the combustion air at the top of the flame tube is adjusted and the volatiles are ignited using a propane torch. With bituminous coal, a sequence of measurements can be made in a single run. This is because the furnace is cooled (essentially linearly with time) by the passage of the trays, so that the VM release rate progressively falls. Measurements at a range of stoichiometries are thus possible by maintaining a steady combustion air flow so that the mixture automatically becomes more lean with time. For the lignite, the VM efflux rate is steady so that stoichiometry in the flame is changed by adjusting the air rate. The trays are reweighed immediately following the run, while still hot, to avoid moisture pick-up by the char. VM deposited on the riser walls is scraped off after each run and weighed, and the VM mass flow rate is adjusted accordingly (generally between 1 and 4 percent).

Two methods of experiment have been used. The first is based on measurements of reaction efficiency at the reactor exit at equivalence ratios near stoichiometric. The second requires mapping extinction loops by increasing or decreasing the air flow rate at a fixed fuel

rate until extinction occurs, and then repeating the experiment at a new fuel flow rate. In these experiments, the first method was used with the 3 coals, propane, and methane; the second method was used for the bituminous coal volatiles, for methane, propane, and CO. The use of both methods for the bituminous coal volatiles has also permitted a direct cross-check of the two different methods.

CHAPTER III

THEORY

3.1 Model Basis and Kinetic Equations. The physical model and basis for the analysis essentially follows that used by Biswas and Essenhigh⁶, and using a two-component reaction as an extension²¹ of Vulis²⁵ treatment of a continuous-flow, perfectly stirred reactor based on a one-component reaction. This treatment includes the analysis of the extinction conditions using Thermal Explosion Theory (TET).

The two primary assumptions used are that: mixing is perfect; and that a global reaction rate expression can be used for the local reaction rate (dc_f/dt) that is rth order in reactant (fuel) and $(n-r)$ th order in oxidant, for an overall reaction order, n , thus²¹

$$dc_f/dt = \rho^{n-1} k_o c_f^r c_{ox}^{(n-r)} \exp (-E/RT) \quad (3.1)$$

In a steady-state reactor, the local reaction rate can be transformed into the reaction efficiency (η) for the whole reactor using

$$\eta = (\rho V_c / J c_f^0) (dc_f / dt) \quad (3.2)$$

The fuel and oxidant concentrations can also be transformed into reaction efficiency using

$$c_f = c_f^0 (1 - \eta) \quad (3.3)$$

$$c_{ox} = c_{ox}^0 (1 - \phi \eta) \quad (3.4)$$

and Eq. (3.1) can be rewritten in the form

$$k = \eta / [(1-\eta)^r (1-\phi\eta)^{(n-r)} c_f^0{}^{(r-1)} c_{ox}^0{}^{(n-r)} \rho^{n-1} \tau_s] = k_0 e^{-E/RT} \quad (3.5)$$

The global rate constants, k_0 and E , are obtainable in two ways. In Method 1 they are obtained directly from appropriate Arrhenius plots, after determination of values of k at different temperatures. In Method 2 they are obtained indirectly by re-formulation of the equations to satisfy the TET extinction criteria. In both cases, the reaction efficiency is first transformed into thermal terms, and the equations are tested using thermal balances.

3.2 Thermal Formulation of Equations: Method 1. The thermal formulation utilizes a heat balance on the reactor. The rate of chemical heat supply, H_f , is given by

$$H_f = J c_f^0 h_f \quad (3.6)$$

In partial combustion in the reactor, only a fraction of the heat is released. This is Q_g , which at steady state is equal to the rate of heat loss, Q_L , which in turn is the sum of the sensible heat in the products of partial combustion (POPC) plus the wall loss (H_w), thus

$$Q_L = J \sum f_i [h_i(T) - h_i(T_0)] + H_w \quad (3.7a)$$

$$= J \bar{c}_p (T - T_0) + H_w \quad (3.7b)$$

Equating heat generation with heat loss, then

$$Q_G = H_f \eta = Q_L \quad (3.8)$$

The detailed measurements required to evaluate these terms are discussed below. For Method 1, however, the procedure is to calculate Q_L and H_f from measurable parameters in the flow at different stoichiometries and temperatures. Their ratio, by Eq. 3.8, is the reaction efficiency. This yields the quantities permitting calculation of k in Eq. 3.5.

3.3 Extinction Analysis: Method 2. The basis of the TET analysis used in Method 2 is satisfaction of the equivalence and tangency

requirements on the Q-T plane²¹. Equation 3.8 is the statement of the equivalence requirement. The tangency requirement is

$$dQ_g/dT = dQ_L/dT \quad (3.9)$$

To evaluate Eq. 3.9 both Q_G and Q_L are transformed into reaction efficiency functions by dividing by H_f . From Eq. 3.8, the equivalence condition takes the form

$$\eta_G = \eta_L \quad (3.10)$$

where η_G and η_L require identifying subscripts since they represent different functions on the Q-T or η -T plane. Equation 3.9 takes the form

$$d\eta_G/dT = d\eta_L/dT \quad (3.11)$$

Equation 3.5 can be re-written in the form

$$\eta_G/(1-\eta_G)^r(1-\phi\eta_G)^{(n-r)} = h_f[\rho^{(n-r)}(\tau_s k_0)c_f^{o(r-1)}c_{ox}^{o(n-r)}]e^{-E/RT} \quad (3.12)$$

whence, differentiating yields:

$$[(1/\eta_G) + r/(1-\eta_G) + \phi(n-r)/(1-\phi\eta_G)] (d\eta_G/dT) = (E/RT)^2 \quad (3.13)$$

From Eqs. 3.7b, 3.8, and 3.6

$$\eta_L = (T - T_0)/\omega^* + (T - T_w)/\gamma^* \quad (3.14)$$

$$\text{where } \omega^* = h_f c_f^0 / c_p \quad (3.15a)$$

$$\text{and } \gamma^* = Jh_f c_f^0 / hA \quad (3.15b)$$

for these purposes dimensional ω^* and γ^* are used in preference to the dimensionless ω and η used elsewhere²¹; the dimensional forms become dimensionless by multiplying by (R/E) . Again, differentiating

$$d\eta_L/dT = (1/\omega^*) + (1/\gamma^*) \quad (3.16)$$

Using Eq. 3.16 in Eq. 3.13, and using Eq. 3.10 to permit removal of the subscripts, the final relation describing the extinction boundary can be written

$$(E/RT)^2 = [(1/\eta) + r/(1-\eta) + (n-r)\phi/(1-\phi\eta)][(1/\omega^* + (1/\gamma^*)\phi] \quad (3.19)$$

3.4 The Uniqueness Problem : Selection of Reaction Order. The equations developed above contain four unknown parameters to be determined: the kinetic constants, k_0 and E ; and the reaction orders, r and n . The literature shows that different measures have been adopted to obtain numerical values of these kinetic parameters from the experimental results. With sufficient experimental values of sufficient precision (repeatability) it is possible to do a 4-parameter optimization. However, when the values obtained are found to be sensitive to the number of points included in the optimization this does not create confidence in the significance of the result. An alternative but broadly similar method is to select successive values of either n and r , or of k_0 and E , and to determine the missing pair by minimizing some designated error residual. In this method, particularly, it is commonly found that optimization must be carried out separately for rich and lean conditions. For lean conditions reaction orders are commonly in the range of 1 or 2; but in rich conditions, the fitting reaction orders can be bizzarely high, at 30 or 40. Clearly, the parameter is then acting only as a fitting factor; it cannot be regarded as a real reaction order and its validity outside the range of experiment is suspect.

Nevertheless, near the stoichiometric, there is considerable unanimity that the fuel reaction order (r) is unity, and the overall order, n , is about 1.8 to 2. Quasi-global treatments²⁶ based on the assumptions of rapid reaction to CO followed by oxidation by OH have resulted in expressions supporting $r = 1$, but adding H_2O as a reactant,

with half order for each of H_2O and O_2 so that overall $n=2$. There are still sufficient questions regarding the quasi-global treatment at this time, however, that the full global expression of Eq. 3.1 is preferred. At the near stoichiometric, then, there is reasonable experimental support from a range of fuels that $r = 1$, and that the oxidant and fuel reaction orders are the same, so that $n = 2$.

Away from the stoichiometric, however, there is only one study to our knowledge that systematically examines the effect of equivalence ratio on reaction order. This is the study by Kretschmer and Odgers²⁷ where the effect of equivalence ratio was examined for 4 different fuels along the bound of the extinction loop so that the equivalence ratio varied all the way from about 0.5 (at the lean limit) to about 2 (at the rich limit). Optimization of the data yielded a common expression for all four fuels as follows²⁷

Lean Side

$$r = (n-r) = \phi \quad (3.20a)$$

Rich Side

$$r = (n-r) = 1/\phi \quad (3.20b)$$

These expressions have the merit that: they are common to several different fuels; they have been validated against experiment all the

way from the lean to the rich limit; they yield $r = 1$ and $n = 2$ at the stoichiometric, in agreement with many other studies; they account for the reports of $n = 1.8$ when corrected for stoichiometry; and they are the only such comprehensive studies known. In a recent communication²⁸, Odgers has advised that a small improvement is obtained using

Lean Side

$$n = 1 + \phi^2 \quad (3.21a)$$

Rich Side

$$n = 1 + 1/\phi^2 \quad (3.21b)$$

with $r = n/2$ near stoichiometric and reaction order for the low concentration component tending toward unity.

On these grounds, the above expressions are used so that the number of unknown kinetic parameters, to be determined from experiment, is reduced to two, these being k_0 and E . As will be shown, the comparison of the results for the bituminous coal volatiles obtained by the two methods provides good support for this choice.

CHAPTER IV

METHODS OF MEASUREMENT

Measurement of many of the various parameters required for the theoretical calculations presents some unusual problems. The simplest measurements using conventional methods are those of the air and gas flows (by rotameter), and various temperatures (by thermocouple, with heat loss corrections if necessary). Other measurements, such as the volatiles mass flow, the VM heat of combustion, the chemical enthalpy of the unburned fuel fraction (H_u), are inherently unconventional and, at this time, less accurate. In principle, accuracy can be improved by using several different methods of measuring the same parameters (redundancy); but, although redundancy in key measurements was planned, as described below, it was found in practice that the additional redundant measurements were not possible, for reasons that will be given. In several instances the redundant measurements failed because of the experimental complexity of the requirements that will require substantial further development for success. Nevertheless, the reasons for present failure of the redundant measurements are regarded to be an important part of the record for insight into the experimental problems to be resolved in carrying out these experiments. It is also intended as a guide in the event of repeat or extension of these experiments by

others.

4.1 Burner Parameters and Constituent Balances. Figure 7 is a schematic of the burner and of the energy and mass balances.

For the mass balance we have: the total mass flow (J) is the sum of the air flow (M_a) and of the fuel (volatiles) mass flow (F): thus

$$J = M_a + F \quad (4.1)$$

For the principal energy balance on the burner, the energy supplied by the volatiles, H_f , is equal to the enthalpy (sensible heat) of the products of partial combustion (POPC), H_g , plus the potential heat of the unburned POPC, H_u , plus wall loss, H_{wl} ; hence

$$H_f = H_{wl} + H_g + H_u \quad (4.2)$$

The energy in the volatiles is primarily chemical, with a heat of reaction h_f^0 , with some additional sensible heat so that (c.f. Eq. 3.6)

$$H_f = F [h_f^0 + (h_v(T_v) - h_v(T_o))] \quad (4.3)$$

so that h_f in Eq. 3.6 is the effective heat of reaction inclusive of the sensible energy of the VM preheat. Likewise, the chemical energy in the unburned constituents of the POPC is the sum from all

Figure 7. Schematic of Burner with Mass and Energy Flows

fractions.

$$H_u = J \sum f_i h_{f,i} \quad (4.4)$$

The exhaust gas enthalpy, H_g , is the sum of the component enthalpies (c.f. Eq. 3.7a)

$$H_g = J \sum f_i [h_i(T) - h_i(T_0)] \quad (4.5)$$

Comparing these equations with Eq. 3.8 it is seen that

$$Q_G = H_f - H_u \quad (4.6)$$

so that:

$$\eta = 1 - H_u/H_f = Q_L/H_f \quad (4.7)$$

Thus Eq. 4.7 is an alternative formulation for the reaction efficiency. This identifies one of the possible redundancy determinations if H_u and Q_L can be calculated independently.

4.2 Supplementary Balances from a Burn-up Section. With a burn-up section fitted, two further balances can be obtained using the final exhaust gas enthalpy, H_e , where this is calculated from the gas

analysis (for stable species: CO, CO₂, O₂), the temperature, and the mass flow: thus

$$H_e = J \sum f_j [h_j(T_e) - h_j(T_o)] \quad (4.8)$$

Inclusive of the wall loss(es) additional measures for H_g and/or H_u arise using

$$H_g + H_u = H_{w2} + H_e \quad (4.9)$$

An additional measure for H_f is also obtained, using:

$$H_f = (H_{w1} + H_{w2}) + H_e \quad (4.10)$$

The precision of measurement of H_e can be improved in principle by adding a water-cooled heat exchanger, and splitting the measurement between the heat exchanger and the POC flow; in particular, the gas temperature can be more accurately measured while at the same time this fraction of the energy flow is less sensitive to accurate measurement of this temperature. The burn-up section was designed with this function to be included but, as noted above, it was not used in any of the quantitative experiments because of the disturbance to the pyrolyzer pressure balance.

4.3 Methods of Primary Measurement. The actual measurements made were as follows.

4.3.1 Mass Flows : M_a , F, and J. Air (and gas) flows were measured by rotameter. Entry pressures were also measured and the nominal volume flow rates were corrected to standard measure using $(P/P_0)^{1/2}$, and then converted to mass flows.

The volatiles mass flow was determined from the rate of loss of weight of the trays passing through the pyrolyzer, calculated from the weight loss and the tray velocity and corrected for mass accumulation on the riser walls. The air rates mostly ranged from 1 to 5 g/s, and the VM rates ranged from about 0.1 to 1 g/s. The ratio of air to VM rates ranged from a high of 25 at the lean limit to a low of 2 at the rich limit. This meant that the accuracy of the total flow rate ($J = M_a + F$) was dominated by the air measurements, but accuracy in F for accuracy in J became increasingly important as the mixture became richer.

4.3.2 Heat of Volatiles Combustion, h_f . This is calculated from an equation that describes the variation of the VM heat of combustion with the pure coal heat of combustion based on a heating value of 14460 Btu/lb for the fixed carbon. The correlation curve is given in STEAM²⁹. The equation is in the form of $h_f(VM)$ as a function of $h_f(p.c.)$, thus

$$h_f(\text{VM}) = \frac{h_f(\text{p.c.}) - 14460 \text{ F.C.}_{\text{p.c.}}/100}{\text{VM}_{\text{p.c.}}/100} \quad (4.11)$$

The graph of the equation is given in Fig. 8 for 10%, 30%, and 50% VM, and the heating values of the 3 coals used are also shown.

This procedure differs from that used by Biswas and Essenhigh⁶ who analyzed gas and condensate samples of the VM flow, obtained by passing the VM mixture through a water-cooled condenser, and used a summation equation of the form of Eq. 4.3 to calculate the effective heat of combustion of the mixture. The cellulose volatiles mixture separated without problems into a liquid condensate and simple gases of which the main combustible constituent was CO. The heat of combustion of the condensate measured in a combustion bomb was determined as 1000 kcal/kg. There was no difficulty in metering the volume of analyzable gas drawn off for association with a measured mass of condensate. The estimated error for the heat of combustion of the mixture was better than 10% and this was cross-checked against the (redundant) estimation using the overall energy balance for the burner given by Eq. 4.2. In that balance, the primary constituent of the unburned gases leaving the burner, for calculating H_u , was carbon monoxide.

