COMBUSTION OF VOLATILE MATTER DURING THE INITIAL STAGES
OF COAL COMBUSTION

Final Technical Report

August 1990

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For
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Stanford University
Stanford, California

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Prepared for
THE UNITED STATES DEPARTMENT OF ENERGY

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Much of the research presented here relies heavily on the work of other students. In particular, our implementation of the radiant coal flow reactor is almost identical to that of John Chen, who designed and developed the reactor in our lab. The measurements by gas chromatography were made possible by Sunghwan Cho, who developed our measurement techniques. And the very complex heat transfer in the radiant coal flow reactor was modeled by Chun Lau.

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1. Background and Motivation

1.1 Introduction

Much effort has been devoted to understanding the combustion of pulverized coal. For several decades, researchers have studied coal devolatilization, and documented the effects of temperature, residence time, heating rate, pressure, and ambient gas composition on the yields of volatile products (see the reviews by Gavallas,¹ Howard,² and Solomon³). Researchers have observed the combustion of volatiles in a diffusion flame surrounding the particle, and the subsequent burnout of the char (see the review by Smith⁴). Char combustion rates and mechanisms have been evaluated (see Smith⁴). The nitrogen chemistry of pulverized coal combustion has been studied, and the effects of combustor configurations and operating parameters on the formation of NO_x and other pollutants have been considered (see the review by Wendt⁵). Many of these areas of coal combustion have been researched in detail. But many of the phenomena of coal combustion remain almost entirely unexplored.

For instance, many researchers⁵ have observed that during devolatilization in an oxidizing environment, a soot cloud and a flame form in the vicinity of a bituminous coal particle. Soot is not observed for the combustion of lignites and anthracites. Researchers propose that the soot is a product of pyrolytic cracking of the volatiles as they escape from the devolatilizing particle, while the flame indicates the combustion of the volatiles. Little more is known about these pyrolysis and combustion processes, beyond the observations that they occur.

However, we can speculate from these observations about the mechanisms of secondary pyrolysis and combustion of the volatiles, and the impact which they have on pulverized coal combustion. It is well known from devolatilization studies that volatiles are composed of light gas hydrocarbons, CO , CO_2 , H_2O , light oils, and high molecular weight tars. Furthermore, bituminous coals produce large amounts of tars, while lignites and anthracites produce less tars. The presence of soot during the combustion of bituminous coals must reflect extensive pyrolytic cracking of the tars. The extent of cracking should have a strong bearing on the pyrolysis products formed, and should thus control the amounts of the reactive species entering the enveloping flame. The reactive species will in turn define the heat release and thickness of the flame, and will have some influence on the destruction and formation of soot. Heat release from the flame will heat the volatiles escaping from the particle,

and accelerate their secondary pyrolysis. The soot formed during pyrolysis will probably incorporate some of the nitrogen in the tars, and the destruction of tars and soot in the flame may have a strong bearing on the formation of NO_x . It is evident from these conjectures that the processes of pyrolysis and combustion of the volatiles are closely linked.

Volatiles chemistry is also linked by heat transfer and mass transport to the other phenomena of coal combustion. The heat release from the volatiles flame will enhance the heating rate and temperature of the coal particles, and increase devolatilization rates. Devolatilization, in turn, creates the volatiles which are pyrolysed and burned in the flame. None of these phenomena can be neglected to fully understand the combustion of a pulverized coal particle.

Volatiles pyrolysis both contributes to and draws upon a variety of research topics. Since coal devolatilization provides the reactant materials for secondary pyrolysis, it is necessary to develop a good understanding of the materials formed by devolatilization, in order to establish the origin of the products of secondary pyrolysis. However, a knowledge of the effects of secondary pyrolysis of the volatiles can also help to clarify the products of devolatilization, since many of the product yields reported from devolatilization experiments are inadvertently skewed by uncontrolled secondary chemistry.