This same procedure was attempted in these experiments, but it was abandoned when it became clear that the simultaneous mass (rate of flow) measurements of the condensibles and fixed gases were unreliable. The primary condensate was a thick tar that coated all the conveying tube surfaces so that measurement of its total mass for a given

Figure 8. Variation of VM Heating Value with Coal Heating Value for Several Values of Fixed Carbon

gas/vapor volume extracted was of low accuracy. As the tar condensate built up the gas flow dropped so that without an integrating flow meter, the gas-flow volume (mass) was also uncertain. In the Biswas experiments with the liquid condensate it was possible to maintain a steady flow rate through a flow meter downstream of the condenser. These problems should be resolvable but resolution will require a sophisticated and expensive quantitative gas-analysis train. As this determination of h_f was redundant to the method described above, and was judged to be of much lower accuracy at this time, it was not pursued.

4.3.3 Sensible Heat in Burner Exhaust : H_g . The primary measurement for this determination was the exhaust temperature, T_g . The calculation using Eq. 4.5 additionally requires the total mass flow, J , and the POPC composition. The mass flow is given by the sum of the metered air and VM flow as described. The POPC composition was not measured, however, on account of additional difficulties, discussed below; estimated values of POC enthalpies were used instead. The accuracy of average POC enthalpies was demonstrated by Rosin 50 years ago (see Spiers³⁰) and was recently re-formulated by Hottel³¹ who has shown that for a very wide range of gaseous, liquid, and solid hydrocarbon and carbonaceous fuels, the normalized POC enthalpy can be described with high accuracy by the same monotonic temperature function. Normalized at 1800K, the following curve-fit equation to Hottel's graph was found to be accurate to $\pm 1\%$.

$$\begin{aligned} & [h(T) - h(298)] / [h(1800) - h(298)] \\ & = f(T) = -.1660 + 5.3807 \cdot 10^{-4} T + 5.9341 \cdot 10^{-8} T^2 \quad (4.12) \end{aligned}$$

Our actual procedure was an iterative approach to estimation of the POPC composition. Using the measured temperature, an efficiency can be calculated assuming that the POPC is air. Then, using this efficiency, the POPC composition can be calculated and a new efficiency found. The POPC composition is again adjusted and this is repeated until the efficiency converges to a final value. Curve-fits for POPC properties from VanWylen and Sonntag³² are used, except for the VM. For most hydrocarbons, the enthalpy per unit mass over the temperature range of interest is similar (see for example Bhatt³³), within $\pm 5\%$, so the value for C_8H_{18} from Ref. 33 was used. Since the fuel concentration in the POPC is low (initial concentration multiplied by the efficiency) any error introduced is very small.

4.4 Problems of Redundancy Measurements. The desirable redundancy measurements that were attempted but not made were as follows.

(1) The VM Heat of Combustion, H_f , from the VM analysis, for the reason given above, that the sampling probe too easily clogged with tars, and associated mass flows of condensate and fixed gases became impossible to measure.

(2) The final (POC) enthalpy, H_f , at the exhaust of the burn-up section, for the reason given above, that the delicate pressure balance in the pyrolyzer was upset and air was drawn into the pyrolyzer from

the end of the muffle tube. It was also found that blow-off conditions were evidently more scattered; there also appeared to be some change in the mixing pattern in the burner but this was difficult to observe directly because the presence of the burn-up section prevented such observation. Nevertheless, this is thought to be the easiest experimental problem to resolve.

(3) The Sensible and Chemical Enthalpies (H_g and H_u) from gas analyses. This refers to the problem identified in Sec. 4.3.3. For both determinations (of H_g and H_u), complete gas analyses of the burner exhaust (POPC) are required. These are conventional measurements at steady state using either on-line analyzers (such as NDIR) or using chromatography on batch samples. This was the procedure used by Biswas and Essenhigh⁶, and it was the planned procedure in these present experiments for measurements near the stoichiometric (Method 1).

Neither procedure can be used with Method 2 (extinction measurements) as these are essentially unsteady state conditions. Batch sampling is impossible. On-line analysis is possible if the analyzer response to gas analysis changes is immediate. The NDIR analyzers used are typical in that their analysis cells respond like stirred reactors to changes in composition; the characteristic time is about 5 sec., so that reequilibration to a step function change requires about 30 sec.

With Method 1, the steady-state procedure was also inappropriate

for the bituminous coal measurements as these were also in unsteady-state.. The procedure could have been used for the other coals but it was not as it was not set up.

4.5 Ancillary Measurements and Determinations. The energy flux calculations and temperature measurements required properties of air and other gases derived as follows.

Air and Gas Density was calculated using the ideal gas law.

Kinematic Viscosity and Thermal Conductivity of air were calculated using third order fitting polynomials for each property

$$p(T) = a + bT_g + cT_g^2 + dT_g^3 \quad (4.13)$$

The coefficient values used were as follows

	a	b	c	d
viscosity (γ)	1.673E-2	8.669E-5	-1.469E-6	1.248E-9
thermal conductivity (λ)	-2.25E-3	1.232E-4	-6.482E-8	2.282E-11

The polynomials were fitted to data compiled by Holman³⁴.

Thermocouple correction used a balance between convection and radiation with conduction along the TC wires neglected so that

convective supply = net radiative loss

$$Nu\lambda A(T_g - T_b)/d = \epsilon\sigma (T_b^4 - T_w^4) \quad (4.14)$$

For the bead sizes used, the Nusselt number, which generally exceeded 2 was calculated from³⁴:

$$Nu = 0.37 (u_{\infty} d / \nu_f)^{0.6} \quad (4.15)$$

with the (exit) reactor velocity given by

$$u_{\infty} = S(T_g/T_o)/A_r \quad (4.16)$$

The reactor cross-section, A_r , was $2.027\text{E-}2 \text{ m}^2$. The gas temperature (T_g) was obtained by iteration.

CHAPTER V

RESULTS

5.1 General Characteristics - The flames stabilized in the intense back-mix (stirred reactor) section at the top of the flame tube. Probing by TC's established that this was a reasonably uniform region with a well-defined lower boundary, as also described by Biswas and Essenhigh⁶. The volume of the back-mix region (needed to define τ_s in Eq. 3.5) is defined by the lower flame boundary, determined by TC measurements, with a jump of 500 to 1000°C across the boundary. The volume is also delineated by the upper boundary of the back-mix region, also determined by TC measurements and identified as the point where the uniform temperature from the back-mix region declines slightly and then begins to rise again. The distance from the bottom to the top boundary was equal to the distance between the two air injection planes. Combustion continued above the top of the tube in straight flow for lean conditions, or as a diffusion flame for rich conditions. The general appearance of this type of flame has been described previously^{6,35} in connection with the cellulose flames. In particular, Ref. 35 presents some color photographs showing a range of burning characteristics, from reddish-yellow, through white with bluish tinges, to essentially non-luminous (blue). The coal VM flames in this

work were closest to the "hard" whitish/blue flames, except at the rich limit where they moved to reddish-yellow. There was some difference in the appearance of the volatile smokes before ignition: the bituminous smokes had a substantial yellow tinge; the lignite smoke was whiter (closer to the cellulose volatiles). The appearance of the flames of the two fuels during combustion, however, was essentially the same.

Two different sets of experiments were carried out. With all three coals, data were obtained during combustion with air and oxygen concentrations varying a little either side of stoichiometric. With the Pittsburgh #8 volatiles, and three gases (CO , CH_4 and C_3H_8) extinction limits were determined. For the coal volatiles, some differences were seen in appearance of the flames, as would be expected, between the lean and rich limits, with the rich limit flames much like the reddish flames of the cellulose volatiles in Ref. 35. At the low limit the flame extinguished completely; at the rich limit, the flame extinguished in the burner but the volatiles continued to burn as a lifted, partially-aerated diffusion flame (see Ref. 35). Other qualitative aspects of ignition, procedures, and general characteristics of the flame behavior are as described earlier^{6,35}.

5.2 Coals: Near-Stoichiometric Measurements - Values of the (global) kinetic constants were obtained for all coals (bituminous and lignite) by measuring the quantities in Eq. 3.7 at stoichiometries slightly rich and slightly lean, and under conditions such that the combustion efficiency, η_v , in the backmix region of the flame was in the region of 0.5. H_g was determined as described in Section 4.3.3 and H_w was

determined by measurement of the temperature rise of the water flowing through the cooling jacket.

These measurements and calculations thus yielded values of the velocity constant, k (Eq. 3.5), as a function of temperature. These data were used to construct the Arrhenius plot of $\ln k$ against $1/T$ shown in Fig. 9. The dashed lines on Fig. 9 are for the results obtained for cellulose smokes by Biswas and Essenhigh⁶ and Shieh and Essenhigh⁷.

As can be seen, the data for the three coals bracket the cellulose kinetics of Biswas, with reaction rates being fastest for lignite VM, followed by Coal "C" (HVBB), and slowest for the Pittsburgh #8 (HVAB). The error values on the slopes show that they do not differ significantly over the experimental temperature range. The coal analyses and VM properties are given in Table 1.

The amount of scatter for the different coals varies with the technique used for data collection. As described in Sec. 2.6 the stoichiometry varied due to the changing VM mass flow rates for the bituminous coals, while the stoichiometry for the lignite was varied by changing the setting of the air control valve. The greater scatter in the lignite kinetic data probably results from the relatively abrupt changes in stoichiometry and the subsequent reequilibration, while the slow, steady and natural changes in stoichiometry in the other cases produced less scatter.

As Fig. 9 shows, the combustion rates for the cellulose volatiles differ significantly. For the lower value, obtained in the test

Figure 9. Arrhenius Plot for Second Order Analysis of VM Data

TABLE 1

Coal Analyses

<u>Fuel</u>	<u>Moist</u>	<u>VM</u>	<u>FC</u>	<u>Ash</u>	<u>Htg. Value</u> <u>(as rec.)</u>	<u>C</u>	<u>H</u>	<u>(d.a.f.)</u>		<u>S</u>
								<u>O</u>	<u>N</u>	
Pitt. #8	2.43	33.11	49.39	15.07	12159	82.69	5.85	7.81	1.65	2.00
Martin Lake	28.10	33.40	29.20	9.30	7658	70.3	5.23	20.02	.75	3.67
Coal "C"	7.59	34.59	52.68	5.14	12754	82.36	5.52	9.07	1.86	1.18

ASTM VM PROPERTIES

VM is $C_a H_b O_c N_d S_e$

<u>Fuel</u>	<u>Heating Value</u>	<u>Normalized to Carbon</u>				
		<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>
Pitt. #8	15800 Btu/lb	1	3.056	.257	.062	.016
Martin Lake	10549	1	2.617	.636	.027	.029
Coal "C"	15067	1	2.988	.310	.073	.010

incinerator⁷, a second measurement (not shown) suggests that the frequency factor in that system was partly controlled by the mixing rate of the smoke and secondary air. In the smaller scale equipment (75 mm and 50 mm dia. tubes) the mixing intensity is much higher and this is probably not a factor except, possibly, at the highest flow rates, as discussed below. In spite of the differences in rates, the activation energies are quite similar. The kinetic constants obtained are summarized in Table 2.

5.3 Gases: Near Stoichiometric Measurements - Values for global kinetics of CH_4 and C_3H_8 were also determined using the method described above. Measurement for CO was also attempted, but the flame did not stabilize within the interjet volume with this fuel. The Arrhenius plots of the velocity constant measurements, and their least squares fits, are shown in Fig. 10. The two fuels show similar behavior, with activation energies of 19.8 and 33.4 kcal/mole, with the two fitted curves intersecting in the experimental temperature range. Figure 11 shows all of the Arrhenius plots for the coal VM and the gases. Over the experimental range the VM and gas kinetics are in the same general range, with the gases showing higher activation energies (steeper slopes) than the VM.

Early results for the gases showed two linear sections in the Arrhenius plot. Figure 12 is an example of such results. The sudden break in the line is thought to point to a change in the physical phenomenon being measured. The temperature for these results was measured at the center of the reactor. A flame corresponding to a

TABLE 2

Kinetic Constants

Fuel	E	Std. Dev.	k_o	Std. Dev.
	(kcal/mole)		($m^3 kg^{-1} s^{-1}$)	$\ln k_o$
Pitt. #8 VM	17.4	.21	$1.79 \cdot 10^6$	.006
Coal "C" VM	17.3	.55	$4.37 \cdot 10^6$	.062
Martin Lake VM	12.2	2.13	$1.63 \cdot 10^6$	.668
Methane	19.8	4.09	$3.99 \cdot 10^7$	2.195
Propane	33.4	3.16	$6.87 \cdot 10^9$	1.231

Figure 10. Arrhenius Plot for Second Order Analysis of Reference Gas Data

Figure 11. Arrhenius Plot for Second Order Least Squares Fits of VM and Reference Gas Data

Figure 12. Arrhenius Plot Showing Change in Apparent Activation Energy for Reference Gas

Figure 13. Temperature Map of High Air/Fuel Flame

condition on the steep part of the line was traversed with a thermocouple to test for mixedness, with the results shown in Fig. 13. The high temperature core surrounded by low temperature gases indicates significant bypass and poor mixing. The flame core (where the temperature was measured for the Arrhenius plots) is not really at the stoichiometry indicated by the fuel and air flows, and the flame volume is no longer the volume between the jets, but some smaller volume, as a result, use of these data in the Arrhenius plots is invalid. After these investigations of the mixing were complete the data in Fig. 10 were taken and evaluated.

5.4 Extinction Loops - The extinction limits (lean and rich) were measured for the Pittsburgh #8 coal, as described above. The results are shown in Fig. 14 with an experimental trend line drawn through the data. Extinction loops were also measured for propane, methane and carbon monoxide and are shown in Figs. 15, 16, and 17 respectively. These three loops show an extended range on the lean side, which will be discussed further. Figure 18 shows the trend lines for all of the measured loops plotted on a heat release basis, which allows comparison among the various fuels, with propane having the largest loop; the methane and coal loops smaller and approximately the same size, and the VM loop the smallest. A loop for bituminous coal measured by Choi et al³⁶ in a jet-stirred reactor is also included for comparison. It is similar in size to the methane loop.

Temperature surveys at various conditions show that there is significant bypass at the leaner conditions as discussed in Section

Figure 14. Experimental Stability Limits for Pittsburgh #8 VM Flame

Figure 15. Experimental Stability Limits for Propane Flame

Figure 16. Experimental Stability Limits for Methane Flame

Figure 17. Experimental Stability Limits for CO Flame

Figure 18. Experimental Stability Limit Trend Lines for All Fuels on a Thermal Basis

Figure 19. Predicted Stability Limits for Pittsburgh #8 VM with Experimental Extinction Points

5.3. This bypass is evident in the large area of "stable" flames which is seen at extremely lean mixtures for both the propane and methane.

5.5 Predicted Extinction Loop for Bituminous Coal VM - The rich and lean extinction limits for the Pittsburgh #8 coal were also calculated using the kinetic constants obtained from the near-stoichiometric measurements (Table 2). The predicted loop is shown with the experimental blow-off points in Fig. 19. The calculations used the classical TET definition of extinction, based on the tangency of the heat loss line to the heat generation line, as described in Section 3.3, and reaction order was adjusted with stoichiometry according to the Kretschmer and Odgers²⁷ rule. The procedure in these calculations followed that used by Biswas and Essenhigh⁶, which was to increase the value for the total mass flow rate through the reactor until extinction occurred (defined by Equations 3.8 and 3.9). To map a loop this was carried out at a number of stoichiometries. The program used for this calculation is included as an Appendix.

5.6 Predicted Extinction Loops for Reference Gases - Extinction loops for the reference gases were also predicted from near-stoichiometric kinetics using the method described above. The predicted loops for methane and propane, along with the experimental trend lines, are shown respectively in Figs. 20 and 21. Fig. 22 shows all of the predicted loops plotted on a heat release basis. The curves show the same trend as the experimental loops, with propane larger than methane, and methane larger than VM, but at different absolute values, not matching the experimental points nearly as well for the reference gases as for

the VM. The predicted loops for the gases were not carried out far to the rich side of stoichiometric due to numerical instabilities.

5.7 Times for Burnout and Pyrolysis - Burning times for VM in an isothermal plug-flow reactor were predicted using the experimentally determined kinetic constants. Burning times were then compared to pyrolysis times from experiments by others (data compiled in Ref. 16). Figure 23 shows predicted burning time for the VM as a function of temperature along with pyrolysis times. It can be seen that burning and pyrolysis times are of the same order for the lignite VM, while burning times tend to be longer than pyrolysis times for the bituminous VM.

Figure 20. Predicted Stability Limits for Methane with Experimental Extinction Points

Figure 21. Predicted Stability Limits for Propane with Experimental Extinction Points

Figure 22. Predicted Stability Loops for All Fuels Plotted on a Thermal Basis

Figure 23. Comparative Burning and Pyrolysis Times

CHAPTER VI

DISCUSSION

6.1 Comparison of Kinetic Constants - The near-stoichiometric experiments for determination of k_0 and E permit comparisons in two ways: between the measurements of this work and previous measurements by others; and among reference gases and coal volatiles. If the same reaction orders are used and mass concentrations are used, then the values of k as a function of T give direct indication of relative reaction rates.

6.1.1 Comparison with Previous Work - An important question to be addressed is: "Are the kinetic constants measured in this work reasonable; are they within the expected range for hydrocarbons?". This can best be seen by comparison with previous measurements of global kinetics in various experiments. Figure 24 is an Arrhenius plot of second order kinetic fits for the data of this work along with data obtained by Clarke³⁷, Herbert³⁸, Westbrook and Dryer³⁹, Vandenabeele et al⁴⁰, and Duterque et al⁴¹ for the fuels methane, propane, benzene, and isooctane. The values from Duterque et al are for the oxidation to CO, and as can be seen, are not fast compared to the global kinetics given. Over the range of flame temperatures, the value of $\ln k$ varies between 1 and 9 at 1000K and between 10 and 17 at 2000K neglecting the outlying

Figure 24. Comparison of Second Order Kinetics of Data from Several Sources

data of Herbert³⁸ and DeZubay⁴².

Several significant features can be seen. The first is the general agreement in activation energies for the pure fuels and the lower activation energies for VM and smoke. Second is the agreement in order of magnitude of the measurements except for those of Herbert and DeZubay. The propane measurement in the present work agrees well with Clarke's and also with the isooctane measurement of Westbrook and Dryer, showing that diverse systems can give similar results.

For previous work in which the data have been analyzed with $n=2$ comparison is more difficult. One way to make the comparison is to re-analyze the data of this study with the reaction orders used by the other workers. Several selected cases are presented here. A widely quoted study is that of Westbrook and Dryer³⁹ for methane, with $n = 1.5$ and $r = 0.8$. The results of analysis of the data of this work at those conditions are shown in Fig. 25. Again, the results are similar to the comparisons for $n=2$.

In previous work using a similar burner Biswas and Essenhigh⁶ made kinetic measurements for the combustion of cellulose smoke. Those results have already been shown in Fig. 9. As can be seen, the activation energy is similar to that for the coal volatiles reported here, and the value of the rate constant falls within the range of those for the various coals.

Thus, comparison with other work shows that the experimental system gives reasonable (order of magnitude) results for the global

Figure 25. Comparison of 1.5 Order Kinetics with Data from Westbrook and Dryer

kinetics and the pure gas measurements agree well with those of other workers from a range of experiments.

6.1.2 Comparison Among VM and Reference Gases - Figure 11 shows the least squares fits for the global kinetics of the VM and reference gases. The lines are solid over the experimental range and dashed beyond it. The reference gases have higher activation energies than the VM, but all activation energies are within the range typical of hydrocarbons, with the VM being near the low end of the scale, and the reference gases nearer the average. The reference gas data shows that the low activation energies for the VM are real, and not just due to the experimental technique, since the reference gas data were obtained in an identical burner. The reduced activation energy for coal volatiles may be due to the nature of the gas mixture which makes up the VM. A similar result is noted by Reuther et al⁴³ in a study of gas mixtures to simulate syn-gas. Although not a well-controlled set of experiments, they do show a general trend toward lower activation energy when moving from pure gases to gas mixtures. A similar phenomenon has been observed in studies of the kinetics of pyrolysis. Howard et al⁴⁴ proposed an explanation shown schematically in Fig. 26. If there are several important reactions with fairly high activation energies occurring over different temperature ranges, the global kinetics will appear to have a lower activation energy. As the number of such reactions increases the low activation energy composite shows less and less scatter, and in the limit of an infinite number of closely spaced lines, the composite itself becomes a straight line.

Figure 26. Schematic Explanation of Apparent Low Activation Energies for Reactions as Proposed by Howard et al.

6.2 Rank Sensitivity of Kinetics - As Fig. 9 shows, the Martin Lake VM (Texas Lignite) had the highest reaction rate, followed by Coal "C" (HVBB), and the Pittsburgh #8 coal volatiles had the lowest rate. The cellulose smoke burning rate was toward the higher end of the range of coal VM. The confidence limits on the least square fits show that the experimental system can measure the rates accurately enough to reveal significant differences between the kinetics of different materials. Since tar production increases with increasing rank while light gas production decreases with increasing rank^{13,14,15} this rank dependence is as expected, with the VM from lower rank coals burning more readily. That the value for the cellulose smoke is in the upper part of the range of coal VM is also in line with intuition, since the cellulose smoke has virtually no tars⁶.

6.3 Comparison of Experimental and Predicted Extinction Loops - The near stoichiometric kinetics gave a good prediction of the stability loop for the Pittsburgh #8 VM using the Kretschmer and Odgers²⁷ rule for reaction order (Fig. 19); however, the fit was not this good for methane and propane. The largest discrepancy between experiment and prediction for all cases is at the tip of the loop (near $\phi=1$). This may be due to the conditions at these highest mass flow rates that are farthest from perfect mixing. It may also be because this is the narrowest section of the stable region. Any small perturbation in either the fuel or air flow may instantaneously move the flame out of the stable region, so that the experiments show a curved tip for the

loop, while theory (which assumes perfectly steady flows) predicts a point.

6.4 Applicability of CO Limited Reaction - As stated in the Introduction, one common assumption is that VM combustion is limited by CO burnout, with a very fast initial reaction from fuel to CO and H₂ (essentially an instantaneous heat release and O₂ consumption). One method for investigating the validity of this assumption was to predict blow-off limits using a model for CO limited combustion. The computer code for this model is included as an Appendix. Initially the model was based on an instantaneous conversion of all fuel to CO and H₂, followed by CO burnout. But instantaneous conversion was found to give extremely large stability loops, since approximately 60% of the available heat is released in this step. A modification to bring the model in line with reality was to impose a delay time on the reaction, and all fuel with residence times of less than the delay time (based on the residence time distribution for a PSR⁴⁵) was assumed to exit the reactor without reaction. The rest of the fuel was then converted to CO and H₂ and burned out with CO kinetics as proposed by Dryer and Glassman⁴⁶. The delay time is a characteristic time for the initial reaction step, but since the kinetics for this step are not well known, there is not any real advantage in using this scheme compared to the use of global kinetics, since a delay time will be required for every fuel, and a delay time coupled with CO kinetics does not provide any more information about relative reactivity of fuels than do global

kinetics. The kinetics of Duterque⁴¹ also show that the rate constant for the initial step is of the same order as the rate constant for global kinetics.

6.5 Relative Time Scales of Pyrolysis and Combustion - Figure 23 shows predicted burning times for VM in an isothermal plug-flow reactor and measured pyrolysis times (data compiled from several workers by Misra and Essenhigh¹⁶). The results seem to indicate that burning times and pyrolysis times are of nearly the same order. This has several implications with regard to total pulverized coal particle behavior. If the two processes are of the same order in time then the pyrolysis/burning/ignition process cannot be modeled as limited by one step or the other, but all must be considered. Flame codes also must model the ignition process properly to follow the VM evolution and temperature history. Proper sequential modeling of these steps may be especially important when pollutant formation is considered.

CHAPTER VII

CONCLUSIONS

The first experimental measurements of the global kinetics for combustion of volatiles from coal have been made. These are the first values based on experiment for quantities which in the past have been only estimated using fairly broad assumptions. The kinetic parameter values now provide an improved basis for testing the sensitivity of modeling to real kinetics.

The rates obtained for the different coals show that coal rank is important; that for calculations of VM combustion we cannot just consider some sort of generic VM, but must consider the coal it originates from. This points as well to necessary future experiments. VM composition varies not only with coal rank but also with heating conditions. The effects of heating rate as well as coal rank must be studied to gain the knowledge base necessary for modeling VM combustion in flames, where heating rates are much higher than in the present experimental system.

The global kinetic constants for VM combustion obtained in this work are reasonable when compared with the measurements of others for hydrocarbon fuels and when compared with measurements for methane and propane in the same burner. The low activation energies for the VM are also real, as shown by comparisons with the methane and propane data.

This result again provides motivation for future studies of gas mixtures to quantify the activation energy effect.

The global combustion rates for the Pittsburgh #8 coal volatiles are significantly reinforced by the comparison in Fig. 19 between the predicted and experimental extinction limits using the Kretschmer and Odgers²⁷ reaction order rule. A problem remains with overprediction at the peak, most likely due to the difference in flow stability between real and ideal systems.

The variation in global kinetics for the VM show that modeling of VM combustion as CO limited may not be very useful, since information (generated experimentally) on the rates of conversion to CO of selected fuels are still important in setting the overall rate. A correlation of global rates with VM composition may be the better approach for engineering models, especially as researchers in the field of pyrolysis are better able to predict VM composition^{13,14}.

Comparison of predicted VM burning times in a plug-flow reactor with pyrolysis times shows the two processes to be of the same order in time under similar conditions. However, now that global kinetics for VM combustion are available, more detailed modeling of realistic systems (e.g. single particle in unsteady state heating) is required to determine rate-limiting steps and to define the details needed for a total flame code.

Future work with this or similar systems should include: detailed measurements of VM composition, modification to allow different particle heating rates, and addition of a burn-up section to permit

redundant measurements. Other related work would be: measurement of gas mixture kinetics to study the effects of mixing on global kinetics (especially upon activation energy), modeling of pyrolyzing/burning particles, and prediction of extinction loops from near stoichiometric kinetics.

REFERENCES

1. Essenhigh, R.H., Coal Conversion Technology (C.Y. Wen and E.S. Lee, eds.) Ch. 3, Addison-Wesley, 1979.
2. Smoot, L.D., Horton, M.D. and Williams, G.A., Sixteenth Symp. (Internat.) on Combust., p. 375, The Combustion Institute, 1977.
3. Kuwata, M. and Essenhigh, R.H., Combust. Flame 20, p. 437, 1973.
4. Finch, D., Fuel 35, p. 415, 1956.
5. Underwood, G. and Thring M.W., "Combustion of Coal Smoke", Conference on Science in the Use of Coal, Paper 30, p. D-27, Inst. Fuel, 1958.
6. Biswas, B.K. and Essenhigh, R.H., Air Pollution and Its Control (R.W. Coughlin, A.F. Sarofim and N.J. Weinstein, eds.), AIChE Symp. Series, No. 126, Vol. 68, p. 207, Amer. Inst. Chem. Eng., 1971.
7. Shieh, W.S. and Essenhigh, R.H., "Combustion of Computer Cards in a Continuous Test Incinerator: A Comparison of Theory and Experiment", Proc. 5th National Incinerator Conference, p. 120, ASME, 1972.
8. Essenhigh, R.H., Chemistry of Coal Utilization (M.A. Elliott, ed.) 2nd Suppl. Vol., Ch. 19, John Wiley and Sons, 1981.
9. Juntgen, H. and van Heek, K.H., "An Update of German non-Isothermal Coal Pyrolysis Work", Fuel Proc. Tech., 2, pp. 261-293, 1979.
10. Howard, J.B., Ch. 12, Chemistry of Coal Utilization, Second Supplementary Volume, M.A. Elliott, Ed., Wiley, N.Y., 1981.
11. Gavalas, G.R., Coal Pyrolysis, Elsevier, Amsterdam, 1982.
12. Kobayashi, H., Howard, J.B. and Sarofim, A.F., 16th Symp. (Internat.) on Combust., pp. 411-425, 1977.
13. Solomon, P.R. and Colket, M.B., "Coal Devolatilization", 17th Symp. (Internat.) on Combust., pp. 131-143, 1979.

14. Suuberg, E.M., Peters, W.A. and Howard, J.B., "Product Compositions and Formation Kinetics in Rapid Pyrolysis of Pulverized Coal - Implications for Combustion", 17th Symp. (Internat.) on Combust., pp. 117-130, 1979.
15. Niksa, S. Paper presented at 22nd Symp. (Internat.) on Combust., Seattle, WA, August, 1988.
16. Misra, M.K. and Essenhig, R.H., "Release of Volatiles from Pyrolyzing Coal Particles: Relative Roles of Kinetics, Heat Transfer, and Diffusion", Energy and Fuels, 2, pp. 371-385, 1988.
17. Badzioch, S. and Hawksley, P.G.W., "Kinetics of Thermal Decomposition of Pulverized Coal Particles", Ind. Eng. Chem. Proc. Des. Dev., 9, pp. 521-530, 1970.
18. Annamalai, K. and Durbetaki, P., "A Theory on Transition of Ignition Phase of Coal Particles", Comb. Flame, 29, pp. 193-208, 1977.
19. Smoot, L.D. and Smith, P.J., Coal Combustion and Gasification, Plenum Press, N.Y., 1985.
20. Strehlow, R.A., Combustion Fundamentals, Ch. 6, McGraw-Hill, New York, 1984.
21. Essenhig, R.H., Combustion Technology: Some Modern Developments (H.B. Palmer and J.M. Beer, eds.), Ch. 14, Academic Press, 1974.
22. Rao, S.T.R., Kuo, T.J. and Essenhig, R.H., "Combustion and Emission Phenomena in Incinerators: Characterization of Stirring Factors by Cold Model Simulation", Proc. 4th National Incinerator Conference, p. 314, ASME, 1970.
23. Rao, S.T.R. and Essenhig, R.H., Thirteenth Symp. (Internat.) on Combust., p. 603, The Combustion Institute, 1971.
24. Zienalov, M.A.O., Kuwata, M. and Essenhig, R.H., 14th Symp. (Internat.) on Combust., pp. 575-583, 1972.
25. Vulis, L.A., Thermal Regimes of Combustion, Ch. 2, McGraw-Hill, 1961.
26. Edelman, R.B. and Fortune, O.F., "A Quasi-Global Chemical Kinetic Model for the Finite-Rate Combustion of Hydrocarbon Fuels with Application to Turbulent Burning and Mixing in Hypersonic Engines and Nozzles", AIAA Paper 69-86, AIAA, 1969.