Because of the complex nature of the tars in volatiles, researchers have attempted to develop a better understanding of the pyrolysis of tars by studying model compounds. By comparing the results of many model compound studies, it may be possible to develop generalizations about the pyrolysis of model compounds and establish mechanisms for the pyrolysis of tars. Observations of product yields from tar pyrolysis, in turn, may suggest generalizations applicable to model compounds. Product yields from volatiles pyrolysis are also of direct interest in gasification and liquefaction studies, in which coal is pyrolysed to form synthetic petroleum.

As with volatiles pyrolysis, the combustion of volatiles is closely connected with several research topics. Volatiles contain many reactive, or fuel, species, and thus the study of the combustion of volatiles actually contributes to research on the combustion of multiple-fuel mixtures. The aromatic oils and tars in volatiles link their combustion with the study of the combustion of aromatic fuels. Since gasolines have recently been made more aromatic to reduce pre-ignition knock, this topic is important to research involving internal combustion engines. Finally, research with

coal dust suspensions has shown that volatiles combustion is important to the prevention of coal dust explosions.⁶

The contributions of each topic to a better understanding of volatiles chemistry, and the questions raised by each topic are explained below.

1.2 Devolatilization of Coal

Coal devolatilization provides the feed stock, or reactant materials, for volatiles pyrolysis and combustion. Many researchers have studied devolatilization, and much fundamental information has been established. Since these studies are the subject of several extensive reviews,^{1,2,3} we will not attempt a comprehensive review here, but will instead focus on the measured yields of the products of devolatilization.

The volatile products of devolatilization divide logically into gases and light oils, which can be detected by gas chromatography, and tars, which condense at room temperature, and tend to deposit on cold surfaces in batch experiments, or be trapped in filters in flow experiments.

Due to the ease with which tars are collected, there are many studies of the weight of tar produced during devolatilization (references 7 through 10 are a very small sample of these). Maximum tar yields vary widely with coal rank, with the lignites and anthracites on either end of the coal rank spectrum having the lowest yields.¹⁰ Bituminous coals in the middle of the rank spectrum typically lose 20 to 30 % of their weight as tar. Elemental analyses for tars indicate that they are enriched in hydrogen, with 20 to 100 % higher hydrogen contents than the parent coal.¹¹ Molecular weight distributions have also been determined for a few tars,^{7,12} and they show that the tars contain species with molecular weights from several hundred to a thousand g/mole, and that the average molecular weights of tars increase slightly with increasing pyrolysis temperature. Yields, elemental analyses, and molecular weight distributions are very useful in determining the specific heats of the tars and their heat release from combustion as discussed in Section 3.4. Elemental analyses also define the partitioning of the elements among the various volatile products.

But they do not provide chemical information about the tars. A handful of studies of the chemical structures of tars have been conducted with ¹³C nmr and ¹H nmr spectroscopy.^{7,12,13,14,15} These studies have determined several structural features of specific tars, such as their aromaticities,^{7,13} and the concentrations of phenolic hydroxyls.¹⁴ Measurements such as these are useful in determining the representative

tar decomposition reactions, and in predicting the products of tar pyrolysis. But the studies are not extensive, and not enough information is yet available to develop a representative chemical structure for tars. However, there are major studies of the chemical structures of coal liquefaction products,¹⁶ and the procedures from these studies might be emulated with devolatilization tars.