27. Kretschmer, D. and Odgers, J., ASME J. Eng. Power 192, p. 173, 1972.
28. Odgers, J., Private Communication, April, 1988.
29. Babcock and Wilcox. Steam: Its Generation and Use, Babcock and Wilcox, N.Y., 1978.
30. Spiers, H.M. (Ed.) Technical Data on Fuel, Brit. Nat. Comm. World Power Conference, 1962.
31. Hottel, H.C. "Comparative Combustion Mechanisms in Dry and Slurry Coal Firing", Engineering Foundation Conference, Santa Barbara, California, Nov. 7-12, 1982.
32. VanWylen, G.J. and Sonntag, R.E., Fundamentals of Classical Thermodynamics, Second Edition, John Wiley and Sons, N.Y., 1973.
33. Bhatt, B.I. and Vora, S.M., Stoichiometry, Second Edition, Tata McGraw-Hill, New Delhi, 1984.
34. Holman, J., Heat Transfer, 5th Edition, McGraw-Hill, 1982.
35. Biswas, B.K. and Essenhigh, R.H., "Some Characteristics of Stabilized Smoke Flames", Comb. Flame, 15, pp. 93-96, 1970.
36. Choi, T., Rahimian, S. and Essenhigh, R.H., "Studies in Coal Dust Explosions: Influence of Additives on Extinction of High Intensity Coal Dust Flames", 21st Symp. (Internat.) on Combust., 1987.
37. Clarke, A.E., Odgers, J., Stringer, F.W. and Harrison, A.J., 10th Symp. (Internat.) on Combust., pp. 1151-1166, 1965.
38. Herbert, M.V., 8th Symp. (Internat.) on Combust., pp. 970-982, 1962.
39. Westbrook, C.K. and Dryer, F.L., "Simplified Reaction Mechanisms for the Oxidation of Hydrocarbon Fuels in Flames", Comb. Sci. Tech., 27, pp. 31-43, 1981.
40. Vandenabeele, H., Corbeels, R. and Van Tiggelen, A., "Activation Energy and Reaction Order in Methane-Oxygen Flames", Combust. Flame, 4, pp. 253-260, 1960.
41. Duterque, J., Gorghi, R. and Tichtinsky, H., "Study of Quasi-Global Schemes for Hydrocarbon Combustion", Comb. Sci. Tech., 26, pp. 1-15, 1981.

42. DeZubay, E.A. and Woodward, E.C., 5th Symp. (Internat.) on Combust., pp. 329-335, 1955.
43. Reuther, J.J., Daley, R.D., Warchol, J.J., and Withum, J.A., "Coal Volatiles Combustion - Coal Pyrolysis Analogy", Fuel, 63, pp. 604-605, 1984.
44. Howard, J.B., Fong, W.S. and Peters, W.A., in Fundamentals of the Physical Chemistry of Pulverized Coal Combustion, pp. 77-97, J. Lahaye and G. Prado, Eds., Nijhoff, The Hague, 1987.
45. Levenspiel, O., Chemical Reaction Engineering, John Wiley and Sons, N.Y., 1962.
46. Dryer, F.L. and Glassman, I., "High Temperature Oxidation of CO and CH₄", 14th Symp. (Internat.) on Combust., pp. 987-1003, 1973.

APPENDIX A
COMPUTER PROGRAMS

Arranged in the following order;

Programs for Data Acquisition

INIT.FOR

DATCOM.FOR

Programs for Data Analysis (Arrhenius Plots)

KEVCONC.FOR

Programs for Calculation of VM Properties

COALPROP.FOR

SMRATIO.FOR

Programs for Prediction of Stability Loops

QGQLCONC.FOR Predicts loops using global kinetics.

COLIM.FOR Predicts loops using CO-limited combustion.

```

C*****
C
C PROGRAM INIT
C
C
C BY DOUGLAS McALLISTER
C
C*****
C
C THIS PROGRAM INITIALIZES PROGRAM DATCOM BY
C ASSIGNING THE NUMBER OF READS AND WHICH
C FILE IS TO BE USED.
C CHARACTER*10 NAME1
C OPEN(UNIT=1,NAME='INITAL.DAT',TYPE='NEW')
C WRITE(5,10)
10 FORMAT(' ENTER DATA FILE NAME [6 CHARACTERS].DAT : ', $)
   READ(5,20)NAME1
20 FORMAT(A10) C
   WRITE(5,30)
30 FORMAT(' HOW MANY HOURS DO YOU WISH THE DATALOGGER',
1 ' TO RECORD ? ', $)
   READ(5,40) HRS
40 FORMAT(F4.0)
   HRS=HRS*3600
   WRITE(1,50)NAME1,HRS
50 FORMAT(A10,F8.0)
C
   CLOSE(UNIT=1)
   END

```

```

C*****
C
C
C PROGRAM DATCOM
C
C
C BY DOUGLAS McALLISTER
C
C*****
C
C this program is to read data from the digitech
C datalogger 3000 and record it in indexed files.
C
C DIMENSION CHAN(71),VALUE(71)
C BYTE BUFFER(40),DATA(75,40),TEMP(80)
C CHARACTER*10 NAME1
C
C-- Open source unit
C
C OPEN(UNIT=1,NAME=' TXB0:',TYPE='OLD')
C
C open initializing data file
C
C OPEN(UNIT=3,NAME='INITAL.DAT',STATUS='OLD')
C READ(3,10)NAME1,TIME
C INTVAL=TIME
10 FORMAT(A10,F8.0)
C
C
C open output file
C
C OPEN(UNIT=2,NAME=NAME1,TYPE='NEW',ACCESS='KEYED',
1 ORGANIZATION='INDEXED',FORM='FORMATTED',RECORDSIZE=18,
2 KEY=(4:12),SHARED)
C
C
C
C T1=SECNDS(0.0)
C CALL PURGE
C
C 100 DO 200 I=1,8
C 105 READ(1,210) LENGTH,(TEMP(K),K=1,LENGTH)
C IF (LENGTH .LT. 4) GOTO 105
C
C J = 1

```

```

DO 120 K = 1,LENGTH
IF (TEMP(K).GE. '0' .AND. TEMP(K) .LE. '9') GOTO 110
IF (TEMP(K).EQ. '.') GOTO 110
IF (TEMP(K).EQ. 'L') GOTO 105
GOTO 120
110 BUFFER(J) = TEMP(K)
J = J + 1
120 CONTINUE
C
DO 140 K=1,9
DATA(I,K)=BUFFER(K+9)
140 CONTINUE
DO 170 K=10,18
DATA(I,K)=BUFFER(K-9)
170 CONTINUE
C
WRITE(2,230)(DATA(I,K),K=1,18)
C
C
200 CONTINUE
T2=SECNDS(T1)
IF(T2.LT.INTVAL) GOTO 100
210 FORMAT(Q,40A1)
230 FORMAT(18A1)
C
C
CLOSE(UNIT=1)
CLOSE(UNIT=2)
CLOSE(UNIT=3)
END
SUBROUTINE PURGE
C
C PURGE, Clears out the typeahead buffer
C
INTEGER*4 SYSSQIO,SYSS$ASSIGN,SYSS$CANCEL
BYTE BUFFER(200)
C
PARAMETER READ_PURGE='831'X
C
ICODE=SYSS$ASSIGN('TT',I_CHAN,,)
C
ICODE=SYSSQIO(%VAL(I_CHAN),%VAL(READ_PURGE),,,,BUFFER,
1 %VAL(200),,,,)
C
ICODE=SYSS$CANCEL(%VAL(I_CHAN))

```

RETURN
END

```

C
C      KEVCONC.FOR
C
C      EVALUATES REAL DATA FROM VOLATILES FLAMES FOR K0, E
C      INCLUDES CALCULATION OF T0 FROM PROPER
C      AVERAGING OF AIR AND FUEL TEMPERTURES
C
C      JULY 20, 1987      D SHAW
C      JAN XX, 1988      MODIFIED TO CORRECT ERROR IN ENTHALPY
C      JAN 21, 1988      MODIFIED REGRESSION TO GIVE CONF LIMITS
C      APR 01, 1988      MODIFIED TO ACCOUNT FOR GAS COMPOSITION
C                          IN CALCULATING ENTHALPY IN REACTOR
C
C      IMPLICIT REAL(A-Z)
C      LOGICAL EXIST
C      LOGICAL YES_NO
C      DIMENSION LGR(100),TINV(100),xlst(2),ylst(2),XH(20),YHMIN(20)
C      DIMENSION YHMAX(20)
C      CHARACTER*10 NAME1,NAME2
C
C      GET DATA ON FUEL COMPOSTION
C
C      WRITE(5,100)
100  FORMAT(' ENTER NAME OF DATA FILE WHICH
      &INCLUDES FUEL PROPERTIES ', $)
      READ(5,110)NAME2
110  FORMAT(A10)
      OPEN (UNIT=1,NAME=NAME2,STATUS='OLD')
      READ(1,*)A,B,D
      READ(1,*)EE,F,G
      READ(1,*)AFSM,HF
      CLOSE(UNIT=1)
C
C
C      WRITE(5,200)
200  FORMAT(' ENTER FILENAME ', $)
      READ(5,210)NAME1
210  FORMAT(A10)
1000 OPEN(UNIT=1,NAME=NAME1,STATUS='OLD')
      READ(1,*)NSETS
C      WRITE(5,300)
C300 FORMAT(' ENTER % OF HEAT LOST TO WALL ', $)
C      READ(5,*)LOSS
      WRITE(5,310)
310  FORMAT(' ENTER REACTION ORDERS : N,R ', $)

```



```

READ(5,*)N,R
DO I=1,NSETS
  ICNT=1
  READ(1,*)SCFMA
  C   AIR FLOW IN SCFM
  READ(1,*)MFUEL
  C   FUEL MASS FLOW RATE (g/sec)
  READ(1,*)FMW
  C   FUEL MOLECULAR WEIGHT
  READ(1,*)AFSM2
  C   STOICH. MASS RATIO
  READ(1,*)HF2
  C   HEAT OF COMBUSTION (J/kg)
  READ(1,*)TA
  TA=TA+273
  C   AMBIENT TEMP (K)
  READ(1,*)T
  T=T+273
  C   FLAME TEMP (K)
  READ(1,*)QWALL
  QWALL=.0126*QWALL
  C   WALL HEAT LOSS (J/sec)
  READ(1,*)TFUEL
  TFUEL=TFUEL+273
  C   FUEL TEMPERATURE (K)
  READ(1,*)TAIR
  TAIR=TAIR+273
  C   COMBUSTION AIR TEMP (K)
  RHO0=1.1774
  C   DENSITY OF AIR (kg/cub meter) at 300 K
  C
  C
  C
  C   T0=300
  RHOF0=RHO0*(FMW/28.9)
  RHOF=RHOF0*(T0/TA)
  RHO=RHO0*(TAIR/TA)
  C   MFUEL=SCFMF*RHOF
  MAIR=SCFMA*RHO
  VOLAIR=SCFMA*.02832/60.
  WRITE(5,*)T
  CALL TCOR(T,VOLAIR)
  WRITE(5,*)T
  MFUEL=MFUEL/1000.
  MAIR=MAIR*.02832/60.
  T0=(MFUEL*TFUEL+MAIR*TAIR)/(MAIR+MFUEL)
  J=MAIR+MFUEL

```

```

CR0=MFUEL/J
COX0=(MAIR/J)*(32/(32+(3.76*28)))
PHI=AFSM/(MAIR/MFUEL)
CPC=1.2
VC=5.149E-5
C ETAC=7
C T=(ETAC*HF*MFUEL+MAIR*CPC*TO)/(J*CPC)
4000 IF(ICNT.EQ.1) THEN
CALL CP(T0,T,CPC)
CPC=CPC*1000
CPC1=CPC/(T-T0)
R1=CPC*j/(HF*CR0)
PSIC=R1/J
ELSE
DUMMY=0.0
CALL ENTH(TA,T,O2,FUEL,CO,CO2,H2O,N2,SO222,ENTHAL)
CALL
ENTH(TA,T0,DUMMY,CR0,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,
& ENTH0)
ENTHALPY=ENTHAL-ENTH0
CPC=ENTHALPY
R1=CPC*j/(HF*CR0)
PSIC=R1/J
END IF
ICNT=ICNT+1
C LOSS=LOSS/100.
C PSIW=LOSS*PSIC
C PSIC=PSIC*(1-LOSS)
C T=T-(T-T0)*LOSS
PSIW=QWALL/(HF*MFUEL)
write(5,*)psic,psiw
ETA=PSIC+PSIW
CALL CONC(PHI,PSIC,A,B,D,EE,F,G,O2,FUEL,CO,CO2,H2O,N2,SO2)
IF (ICNT.EQ.2) THEN
ETASAV=ETA
GOTO 4000
END IF
END IF
IF((ETASAV-ETA).GT..0001) THEN
ETASAV=ETA
GOTO 4000
END IF
C
C
C
C
R2=1-PSIC-PSIW
R3=1-PHI*(PSIC+PSIW)

```

```

RHO=RHO0*(300./T)
DENOM=VC*(RHO**N)*(CR0**(R-1))*(COX0**(N-R))
GROUP=(PSIC+PSIW)*J/((R2**R)*(R3**(N-R))*DENOM)
LGR(I)=ALOG(GROUP)
TINV(I)=1/T
WRITE(5,500)
500 FORMAT(' THE RESULTS ARE: ')
WRITE(5,520)GROUP,LGR(I),TINV(I)
520 FORMAT(' [ ] = ',F12.4,' LN[ ] = ',F12.4,' 1/T = ',F8.5)
WRITE(5,*)' NO. OF INERATIONS = ',ICNT
END DO
CLOSE(UNIT=1)
C
C DO THE LINEAR REGRESSION
C
CALL LINREG(TINV,LGR,NSETS,C1,C2,RSQ,XH,YHMIN,YHMAX)
WRITE(5,*)C1,C2,RSQ
C
C DRAW THE ARRHENIUS PLOT
C
C
WRITE(5,600)
600 FORMAT(' ENTER THE MIN AND MAX X VALUES',)
READ(5,*)XMIN,XMAX
xlst(1)=xmin
xlst(2)=xmax
ylst(1)=c1+ c2*xmin
ylst(2)=c1+ c2*xmax
WRITE(5,620)
620 FORMAT(' ENTER THE MIN AND MAX Y VALUES',)
READ(5,*)YMIN,YMAX
CALL QP_START
YES_NO=.FALSE.
CALL QP_BDR(YES_NO)
CALL QP_TICKS(5,4)
call qp_font(1)
CALL QP_AX(XMIN,XMAX,4,5,YMIN,YMAX,5,2)
CALL QP_LSTYL(129)
CALL QP_PTS(TINV,LGR,NSETS,2,3)
call qp_pts(xlst,ylst,2,1,1)
CALL QP_PTS(XH,YHMIN,8,1,1)
CALL QP_PTS(XH,YHMAX,8,1,1)
CALL QP_TTL(' '1/T','LN(GROUP)')
CALL QP_PAUSE
CALL QP_CLEAR

```

```

C  CALL QP_END
C
  write(5,630)c1,c2
630  format(' Slope = ',f12.5,' Intercept = ',f12.5)
  WRITE(5,640)
640  FORMAT(/,' CHANGE VALUES? (1=YES, 2=NO) ', $)
  READ(5,*)ANS2
  call qp_clear
  CALL QP_END
  IF(ANS2.EQ.1)GOTO 1000
  STOP
  END

C
C
C
C
  SUBROUTINE CP(T0,T,CPC)
  IMPLICIT REAL(A-Z)
  THETA=T/100.
  THETA0=T0/100.
  H=THETA
  H0=THETA0
  CPO2=37.432*(H-H0)+.020102*(H**2.5-H0**2.5)/2.5+
%178.57*(H**-.5-H0**-.5)/.5-236.88*(H**-1-H0**-1)
  CPN2=39.060*(H-H0)+2*512.79*(H**-.5-H0**-.5)-
%1072.7*(H**-1-H0**-1)+.5*820.4*(H**-2-H0**-2)
  CPC=CPO2/4.76+CPN2*3.76/4.76
  CPC=100.*CPC/28.9
  RETURN
  END

C
C
  SUBROUTINE LINREG(X,Y,N,C1,C2,R2,XHH,YHMIN,YHMAX)
  IMPLICIT REAL (A-Z)
  DIMENSION X(100),Y(100),XHH(20),YHMIN(20),YHMAX(20)

C
C  JAN 21, 1988 - ADDED ABILITY TO CALC. CONFIDENCE LIMITS
C
  SX=0
  SY=0
  SXX=0
  SYY=0
  SXY=0
  MSE=0
  XDELT=0
  II=0

```

```

C      DO I=1,N
        SX=SX+X(I)
        SY=SY+Y(I)
        SXX=SXX+X(I)*X(I)
        SYY=SYY+Y(I)*Y(I)
        SXY=SXY+X(I)*Y(I)
      END DO
      XBAR=SX/N
C
C
C      WRITE(5,*)SX,SY,SXX,SYY,SXY,N
      C2=(SXY-SX*SY/N)/(SXX-SX*SX/N)
      C1=(SY-C2*SX)/N
      R2=C2*(SXY-SX*SY/N)/(SYY-SY*SY/N)
C
C      COMPUTE ERROR MEAN SQUARE AND SUM OF SQ. DIF. OF X AND XBAR
C
      DO I=1,N
        MSE=MSE+((Y(I)-C1-C2*X(I))**2)/(N-2)
        XDELT=XDELT+(X(I)-XBAR)**2
      END DO
C
C      COMPUTE VARIANCE OFF Y(H) OVER A RANGE OF X
C
      WRITE(5,200)N
200  FORMAT(' ENTER F STATISTIC FOR N= ',F5.2,' : ',F5.2)
      READ(5,*)FST
      W=SQRT(2*FST)
      DO XH=.0006,.001,.00005
        II=II+1
        SYH=SQRT(MSE*(1/N+((XH-XBAR)**2)/XDELT))
        YHMIN(II)=C1+C2*XH-W*SYH
        YHMAX(II)=C1+C2*XH+W*SYH
        XHH(II)=XH
        YH=C1+C2*XH
        WRITE(5,*)XHH(II),YHMIN(II),YHMAX(II),YH
      END DO
C
C
C      RETURN
      END
C
C      SUBROUTINE TCOR(T,VOL)

```

```

      IMPLICIT REAL(A-Z)
      EPS=.191
      SIGMA=5.669E-8
      AREA=2.027E-3
      DIA=.6E-3
      TI=T
      TW=600
      ICOUNT=1
5000  NU=-.70384E1+.58051E-1*TI+.68187E-4*TI**2-.15741E-8*TI**3
      NU=NU*1E-6
      LAMBDA=-.225E-2+.1121E-3*TI-.6482E-7*TI**2+.2282E-10*TI**3
      NUS=NU*300.*AREA/(VOL*TI*DIA)
      DELTA=EPS*SIGMA*DIA*NUS**.6*(T**4-TW**4)/(LAMBDA*.37)
      IF(ICOUNT.EQ.1)THEN
        DELTASAV=DELTA
        TI=TI+DELTA
        ICOUNT=ICOUNT+1
        GOTO 5000
      END IF
      ICOUNT=ICOUNT+1
C   WRITE(5,*)ICOUNT,DELTA
      DELTEST=TI-T
C   WRITE(5,*)DELTEST
      IF(ABS(DELTA-DELTEST).LT.1.)GOTO 6000
      IF(DELTA.GT.DELTEST)THEN
        DELTASAV=DELTA
        TI=TI+1
        GOTO 5000
      ELSE IF(DELTA.LT.DELTEST)THEN
        DELTASAV=DELTA
        TI=TI-1
        GOTO 5000
      END IF
6000  DEL=DELTA-DELTEST
      WRITE(5,*)T,TI,ICOUNT,DEL
      T=TI
      RETURN
      END
C
C   SUBROUTINE CONC(PHI,EPS,A,B,D,E,F,G,O2,FUEL,CO,CO2,
C   &H2O,N2,SO2)
C   IMPLICIT REAL(A-Z)
C
C   CALCULATES MASS CONCENTRATIONS IN REACTOR BASED ON
C   GIVEN EFFICIENCY AND STOICHIOMETRY
C

```

```

C   AUTHOR: D.W. SHAW
C   DATE: MARCH 31, 1988
C
C   IF (PHI.GT.1) THEN
C       Y=1
C   ELSE
C       Y=PHI
C   END IF
C
C   CALCULATE CONVENIENT GROUPS
C
C   GR1=A+B/4-D/2+F
C   GR2=1-EPS*Y
C   GR3=PHI*(1-EPS)
C   GR4=PHI*EPS*D
C   GR5=A*PHI*EPS
C   GR6=B*PHI*EPS/2
C   GR7=EPS*PHI*G
C
C   MASSES OF EACH COMPONENT
C
C   O2=(GR1*GR2)*31.998
C   WRITE(5,*) GR3='GR3,' A='A,' B='B,' D='D
C   WRITE(5,*) E='E,' F='F,' G='G
C   FUEL=GR3*(12.011*A+1.008*B+15.999*D+14.007*E+32.06*F
C   &+18.015*G)
C   CO=(2*GR5+GR6+2*F*eps*phi-2*GR1*EPS*Y-GR4)*28.01
C   CO2=(2*GR1*EPS*Y+GR4-GR5-GR6-2*F*eps*phi)*44.009
C   IF(CO2.LE.0) CO2=0.0
C   H2O=(GR6+EPS*PHI*G)*18.015
C   N2=(3.76*GR1+phi*eps*E/2)*28.014
C   SO2=F*64.058*eps*phi
C   write(5,*) O2 = ',O2,' FUEL = ',FUEL,' CO = ',CO
C   WRITE(5,*) CO2= ',CO2,' H2O= ',H2O
C   WRITE(5,*) N2 = ',N2,' SO2= ',SO2
C
C   DENOMINATOR
C
C   DENOM=O2+FUEL+CO+CO2+H2O+N2+SO2
C
C   MASS FRACTIONS
C
C   O2=O2/DENOM
C   FUEL=FUEL/DENOM
C   CO=CO/DENOM

```

```

CO2=CO2/DENOM
H2O=H2O/DENOM
N2=N2/DENOM
SO2=SO2/DENOM

```

```

C RETURN
C END

```

```

C SUBROUTINE ENTH(T10,T20,O2,FUEL,CO,CO2,H2O,N2,SO2,ENTHAL)

```

```

C
C AUTHOR: HAI NGYUEN
C MODIFIED MARCH 31, 1988 BY D.W. SHAW
C TO INCLUDE A VALUE FOR THE FUEL,
C TO BE A SUBROUTINE RATHER THAN A STAND-ALONE PROGRAM
C TO GIVE ENTHALPIES IN J/KG RATHER THAN KJ/KMOL
C TO BE USED BETWEEN ANY TWO TEMPERATURES SPECIFIED
C

```

```

C
C          c
c This subroutine calculates the enthalpy of      c
c several gases. The enthalpy of each gas is de- c
c noted below :                                c
c   h(1): enthalpy of nitrogen.                  c
c   h(2): enthalpy of oxygen.                    c
c   h(3): enthalpy of hydrogen.                  c
c   h(4): enthalpy of carbon-monoxide.           c
c   h(5): enthalpy of water.                     c
c   h(6): enthalpy of carbon-dioxide.            c
c   h(7): enthalpy of nitrogen-dioxide.          c
c
c          c
c Where enthalpy is obtained by integrating      c
c formulas for specific heat from T1 to T2      c
c (source of polynomials, VanWylen and Sonntag c
c

```

```

C IMPLICIT REAL(A-Z)
C REAL H(10),MW(10)
C REAL T,T1,T2,A,B,C,D,E
C REAL F,G,H1,Q,P,R,S
C DATA MW/28.014,31.998,2.016,28.01,18.015,44.009,46.005,0,0,0/
C T1=T10/100
C T2=T20/100

```

```

C
C Calculate differences of powers of temperature
C

```

```

C   T = T2-T1
C   A = ((1/T2**.5)-(1/T1**.5))
C   B = (1/T2-1/T1)

```



```

C = ((1/T2**2.)-(1/T1**2.))
D = (T2**2.5-T1**2.5)
E = LOG(T2/T1)
F = (T2**1.75-T1**1.75)
G = (T2**1.5-T1**1.5)
H1 = (T2**1.25-T1**1.25)
Q = (T2**1.5-T1**1.5)
P = (T2**2.-T1**2.)
R = (T2**3.-T1**3.)
S = (T2**2.5-T1**2.5)

C
C
C  CALCULATE ENTHALPIES IN KJ/KMOL
C
H(1)=100*((39.06*T)+(1025.58*A)-(1072.7*B)+(410.2*C))
H(2)=100*((37.432*T)+(0.0080408*D)+(357.14*A)-(236.88*B))
H(3)=100*((56.505*T)-(2810.96*S)+(1165.0*E)+(1121.4*A))
H(4)=100*((69.145*T)-(.4026457*F)-(401.54*G)+(707.04*S))
H(5)=100*((143.05*T)-(146.832*H1)+(55.1673*Q)-(1.84945*P))
H(6)=100*((-3.7357*T)+(20.3527*Q)-(2.0517*P)+(0.008066*R))
H(7)=100*((46.045*T)+(432.2*G)-(1454.64*S)-(232.55*B))

C
C
C  CONVERT TO J/KG
C
DO I=1,7
  H(I)=H(I)*1000./MW(I)
END DO

C
C
C  CALCULATE ENTHALPY OF THE FUEL
C  (ACTUALLY THE VALUE FOR C3H8, BUT ALL
C  ARE FAIRLY CLOSE ON A MASS BASIS)
C
HFUEL=-4.042*T+15.23*P-.5237*R+.00793*(T2**4.-T1**4.)
HFUEL=100.*HFUEL*1000./44.097

C
C
C  CALCULATE TOTAL ENTHALPY PER KG OF MIXTURE
C
ENTHAL=N2*H(1)+O2*H(2)+CO*H(4)+H2O*H(5)+CO2*H(6)
& +SO2*H(6)+FUEL*HFUEL

C
C
C
C
DO 10 N=1,7
  WRITE(5,*) ' h('N,') =',H(N)
  CONTINUE
10
C
RETURN

```

END

```

C
C THIS PROGRAM TAKES THE AS RECEIVED ANALYSIS OF THE
C COAL AND CALCULATES THE PARR FORMULAS AND
C THE HEATING VALUE OF THE VM USING EQ. 12 FROM
C CHAPTER 5 OF B&W, STEAM
C
C AUTHOR: DAVID W. SHAW
C DATE: MARCH 14, 1988
C
C IMPLICIT REAL(A-Z)
C WRITE (5,100)
100 FORMAT(' ENTER THE % FIXED CARBON (PROXIMATE) ', $)
C READ (5,*)FC
C WRITE (5,120)
120 FORMAT(' ENTER THE % SULFUR ', $)
C READ (5,*)SULF
C WRITE (5,140)
140 FORMAT(' ENTER THE % MOISTURE ', $)
C READ (5,*)MOIST
C WRITE (5,160)
160 FORMAT(' ENTER THE % ASH ', $)
C READ (5,*)ASH
C WRITE (5,180)
180 FORMAT(' ENTER THE HIGHER HEATING VALUE BTU/LB ', $)
C READ (5,*)BTU
C VM=100-(FC+MOIST+ASH)
C
C CALCULATE THE PARR FORMULAS, EQ. 1-3
C
C FCDMMF=(FC-.15*SULF)*100/(100-(MOIST+1.08*ASH+.55*SULF))
C VMDMMF=100-FCDMMF
C BTUMMMF=(BTU-50*SULF)*100/(100-(1.08*ASH+1.01*SULF))
C
C CALCULATION OF "PURE COAL" VALUES, EQ. 9-12
C
C DENOM=100-(1.08*ASH+.2625*SULF+MOIST)
C VMPC=100*(VM-(.08*ASH+.2*SULF))/DENOM
C FCPC=100*(FC-.0625*SULF)/DENOM
C BTUPC=100*(BTU-26.2*SULF)/DENOM
C BTUVM=100*(BTUPC-(144.6*FCPC))/VMPC
C BTUVMSI=BTUVM*2.326*1000
C
C WRITE THE RESULTS TO THE SCREEN
C
C WRITE(5,1000)

```

```
1000 FORMAT(' THE RESULTS ARE: ',/)
      WRITE(5,1020)VMPC
1020 FORMAT(' "PURE COAL" VM ',F10.5,' %')
      WRITE(5,1040)FCPC
1040 FORMAT(' "PURE COAL" FC ',F10.5,' %')
      WRITE(5,1060)BTUPC
1060 FORMAT(' "PURE COAL" HEATING VALUE ',F10.1,' BTU/LB')
      WRITE(5,1080)BTUVM,BTUVMSI
1080 FORMAT(' VM HEATING VALUE ',F10.1,' BTU/LB ',E10.4,' J/KG')
      WRITE(5,1100)FCDMMF
1100 FORMAT(' FC (DRY, MM FREE) ',F10.5,' %')
      WRITE(5,1120)VMDMMF
1120 FORMAT(' VM (DRY, MM FREE) ',F10.5,' %')
      WRITE(5,1140)BTUMMMF
1140 FORMAT(' HEATING VALUE (MOIST, MM FREE) ',F10.1,' BTU/LB')
C
C
C
      STOP
      END
```

```

C THIS PROGRAM CALCULATES THE STOICHIOMETRIC MASS
C RATIO FOR VOLATILES FROM A GIVEN COAL, USING
C THE ULTIMATE AND PROXIMATE ANALYSES ON AN
C AS RECEIVED BASIS
C
C AUTHOR: D.W. SHAW
C DATE : MAY 9, 1988
C
C WRITE(5,*)' ENTER THE PROPERTIES ON AS RECEIVED BASIS'
C WRITE(5,*)' PROXIMATE ANALYSIS'
C WRITE(5,*)'
C WRITE(5,*)' FIXED CARBON = '
C READ(5,*)FC
C WRITE(5,*)' VM = '
C READ(5,*)VM
C WRITE(5,*)' ASH = '
C READ(5,*)ASH
C WRITE(5,*)' MOISTURE = '
C READ(5,*)RMOIST
C WRITE(5,*)'
C WRITE(5,*)' ULTIMATE ANALYSIS'
C WRITE(5,*)'
C WRITE(5,*)' HYDROGEN'
C READ(5,*)H
C WRITE(5,*)' CARBON = '
C READ(5,*)C
C WRITE(5,*)' OXYGEN = '
C READ(5,*)O
C WRITE(5,*)' NITROGEN = '
C READ(5,*)RN
C WRITE(5,*)' SULFUR = '
C READ(5,*)S
C
C
C CONVERT TO DRY BASIS
C
C DRYCO=VM+ASH+FC
C WRITE(5,*)' DRYCO = ',DRYCO
C VM=100*VM/DRYCO
C SAVE=ASH
C ASH=100*ASH/DRYCO
C FC=100*FC/DRYCO
C
C CONVERT ULTIMATE ANALYSIS

```

```

C
  PERCH=2*1.008/(2*1.008+15.999)
  PERCO=15.999/(2*1.008+15.999)
  WRITE(5,*) PERCH = ',PERCH,' PERCO = ',PERCO
  H=H-RMOIST*PERCH
  O=O-RMOIST*PERCO
  WRITE(5,*) H = ',H,' O = ',O
  DRYCO=H+C+O+RN+S+SAVE
  WRITE(5,*) DRYCO = ',DRYCO
  H=100*H/DRYCO
  C=100*C/DRYCO
  O=100*O/DRYCO
  RN=100*RN/DRYCO
  S=100*S/DRYCO
  ASH=100*SAVE/DRYCO

C
C  CALCULATE VM PROPERTIES
C
  DENOM=C-FC+H+O+RN+.5*S
  C=(C-FC)/DENOM
  H=H/DENOM
  O=O/DENOM
  RN=RN/DENOM
  S=.5*S/DENOM

C
C  CONVERT TO MOLES
C
  C=C/12.011
  H=H/1.008
  O=O/15.999
  RN=RN/14.007
  S=S/32.06

C
C  NORMALIZE ON CARBON
C
  H=H/C
  O=O/C
  RN=RN/C
  S=S/C
  C=1.0

C
C
C
  WRITE(5,*) CARBON IS ',C
  WRITE(5,*) HYDROGEN IS ',H
  WRITE(5,*) OXYGEN IS ',O

```

```
WRITE(5,*)' NITROGEN IS ',RN
WRITE(5,*)' SULFUR IS ',S
C
C  NOW CALCULATE STOICH. MASS RATIO
C
AIR=C+H/4+S-O/2
AIRMASS=AIR*(2*15.999+3.76*2*14.007)
FUELMASS=C*12.011+H*1.008+O*15.999+RN*14.007+S*32.06
SMRATIO=AIRMASS/FUELMASS
WRITE(5,*)' STOICH MASS RATIO = ',SMRATIO
C
C
STOP
END
```

**CALCULATES STABLE TEMPERATURE FOR GIVEN KINETICS AT
FIXED MASS FLOW RATE AND STOICHIOMETRY
(WILL BE MODIFIED TO DETECT LIMITS BY VARYING
MASS FLOW RATE AT FIXED STOICHIOMETRY)**

**JANUARY 5, 1988 CHANGED TO SI UNITS, CORRECT ERROR IN
UNITS OF CPC (*1000)**

**FEBRUARY 1, 1988 MODIFIED TO INCLUDE DECREASED HEAT
RELEASE FOR RICH MIXTURES WHERE NOT
ALL CARBON GOES TO CO2, BUT SOME
GOES TO CO**

**MARCH 31, 1988 MODIFIED TO INCLUDE ACTUAL ENTHALPY
OF THE MIXTURE IN THE REACTOR.
HEAT LOSS IS NOW BASED ON THE MIXTURE
WHICH RESULTS FROM A REACTION WHICH
WHICH GIVES OG AT TEMPERATURE T.**

CHARACTER*10 NAME1,FILE1

CCCCCCCC

G IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR WATER

```
READ(1,*)AFSM,HF
```



```

CLOSE(UNIT=1)
C  WRITE(5,*) A = 'A,' B = 'B,' D = 'D
C  WRITE(5,*) EE = 'EE,' F = 'F,' G = 'G
C  WRITE(5,*) AFSM;' AFSM,' HF = 'HF
  QG=.1
C
C                                     A=1.0
C                                     B=1.8
  VC=5.149E-5
  T0=700.
  TA=298.
  TW=500.
C  HF=3.5E7
C  AFSM=6.9
  HA=0.0
  RCON=1.98
  RHO0=1.1774
C
C  VC - COMBUSTOR VOLUME IN CUBIC METERS
C  T0 - INITIAL GAS MIXTURE TEMPERATURE - K
C  TA - AMBIENT TEMP - K
C  TW - REACTOR WALL TEMP - K - USED TO CALC. HEAT LOSS
C  HF - HEAT OF COMBUSTION OF FUEL - J/KG
C  AFSM - STOICH. MASS RATIO
C  HA - CONVECTIVE HEAT TRANSFER COEFF. - W/SQUARE METER
C  RCON - UNIVERSAL GAS CONSTANT
C  RHO0-DENSITY OF AIR (kg/cub meter) at 300 K
C
  WRITE(5,310)
310  FORMAT(' ENTER REACTION ORDERS : N,R ', $)
  READ(5,*)N,R
  WRITE(5,320)
320  FORMAT(' ENTER ACT. ENERGY - E (kcal/mol) ', $)
  READ(5,*)E
  E=E*1000
  WRITE(5,330)
330  FORMAT(' ENTER VELOCITY CONSTANT k0 (SI units) ', $)
  READ(5,*)k0
C  IF (N.EQ.2.)THEN
C    K0=K0*1.E-6
C  END IF
  WRITE(5,340)
340  FORMAT(' ENTER EQUIVALENCE RATIO - PHI ', $)
  READ(5,*)PHI
  WRITE(5,350)

```

```

350 FORMAT(' ENTER TOTAL MASS FLOW RATE (kg/s) ', $)
    READ(5,*)J
    WRITE(5,360)
360 FORMAT(' ENTER INITIAL TEMPERATURE RANGE ', $)
    READ(5,*)T1,T2
    T=T1
C
C   CALCULATE CONSTANT (AT FIXED PHI) PARAMETERS
C
800 CR0=1./(1+AFSM/PHI)
    COX0=(32./(32.+3.76*28.))/(1+PHI/AFSM)
    CN20=1-CR0-COX0
C
C   CALCULATE PARAMETERS WHICH CHANGE WITH TEMPERATURE
C
900 NN=0
    DO T=T1,T2,10.
        NN=NN+1
        RHO=RHO0*(TA/T)
C
C   CALCULATE HEAT GENERATION TERM
C
    RHS=RHO**N*VC*K0*CR0**(R-1)*COX0**(N-R)*EXP(-E/(RCON*T))/J
    CALL SOLVER (RHS,N,R,PHI,QG)
    IF((PHI.GT.1).AND.(QG.GE..001))THEN
        CALL HFADJUST(PHI,A,B,QG,HF,HFMOD)
        QG=QG*HFMOD/HF
    END IF
C   WRITE(5,*)' T = ',T,' EPS = ',QG
C
C   CALCULATE CONCENTRATIONS BASED ON QG
C
    CALL CONC(PHI,QG,A,B,D,EE,F,G,O2,FUEL,CO,CO2,H2O,N2,SO2)
C   WRITE (5,*) ' O2  = ',O2
C   WRITE (5,*) ' FUEL = ',FUEL
C   WRITE (5,*) ' CO   = ',CO
C   WRITE (5,*) ' CO2  = ',CO2
C   WRITE (5,*) ' H2O  = ',H2O
C   WRITE (5,*) ' N2   = ',N2
C   WRITE (5,*) ' SO2  = ',SO2
C
C   CALCULATE LOSSES
C
    DUMMY=0.0
    CALL ENTH(TA,T,O2,FUEL,CO,CO2,H2O,N2,SO2,ENTHAL)
    CALL

```

```

ENTH(TA,T0,DUMMY,CR0,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,ENT
H0)
    ENTHALPY=ENTHAL-ENTH0
    CPC=ENTHALPY
    CALL CP(T0,T,CPC)

C
C
CPC=cpc*1000.

    PSIC=CPC/(HF*CR0)
    QWALL=HA*(T-TW)
    PSIW=QWALL/(HF*CR0*J)
    ETA=PSIC+PSIW

C
C
    IF (PHI.GT.1.0)THEN
        END IF

    LHS=ETA*(1-ETA)**(-R)*(1-PHI*ETA)**(R-N)
    QL=ETA
    IF (N.EQ.1)THEN
        QG=RHS/(1+RHS)
    ELSE IF (N.EQ.2)THEN
        TEMP=PHI+1+1/RHS
        QG=(TEMP-SQRT(TEMP**2-4*PHI))/(2*PHI)
    END IF
    QL=RHS*((1-ETA)**R)*((1-PHI*ETA)**(N-R))
    ETAL(NN)=ETA
    ETAG(NN)=QG
    TG(NN)=T
    WRITE(5,*)rhs,QG,QL,T
    END DO

C
C
    PLOTTING SECTION
C
    XMIN=T1
    XMAX=T2
    YMIN=0
    YMAX=1.
    NTICKS=(T2-T1)/400
    WRITE(5,*)NTICKS
    READ(5,*)JUNK
    YES_NO=FALSE.
    CALL OP_START
    CALL OP_BDR(YES_NO)
    CALL OP_TICKS(O,O)
    CALL OP_AX(XMIN,XMAX,NTICKS,4,YMIN,YMAX,5,4)
    CALL OP_PTS(TG,ETAG,NN,1,1)
    CALL OP_PTS(TG,ETAL,NN,1,1)

```

```

CALL QP_PAUSE
CALL QP_CLEAR
CALL QP_END
WRITE(5,999)
999  FORMAT(' ENTER 999 FOR NEW MASS FLOW RATE',/,
@' 9999 FOR NEW STOICHIOMETRY',/,
@' 9998 TO EXIT', $)
1000 FORMAT(' ENTER NEW VALUE OF T ', $)
READ (5,*)T
IF(T.EQ.999)THEN
WRITE(5,950)
950  FORMAT(' ENTER NEW VALUE OF MASS FLOW RATE (kg/s) ', $)
READ(5,*)J
C   WRITE(5,1000)
C   READ(5,*)T
END IF
IF(T.EQ.9999)THEN
WRITE(5,960)
960  FORMAT(' ENTER NEW EQUIVALENCE RATIO ', $)
READ(5,*)PHI
WRITE(5,950)
READ(5,*)J
C   WRITE(5,1000)
C   READ(5,*)T
goto 800
END IF
IF (T.EQ.9998) GOTO 2000
GOTO 900
C
C
C
2000  STOP
END
C
C
C
C
SUBROUTINE CP(T0,T,CPC)
IMPLICIT REAL(A-Z)
THETA=T/100.
THETA0=T0/100.
H=THETA
H0=THETA0
CPO2=37.432*(H-H0)+.020102*(H**2.5-H0**2.5)/2.5+
%178.57*(H**-.5-H0**-.5)/.5-236.88*(H**-1-H0**-1)
CPN2=39.060*(H-H0)+2*512.79*(H**-.5-H0**-.5)-

```

```

%1072.7*(H**-1.-H0**-1.)+.5*820.4*(H**-2-H0**-2)
CPC=CPO2/4.76+CPN2*3.76/4.76
CPC=100.*CPC/28.9
RETURN
END
C
C
SUBROUTINE SOLVER (RHS,N,R,PHI,ETAG)
IMPLICIT REAL(A-Z)
ETAT=QG
100 TEST=ETAT/((1-ETAT)**R*(1-PHI*ETAT)**(N-R))
DELTA = TEST-RHS
C WRITE(5,*)RHS,TEST,DELTA,ETAT
IF(ABS(DELTA).GT.0.005)THEN
ETAT = ETAT-0.05*DELTA*(1-ETAT)**R*(1-PHI*ETAT)**(N-R)
IF(ETAT.GE.1.0)ETAT=.99
GOTO 100
END IF
ETAG=ETAT
RETURN
END
C
SUBROUTINE HFADJUST(PHI,A,B,ETAG,HF,HFMOD)
IMPLICIT REAL(A-Z)
C
C THIS SUBROUTINE ADJUSTS HF FOR INCOMPLETE COMBUSTION
C IN RICH REGION, BASED ON ASSUMPTION THAT
C ALL HYDROGEN GOES TO WATER, BUT CARBON GOES
C TO CO AND CO2 UNTIL ALL OXYGEN IS CONSUMED
C
C HF FOR CO IN J/KG
C FUEL IS C(A)H(B)
C
HFCO=1.0107E7
VAR1=A+B/4.
Y=1
EPS=ETAG
C WRITE(5,*)EPS,PHI
DENOM=VAR1*(1-EPS)*32+PHI*(1-EPS)*(12*A+B)+12*A*PHI*EPS+
@B*PHI*EPS+3.76*28*VAR1
CO2=32*VAR1*(1-EPS)/DENOM
CFUEL=PHI*(1-EPS)*(12*A+B)/DENOM
CCO2=44*(2*VAR1*EPS-A*PHI*EPS-.5*B*PHI*EPS)/DENOM
CCO=28*(2*A*PHI*EPS+.5*B*PHI*EPS-2*VAR1*EPS)/DENOM
CSUM=CCO+CCO2
C WRITE(5,*)CO2,CFUEL,CCO2,CCO,CSUM

```

```

      HFMOD=(CCO2/CSUM)*HF+(CCO/CSUM)*(HF-HFCO)
C    WRITE(5,*)HF,HFCO,HFMOD
      RETURN
      END
C
C
C
      SUBROUTINE CONC(PHI,EPS,A,B,D,E,F,G,O2,FUEL,CO,CO2,
&H2O,N2,SO2)
      IMPLICIT REAL(A-Z)
C
C    CALCULATES MASS CONCENTRATIONS IN REACTOR BASED ON
C    GIVEN EFFICIENCY AND STOICHIOMETRY
C
      IF (PHI.GT.1)THEN
        Y=1
      ELSE
        Y=PHI
      END IF
C
C    CALCULATE CONVENIENT GROUPS
C
      GR1=A+B/4-D/2+F
      GR2=1-EPS*Y
      GR3=PHI*(1-EPS)
      GR4=PHI*EPS*D
      GR5=A*PHI*EPS
      GR6=B*PHI*EPS/2
      GR7=EPS*PHI*G
C
C    MASSES OF EACH COMPONENT
C
      O2=(GR1*GR2)*31.998
C    WRITE(5,*) GR3='GR3,' A='A,' B='B,' D='D
C    WRITE(5,*) E='E,' F='F,' G='G
      FUEL=GR3*(12.011*A+1.008*B+15.999*D+14.007*E+32.06*F
&+18.015*G)
      CO=(2*GR5+GR6+2*F*eps*phi-2*GR1*EPS*Y-GR4)*28.01
      CO2=(2*GR1*EPS*Y+GR4-GR5-GR6-2*F*eps*phi)*44.009
C    IF(CO2.LE.0)CO2=0.0
      H2O=(GR6+EPS*PHI*G)*18.015
      N2=(3.76*GR1+phi*eps*E/2)*28.014
      SO2=F*64.058*eps*phi
C    write(5,*) O2 = ',O2,' FUEL = ',FUEL,' CO = ',CO
C    WRITE(5,*) CO2=',CO2,' H2O=',H2O
C    WRITE(5,*) N2 = ',N2,' SO2=',SO2

```

```

C
C DENOMINATOR
C
DENOM=O2+FUEL+CO+CO2+H2O+N2+SO2
C
C MASS FRACTIONS
C
O2=O2/DENOM
FUEL=FUEL/DENOM
CO=CO/DENOM
CO2=CO2/DENOM
H2O=H2O/DENOM
N2=N2/DENOM
SO2=SO2/DENOM
C
RETURN
END
C
C
C
SUBROUTINE ENTH(T10,T20,O2,FUEL,CO,CO2,H2O,N2,SO2,ENTHAL)
C
C      This subroutine calculates the enthalpy of      C
C      several gases. The enthalpy of each gas is de- C
C      noted below :      C
C      h(1): enthalpy of nitrogen.      C
C      h(2): enthalpy of oxygen.      C
C      h(3): enthalpy of hydrogen.      C
C      h(4): enthalpy of carbon-monoxide.      C
C      h(5): enthalpy of water.      C
C      h(6): enthalpy of carbon-dioxide.      C
C      h(7): enthalpy of nitrogen-dioxide.      C
C
C      Where enthalpy is obtained by integrating      C
C      formulas for specific heat from T1 to T2      C
C      (source of polynomials, VanWylen and Sonntag C
C
C      IMPLICIT REAL(A-Z)
C      REAL H(10),MW(10)
C      REAL T,T1,T2,A,B,C,D,E
C      REAL F,G,H,I,Q,P,R,S
C      DATA MW/28.014,31.998,2.016,28.01,18.015,44.009,46.005,0,0,0/
C      T1=T10/100
C      T2=T20/100
C
C      Calculate differences of powers of temperature

```

C

```

T = T2-T1
A = ((1/T2**.5)-(1/T1**.5))
B = (1/T2-1/T1)
C = ((1/T2**2.)-(1/T1**2.))
D = (T2**2.5-T1**2.5)
E = LOG(T2/T1)
F = (T2**1.75-T1**1.75)
G = (T2**.5-T1**.5)
H1 = (T2**1.25-T1**1.25)
Q = (T2**1.5-T1**1.5)
P = (T2**2.-T1**2.)
R = (T2**3.-T1**3.)
S = (T2**.25-T1**.25)

```

C

C

C

CALCULATE ENTHALPIES IN KJ/KMOL

```

H(1)=100*((39.06*T)+(1025.58*A)-(1072.7*B)+(410.2*C))
H(2)=100*((37.432*T)+(.0080408*D)+(357.14*A)-(236.88*B))
H(3)=100*((56.505*T)-(2810.96*S)+(1165.0*E)+(1121.4*A))
H(4)=100*((69.145*T)-(.4026457*F)-(401.54*G)+(707.04*S))
H(5)=100*((143.05*T)-(146.832*H1)+(55.1673*Q)-(1.84945*P))
H(6)=100*((-3.7357*T)+(20.3527*Q)-(2.0517*P)+(.008066*R))
H(7)=100*((46.045*T)+(432.2*G)-(1454.64*S)-(232.55*B))

```

C

C

C

CONVERT TO J/KG

```

DO I=1,7
  H(I)=H(I)*1000./MW(I)
END DO

```

C

C

C

C

C

CALCULATE ENTHALPY OF THE FUEL
(ACTUALLY THE VALUE FOR C3H8, BUT ALL
ARE FAIRLY CLOSE ON A MASS BASIS)

```

HFUEL=-4.042*T+15.23*P-.5237*R+.00793*(T2**4.-T1**4.)
HFUEL=100.*HFUEL*1000./44.097

```

C

C

C

CALCULATE TOTAL ENTHALPY PER KG OF MIXTURE

```

ENTHAL=N2*H(1)+O2*H(2)+CO*H(4)+H2O*H(5)+CO2*H(6)
& +SO2*H(6)+FUEL*HFUEL

```

C

C

C

DO 10 N=1,7


```
C      WRITE(5,*) ' h(',N,') =',H(N)
10    CONTINUE
C
      RETURN
END
```

119

COLIM.FOR

CALCULATES STABLE TEMPERATURE FOR GIVEN KINETICS AT
FIXED MASS FLOW RATE AND STOICHIOMETRY USING
CO LIMITED COMBUSTION
(WILL BE MODIFIED TO DETECT LIMITS BY VARYING
MASS FLOW RATE AT FIXED STOICHIOMETRY)

DECEMBER 18, 1987 D SHAW

JANUARY 5, 1988 CHANGED TO SI UNITS, CORRECT ERROR
IN UNITS OF CPC (*1000)

JANUARY 28, 1988 ADDED GENERAL SOLVER TO FIND ETAG

FEBRUARY 1, 1988 MODIFIED TO INCLUDE DECREASED HEAT
RELEASE FOR RICH MIXTURES WHERE NOT
ALL CARBON GOES TO CO₂, BUT SOME
GOES TO CO

MARCH 31, 1988 MODIFIED TO INCLUDE ACTUAL ENTHALPY
OF THE MIXTURE IN THE REACTOR.

HEAT LOSS IS NOW BASED ON THE MIXTURE
WHICH RESULTS FROM A REACTION WHICH
WHICH GIVES QG AT TEMPERATURE T.

JULY 21-25, 1988 MODIFIED TO CONSIDER COMBUSTION AS
INFINITELY FAST CONVERSION TO CO AND WATER,
WITH CO BURNING AS THE RATE LIMITING STEP.

JULY 29, 1988 MODIFIED TO ACCOUNT FOR UNBURNED FUEL
BY COMBUSTION DELAY TIME AND RTD.

IMPLICIT REAL(A-Z)

INTEGER NN,NTICKS

LOGICAL EXIST

LOGICAL YES_NO

DIMENSION LGR(100),TINV(100),xlst(2),ylst(2),ETAG(500),ETAL(500)

DIMENSION TG(500)

CHARACTER*10 NAME1,FILE1

A IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR CARBON

B IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR HYDROGEN

D IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR OXYGEN

EE IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR NITROGEN

F IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR SULFUR

G IS THE SUBSCRIPT GIVING EQUIVALENT MOLECULAR WATER

95 WRITE(5,100)

100 FORMAT(' ENTER NAME OF DATA FILE WHICH
&INCLUDES FUEL PROPERTIES ', \$)

```

      READ(5,110)FILE1
110  FORMAT(A10)
      OPEN (UNIT=1,NAME=FILE1,STATUS='OLD',ERR=95)
      READ(1,*)A,B,D
      READ(1,*)EE,F,G
      READ(1,*)AFSM,HF
      CLOSE(UNIT=1)
      QG=.1
      VC=5.149E-5
      T0=700.
      TA=298.
      TW=500.
C    HF=3.5E7
C    AFSM=6.9
      HA=0.0
      RCON=1.98
      RHO0=1.1774
C
C    VC - COMBUSTOR VOLUME IN CUBIC METERS
C    T0 - INITIAL GAS MIXTURE TEMPERATURE - K
C    TA - AMBIENT TEMP - K
C    TW - REACTOR WALL TEMP - K - USED TO CALC. HEAT LOSS
C    HF - HEAT OF COMBUSTION OF FUEL - J/KG
C    AFSM - STOICH. MASS RATIO
C    HA - CONVECTIVE HEAT TRANSFER COEFF. - W/SQUARE METER
C    RCON - UNIVERSAL GAS CONSTANT
C    RHO0-DENSITY OF AIR (kg/cub meter) at 300 K
C
C
C    CO KINETICS
C
      N=1.75
      R=1.00
      GAMMA=0.5
      K0=2.2177E11
      E=40.0
      E=E*1000.
C
      WRITE(5,340)
340  FORMAT(' ENTER EQUIVALENCE RATIO - PHI ',)$)
      READ(5,*)PHI
      WRITE(5,350)
350  FORMAT(' ENTER TOTAL MASS FLOW RATE (kg/s) ',)$)
      READ(5,*)J
      WRITE(5,360)

```

```

360 FORMAT(' ENTER INITIAL TEMPERATURE RANGE ', $)
    READ(5,*)T1,T2
    T=T1
    WRITE(*)' ENTER DELAY TIME FOR COMBUSTION OF FUEL'
    READ(5,*)TDEL
C
C  CALCULATE CONSTANT (AT FIXED PHI) PARAMETERS
C    -CONCENTRATIONS IN THE FEED STREAM
C
800  CR0=1./(1+AFSM/PHI)
    COX0=(32./(32.+3.76*28.))/(1+PHI/AFSM)
    CN20=1-CR0-COX0
C
C  CALCULATE HEAT RELEASE AND NEW CONCENTRATIONS AFTER
CONVERSION
C    TO CO AND WATER.
C
    CFUEL0=CR0
    COX0SAV=COX0
    PHISAV=PHI
C
C  CALCULATE PARAMETERS WHICH CHANGE WITH TEMPERATURE
C
900  NN=0
    DO T=T1,T2,10.
    NN=NN+1
    RHO=RHO0*(TA/T)
    TAUS=RHO*VC/J
    PHI=PHISAV
    CR0=CFUEL0
    COX0=COX0SAV
    CALL PCOMB(A,B,D,EE,F,G,PHI,CR0,COX0,CH2O0,
&QGPC,ETAPC,DELTQG,QGMAX,AFSM,J,HF,TDEL,TAUS,ETAF)
C    WRITE(5,*)ETAPC,QGPC,QGMAX,DELTQG
C
C  CALCULATE HEAT GENERATION TERM
C
    RHS=RHO**N*VC*K0*CR0**(R-1)*COX0**(N-R-GAMMA)
    &*CH2O0**GAMMA*EXP(-E/(RCON*T))/J
    CALL SOLVER (RHS,N,R,PHI,QG)
    ETACO=QG
    QGTOT=QGPC+ETACO*DELTQG
    ETAGG=QGTOT/QGMAX
C    IF((PHI.GT.1).AND.(QG.GE..001))THEN
C        CALL HFADJUST(PHI,A,B,QG,HF,HFMOD)
C        QG=QG*HFMOD/HF

```

```

C   END IF
C   WRITE(5,*) ' T = ',T,' EPS = ',QG
C
C   CALCULATE CONCENTRATIONS BASED ON QG
C
C   CALL CONCMOD(PHI,ETACO,A,B,D,EE,F,G,O2,FUEL,CO,CO2,H2O,N2,
&   SO2,ETAF)
C   WRITE (5,*) ' O2 = ',O2
C   WRITE (5,*) ' FUEL = ',FUEL
C   WRITE (5,*) ' CO = ',CO
C   WRITE (5,*) ' CO2 = ',CO2
C   WRITE (5,*) ' H2O = ',H2O
C   WRITE (5,*) ' N2 = ',N2
C   WRITE (5,*) ' SO2 = ',SO2
C
C   CALCULATE LOSSES
C
C   DUMMY=0.0
C   CALL ENTH(TA,T,O2,FUEL,CO,CO2,H2O,N2,SO2,ENTHAL)
C   CALL
C   ENTH(TA,T0,DUMMY,CFUEL0,DUMMY,DUMMY,DUMMY,DUMMY,DUMMY,E
NTH0)
C   ENTHALPY=ENTHAL-ENTH0
C   CPC=ENTHALPY
C   PSIC=CPC/(HF*CFUEL0)
C   WRITE(8,*)CPC,PSIC,PHISAV
C   QWALL=HA*(T-TW)
C   PSIW=QWALL/(HF*CFUEL0*I)
C   ETA=PSIC+PSIW
C   LHS=ETA*(1-ETA)**(-R)*(1-PHI*ETA)**(R-N)
C   QL=ETA
C   ETAL(NN)=ETA
C   ETAG(NN)=ETAGG
C   TG(NN)=T
C   WRITE(5,*)rhs,ETAGG,QL,T
C   END DO
C
C   PLOTTING SECTION
C
C   XMIN=T1
C   XMAX=T2
C   YMIN=0
C   YMAX=1.
C   NTICKS=(T2-T1)/400
C   WRITE(5,*)NTICKS
C   READ(5,*)JUNK

```

```

YES_NO=.FALSE.
CALL QP_START
CALL QP_BDR(YES_NO)
CALL QP_TICKS(O,O)
CALL QP_AX(XMIN,XMAX,NTICKS,4,YMIN,YMAX,5,4)
CALL QP_PTS(TG,ETAG,NN,1,1)
CALL QP_PTS(TG,ETAL,NN,1,1)
CALL QP_PAUSE
CALL QP_CLEAR
CALL QP_END
WRITE(5,999)
999  FORMAT(' ENTER 999 FOR NEW MASS FLOW RATE',/,
@' 9999 FOR NEW STOICHIOMETRY',
@' 9998 TO EXIT',)$)
1000 FORMAT(' ENTER NEW VALUE OF T ',)$)
    READ(5,*)T
    IF(T.EQ.999)THEN
        WRITE(5,950)
950  FORMAT(' ENTER NEW VALUE OF MASS FLOW RATE (kg/s) ',)$)
        READ(5,*)J
C    WRITE(5,1000)
C    READ(5,*)T
    END IF
    IF(T.EQ.9999)THEN
        WRITE(5,960)
960  FORMAT(' ENTER NEW EQUIVALENCE RATIO ',)$)
        READ(5,*)PHI
        WRITE(5,950)
        READ(5,*)J
C    WRITE(5,1000)
C    READ(5,*)T
        goto 800
    END IF
    IF (T.EQ.9998) GOTO 2000
    GOTO 900
C
C
C
2000  STOP
    END
C
C
C
C
SUBROUTINE SOLVER (RHS,N,R,PHI,ETAG)
IMPLICIT REAL(A-Z)

```

```

      ICT=0
      ETAT=QG
100  TEST=ETAT/((1-ETAT)**R*(1-PHI*ETAT)**(N-R))
      DELTA = TEST-RHS
      ICT=ICT+1
      IF (ICT.GT.100)THEN
        WRITE(*)' DID NOT CONVERGE AFTER 100 ITERATIONS'
        GOTO 200
      END IF
C    WRITE(5,*)RHS,TEST,DELTA,ETAT
      IF(ABS(DELTA).GT.0.005)THEN
        ETAT = ETAT-0.05*DELTA*(1-ETAT)**R*(1-PHI*ETAT)**(N-R)
        IF(ETAT.GE.1.0)ETAT=.99
        GOTO 100
      END IF
200  ETAG=ETAT
      RETURN
      END
C
      SUBROUTINE HFADJUST(PHI,A,B,ETAG,HF,HFMOD)
      IMPLICIT REAL(A-Z)
C
C    THIS SUBROUTINE ADJUSTS HF FOR INCOMPLETE COMBUSTION
C    IN RICH REGION, BASED ON ASSUMPTION THAT
C    ALL HYDROGEN GOES TO WATER, BUT CARBON GOES
C    TO CO AND CO2 UNTIL ALL OXYGEN IS CONSUMED
C
C    HF FOR CO IN J/KG
C    FUEL IS C(A)H(B)
C
      HFCO=1.0107E7
      VAR1=A+B/4.
      Y=1
      EPS=ETAG
C    WRITE(5,*)EPS,PHI
      DENOM=VAR1*(1-EPS)*32+PHI*(1-EPS)*(12*A+B)+12*A*PHI*EPS+
      @B*PHI*EPS+3.76*28*VAR1
      CO2=32*VAR1*(1-EPS)/DENOM
      CFUEL=PHI*(1-EPS)*(12*A+B)/DENOM
      CCO2=44*(2*VAR1*EPS-A*PHI*EPS-.5*B*PHI*EPS)/DENOM
      CCO=28*(2*A*PHI*EPS+.5*B*PHI*EPS-2*VAR1*EPS)/DENOM
      CSUM=CCO+CCO2
C    WRITE(5,*)CO2,CFUEL,CCO2,CCO,CSUM
      HFMOD=(CCO2/CSUM)*HF+(CCO/CSUM)*(HF-HFCO)
C    WRITE(5,*)HF,HFCO,HFMOD
      RETURN

```

```

END
C
C
C
SUBROUTINE CONCMOD(PHI, EPS, A, B, D, E, F, G, O2, FUEL, CO, CO2,
&H2O, N2, SO2, ETAF)
IMPLICIT REAL(A-Z)
C
C  CALCULATES MASS CONCENTRATIONS IN REACTOR BASED ON
C  GIVEN EFFICIENCY AND STOICHIOMETRY
C
IF (PHI.GT.1) THEN
  Y=1
ELSE
  Y=PHI
END IF
C
C  CALCULATE CONVENIENT GROUPS
C
MWFUEL=12.011*A+1.008*B+15.999*D+14.007*EE+32.*F+18.015*G
GR1=A+B/4-D/2+F
GR2=(1-EPS)*A*PHI*ETAF
GR3=PHI*A*EPS*ETAF
GR4=PHI*(G+B/2)*ETAF
GR5=.5*PHI*E*ETAF+3.76*GR1
GR6=GR1+.5*D*PHI*ETAF-.5*GR2-.25*B*PHI*ETAF-PHI*F*ETAF-GR3
GR7=EPS*PHI*G
C
C  MASSES OF EACH COMPONENT
C
O2=GR6*31.998
C  WRITE(5,*) GR3= ',GR3,' A= ',A,' B= ',B,' D= ',D
C  WRITE(5,*) E= ',E,' F= ',F,' G= ',G
FUEL= (1-ETAF)*PHI*MWFUEL
CO=GR2*28.01
CO2=GR3*44.009
c  IF(CO2.LE.0) CO2=0.0
H2O=GR4*18.015
N2=GR5*28.014
SO2=F*64.058*phi*ETAF
C  write(5,*) O2 = ',O2,' FUEL = ',FUEL,' CO = ',CO
C  WRITE(5,*) CO2= ',CO2,' H2O= ',H2O
C  WRITE(5,*) N2 = ',N2,' SO2= ',SO2
C
C  DENOMINATOR
C

```



```

DENOM=O2+FUEL+CO+CO2+H2O+N2+SO2
C
C  MASS FRACTIONS
C
O2=O2/DENOM
FUEL=FUEL/DENOM
CO=CO/DENOM
CO2=CO2/DENOM
H2O=H2O/DENOM
N2=N2/DENOM
SO2=SO2/DENOM
C
RETURN
END
C
C
C
SUBROUTINE ENTH(T10,T20,O2,FUEL,CO,CO2,H2O,N2,SO2,ENTHAL)
c
c      This subroutine calculates the enthalpy of      c
c      several gases. The enthalpy of each gas is de- c
c      noted below :      c
c      h(1): enthalpy of nitrogen.      c
c      h(2): enthalpy of oxygen.      c
c      h(3): enthalpy of hydrogen.      c
c      h(4): enthalpy of carbon-monoxide.      c
c      h(5): enthalpy of water.      c
c      h(6): enthalpy of carbon-dioxide.      c
c      h(7): enthalpy of nitrogen-dioxide.      c
c
c      Where enthalpy is obtained by integrating      c
c      formulas for specific heat from T1 to T2      c
c      (source of polynomials, VanWylen and Sonntag c
c
IMPLICIT REAL(A-Z)
REAL H(10),MW(10)
REAL T,T1,T2,A,B,C,D,E
REAL F,G,H1,Q,P,R,S
DATA MW/28.014,31.998,2.016,28.01,18.015,44.009,46.005,0,0,0/
T1=T10/100
T2=T20/100
C
C  Calculate differences of powers of temperature
C
T = T2-T1
A = ((1/T2**.5)-(1/T1**.5))

```

```

      B = (1/T2-1/T1)
      C = ((1/T2**2.)-(1/T1**2.))
      D = (T2**2.5-T1**2.5)
      E = LOG(T2/T1)
      F = (T2**1.75-T1**1.75)
      G = (T2**1.5-T1**1.5)
      H1 = (T2**1.25-T1**1.25)
      Q = (T2**1.5-T1**1.5)
      P = (T2**2.-T1**2.)
      R = (T2**3.-T1**3.)
      S = (T2**.25-T1**.25)

C
C  CALCULATE ENTHALPIES IN KJ/KMOL
C
      H(1)=100*((39.06*T)+(1025.58*A)-(1072.7*B)+(410.2*C))
      H(2)=100*((37.432*T)+(.0080408*D)+(357.14*A)-(236.88*B))
      H(3)=100*((56.505*T)-(2810.96*S)+(1165.0*E)+(1121.4*A))
      H(4)=100*((69.145*T)-(.4026457*F)-(401.54*G)+(707.04*S))
      H(5)=100*((143.05*T)-(146.832*H1)+(55.1673*Q)-(1.84945*P))
      H(6)=100*((-3.7357*T)+(20.3527*Q)-(2.0517*P)+(.008066*R))
      H(7)=100*((46.045*T)+(432.2*G)-(1454.64*S)-(232.55*B))

C
C  CONVERT TO J/KG
C
      DO I=1,7
        H(I)=H(I)*1000./MW(I)
      END DO

C
C  CALCULATE ENTHALPY OF THE FUEL
C  (ACTUALLY THE VALUE FOR C3H8, BUT ALL
C  ARE FAIRLY CLOSE ON A MASS BASIS)
C
      HFUEL=-4.042*T+15.23*P-.5237*R+.00793*(T2**4.-T1**4.)
      HFUEL=100.*HFUEL*1000./44.097

C
C  CALCULATE TOTAL ENTHALPY PER KG OF MIXTURE
C
      ENTHAL=N2*H(1)+O2*H(2)+CO*H(4)+H2O*H(5)+CO2*H(6)
      & +SO2*H(6)+FUEL*HFUEL

C
C
C
      DO 10 N=1,7
        WRITE(5,*)  h('N,') =,H(N)
      10 CONTINUE
C

```

```

      RETURN
      END
C
C
C
      SUBROUTINE PCOMB(A,B,D,E,F,G,PHI,CR0,COX0,CH2O0,QGPC,ETAPC,
&   DELTQG,QGMAX,AFSM,J,HF,TDEL,TAUS,ETAF)
C
C   THIS SUBROUTINE CALCULATES CONCENTRATIONS AND HEAT
C   RELEASE
C   AFTER CONVERSION OF FUEL TO CO AND WATER.
C
C   IMPLICIT REAL(A-Z)
C
C   CALCULATE MAXIMUM HEAT RELEASE POSSIBLE (100% EFFICIENCY)
C
      HFCO=1.0103E7
      QGMAX=HF*J*CR0
      MWFUEL=12.011*A+1.008*B+15.999*D+14.007*EE+32.*F+18.015*G
      MWCO=12.011+15.999
      DELTQG=A*MWCO*J*CR0*HFCO/MWFUEL
C
C   CALCULATE AMOUNT OF FUEL CONSUMED USING DELAY TIME AND
C   RESIDENCE TIME DISTRIBUTION
C
      ETAF=EXP(-TDEL/TAUS)
      QGPC=ETAF*(QGMAX-DELTQG)
      ETAPC=QGPC/QGMAX
C
C   CALCULATE CONVENIENT GROUPS
C
      GR1=A+B/4-D/2+F
      GR2=A*PHI*ETAF
      GR3=PHI*A*EPS
      GR4=PHI*(G+B/2)*ETAF
      GR5=.5*PHI*E*ETAF+3.76*GR1
      GR6=GR1+.5*D*PHI*ETAF-.5*GR2-.25*B*PHI*ETAF-PHI*F*ETAF
      GR7=EPS*PHI*G
C
C   MASSES OF EACH COMPONENT
C
      O2=GR6*31.998
C   WRITE(5,*)' GR3= ',GR3,' A= ',A,' B= ',B,' D= ',D
C   WRITE(5,*)' E= ',E,' F= ',F,' G= ',G
      FUEL=(1-ETAF)*PHI*MWFUEL
      CO=GR2*28.01

```

```

      CO2=0.0
c    IF(CO2.LE.0)CO2=0.0
      H2O=GR4*18.015
      N2=GR5*28.014
      SO2=F*64.058*phi*ETAF
C    write(5,*)' O2 = ',O2,' FUEL = ',FUEL,' CO = ',CO
C    WRITE(5,*)' CO2= ',CO2,' H2O= ',H2O
C    WRITE(5,*)' N2 = ',N2,' SO2= ',SO2
C
C    DENOMINATOR
C
C    DENOM=O2+FUEL+CO+CO2+H2O+N2+SO2
C
C    MASS FRACTIONS
C
      O2=O2/DENOM
      FUEL=FUEL/DENOM
      CO=CO/DENOM
      CO2=CO2/DENOM
      H2O=H2O/DENOM
      N2=N2/DENOM
      SO2=SO2/DENOM
      CR0=CO
      COX0=O2
      CH2O0=H2O
      AFSMNEW=0.5*(31.998+3.76*28.014)/(12.011+15.999)
      O2FSM=0.5*31.998/(12.011+15.999)
      PHI=O2FSM/(O2/CO)
C
C    RETURN
C    END
C

```

APPENDIX B
Experimental Kinetic Data

Fuel: Coal "C"

Date: 4/25/88

$\dot{m}_{\text{fuel}}$ (g/s)	Air Flow (scfm)	T(K) Uncorrected	T(K) Corrected	Q_{water} (J/s)
0.566	3.902	989.8	1031.5	501.1
0.476	3.902	1026.0	1074.6	685.1
0.461	3.902	1030.2	1079.5	701.8
0.452	3.902	1057.4	1111.3	721.2
0.442	3.902	1037.1	1087.8	748.4
0.425	3.902	1059.4	1113.8	771.5
0.394	3.902	1064.8	1120.3	774.0
0.365	3.902	1066.6	1122.4	781.8
0.329	3.902	1079.5	1138.1	794.6
0.323	3.902	1105.0	1169.5	797.3
0.305	3.902	1108.6	1174.0	788.2
0.308	3.902	1127.7	1197.7	741.8
0.303	3.902	1119.4	1187.4	743.1

Fuel mass flow rate corrected for mass lost to walls.

Fuel: Martin Lake

Date: 12/21/87

$\dot{m}_{\text{fuel}}$ (g/s)	Air Flow (scfm)	T(K) Uncorrected	T(K) Corrected	$\dot{Q}_{\text{water}}$ (J/s)
0.837	3.070	1070.5	1136.1	424.5
0.923	3.070	1061.1	1124.3	447.2
0.893	3.070	1062.9	1126.6	460.5
0.821	4.070	1212.3	1300.7	449.2
0.804	4.070	1217.1	1306.9	437.8
0.785	4.070	1222.9	1314.4	429.8
0.674	4.570	1316.3	1427.0	278.2
0.672	4.570	1312.6	1422.2	283.5
0.670	4.570	1314.6	1424.8	283.5
0.667	5.070	1334.0	1443.1	286.2
0.662	5.070	1330.0	1437.9	284.8
0.659	5.070	1311.3	1414.6	291.4
0.654	5.070	1307.1	1409.1	283.5
0.624	5.070	1223.2	1304.1	244.9
0.611	3.570	1191.5	1281.2	242.3

Fuel mass flow rate corrected for mass lost to walls.

Fuel: Pittsburgh #8

Date: 11/27/87

$\dot{m}_{\text{fuel}}$ (g/s)	Air Flow (scfm)	T(K) Uncorrected	T(K) Corrected	$\dot{Q}_{\text{water}}$ (J/s)
0.609	3.902	1169.3	1249.0	381.8
0.603	3.902	1186.3	1270.6	396.0
0.576	3.902	1203.0	1291.1	477.4
0.545	3.902	1207.6	1297.0	506.9
0.534	3.902	1213.3	1304.4	514.7
0.522	3.902	1229.4	1325.2	526.3
0.501	3.902	1233.1	1330.1	535.3
0.482	3.902	1236.7	1334.8	537.9
0.456	3.902	1257.9	1361.6	544.3
0.435	3.902	1272.5	1380.9	544.2
0.408	3.902	1289.4	1418.5	540.4
0.376	3.902	1298.4	1414.4	550.7
0.350	3.902	1335.9	1463.1	548.2

Fuel mass flow rate corrected for mass lost to walls.

Fuel: Methane

Date: 8/17/88

$\dot{m}_{\text{fuel}}$ (g/s)	Air Flow (scfm)	T(K) Uncorrected	T(K) Corrected	$\dot{Q}_{\text{water}}$ (J/s)
0.153	5.800	1089.0	1137.7	1238.9
0.231	8.000	1455.0	1567.0	875.1
0.154	4.749	1079.7	1131.8	1552.3
0.154	5.498	1162.7	1226.8	1384.0
0.154	5.998	1197.5	1265.7	1387.8
0.154	6.498	1269.0	1348.9	1412.2
0.154	6.911	1302.0	1385.8	1439.2
0.154	7.426	1329.6	1416.3	1444.4
0.154	7.921	1401.2	1501.3	1436.8
0.212	6.180	1346.1	1446.8	1018.2
0.212	6.930	1404.7	1513.4	1084.5
0.212	7.426	1442.5	1556.2	1089.6
0.212	7.921	1402.7	1503.2	1251.9
0.212	8.416	1435.6	1539.8	1278.8
0.212	8.911	1444.0	1546.7	1337.4
0.212	9.406	1465.8	1570.6	1394.9

Fuel: Propane

Date: 8/20/88

$\dot{m}_{\text{fuel}}$ (g/s)	Air Flow (scfm)	T(K) Uncorrected	T(K) Corrected	$\dot{Q}_{\text{water}}$ (J/s)
0.512	11.850	1350.0	1419.6	1766.1
0.512	12.840	1362.1	1430.5	1835.0
0.512	13.830	1389.8	1460.2	1878.6
0.512	14.780	1409.3	1480.4	1872.0
0.512	15.760	1413.4	1482.4	1879.8
0.512	16.750	1421.8	1489.7	1892.5
0.512	17.730	1418.1	1484.0	1872.0
0.512	18.720	1440.7	1507.2	1939.8
0.512	19.700	1462.6	1530.5	1949.9
0.512	20.690	1500.5	1572.6	1922.9
0.512	21.670	1518.7	1591.8	1910.4
0.512	22.660	1531.9	1605.1	1896.3
0.509	10.510	1126.0	1165.0	1302.9
0.509	14.340	1308.0	1363.9	1317.6
0.509	16.160	1322.1	1376.2	1181.1
0.509	20.160	1491.9	1563.7	1215.5
0.509	23.770	1609.6	1692.7	1239.7
0.518	10.000	1102.5	1139.4	1479.8
0.518	15.000	1407.4	1477.5	1593.7
0.518	20.000	1499.9	1573.4	1609.0
0.368	9.850	1238.2	1295.4	2147.2
0.368	10.850	1293.3	1356.9	2101.4
0.368	11.820	1311.6	1375.2	2107.7
0.368	12.810	1373.8	1444.5	2172.6
0.368	13.790	1371.7	1438.9	2190.5
0.368	14.780	1395.5	1464.1	1918.4
0.368	15.760	1413.8	1482.9	1880.2
0.368	16.750	1430.1	1499.4	1884.9
0.368	17.730	1438.2	1506.5	1851.9
0.714	15.000	1139.5	1172.5	1136.1
0.714	20.000	1503.2	1577.3	1274.2