Measurements of gas and light oil yields have been reported by Bautista et al.,¹⁷ Suuberg,⁸ Freihaut et al.,¹¹ Howard,² and Xu and Tomita.¹⁰ The most extensive measurements were made by Xu and Tomita, who reported yields of C₁ through C₇ hydrocarbons (including CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, benzene, toluene, xylene, phenol, and cresol), and inorganic gases (H₂, CO₂, CO, and H₂O) for 17 coals from Australia and Japan (Figure 1.2.1). It should be noted that Xu and Tomita measured these yields in an apparatus which is observed to cause secondary pyrolysis (see the discussion in the following paragraphs), and that their maximum operating temperature of 1037 K should have caused extensive secondary pyrolysis (see Tables 1.2.1 and 1.2.2). However, these are the most extensive measurements that we are aware of which show the variations with coal rank of the yields of gases and light oils. As seen in Figure 1.2.1, the chief gaseous products are CO₂, H₂O, and CO. For the low rank lignites, these products account for a quarter of the original weight of the coal, while for the high rank anthracites their yields have decreased to about 2 % of the original weight. CH₄ accounts for 2 to 3 % of the weight, and its yield increases slightly with increasing coal rank. The H₂ yield remains at about 0.5 % of the original weight for the entire range of coals. The light oils, C₂ and C₃ hydrocarbons, and tars all show similar basic trends with coal rank, with their maximum yields occurring for bituminous coals. The light oil and C₂ and C₃ hydrocarbon yields comprise about 5 wt. %. Due to the large amounts of CO₂, CO, and H₂O produced, the gases and light oils have a much higher oxygen level than the original coal (about a factor of 2 higher), but their H/C ratio is about the same. Despite these high oxygen levels, the combustible fraction of the gases and light oils accounts for about 15 % of the original weight of bituminous coals, and is thus expected to contribute a significant portion of the heat release of combustion.

One difficulty in interpreting devolatilization experiments is determining the degree to which product yields have been skewed by undesired secondary pyrolysis. The extent of secondary pyrolysis depends greatly on the apparatus used. Reactors in which coal particles are entrained into a heated gas^{18,19,20} cause the most extensive secondary pyrolysis; as volatiles leave the particle surface, they decompose rapidly, making the collection and identification of primary pyrolysis products nearly impossible. Radiatively heated fixed beds of coal^{21,22} also tend to exhibit secondary

Figure 1.2.1. Effect of coal rank on yields of various devolatilization products; (a) gas including water, tar, and hydrocarbon liquids (HCL), and char; (b) oxygen-containing gases; (c) CH₄ and H₂; (d) C₂ and C₃ hydrocarbons; (e) benzene (B), toluene (T), xylene (X), phenol (P), creson (C); (f) tar (the small circles are yields reported from other sources).¹⁰

pyrolysis due to the preheating of the sweep gas as it flows over heated surfaces. But, radiatively heated beds generally create lower levels of secondary pyrolysis than entrained flow reactors, and they are often operated at temperatures below 900 K to avoid significant secondary reactions.^{21,22} This low temperature ceiling severely limits the study of devolatilization. The lowest levels of secondary pyrolysis are achieved in electrically heated coal beds, such as wire-grid heaters and Curie-point analysers.^{8,9,10,17} These reactors heat a small sample of coal wrapped in a metal foil or wire grid by passing an electric current through the metal. Very high heating rates are achieved in this way. However, even in electrically heated grids secondary pyrolysis can occur at the highest temperatures due to tar deposition on the electrically heated surfaces, or due to heating of the sweep gas as it passes through the wire grid and the coal bed.

Unwanted secondary pyrolysis in metal foil heater experiments can be very misleading, since these experiments are generally assumed to be free from secondary reactions. An example of this is the study of Xu and Tomita,²³ in which they claim to have minimized secondary pyrolysis, despite ample evidence of extensive secondary reactions. Table 1.2.1 shows their measured tar yields for several different lignite and bituminous coals as a function of pyrolysis temperature. In each case the tar has reached its maximum yield before ultimate weight loss is achieved, and in some cases the tar yield appears to decrease, as it would if gas phase tar decomposition were occurring. As tar yields decrease, the yields of H_2 , CH_4 , and CO (shown in Table 1.2.2) increase dramatically. Since several experimenters have observed that the major products of tar decomposition are H_2 , CH_4 , and CO ,^{24,25} the gas yields provide further evidence that the tars are decomposing. Of course, the variations in tar yield are small, and could probably be attributed to experimental error, but when the trends in the gas yields are also considered, the influence of secondary pyrolysis becomes apparent.

Table 1.2.1. Product yields (wt % daf) from pyrolysis of several lignite and bituminous coals, as measured by Xu and Tomita.²³

T(K)	Wt. loss	Tar yield	Wt. loss	Tar yield
Wandoan			Hunter Valley	
718	17	11	8	5
773	30	20	15	10
863	43	28	28	19
923	47	27	35	24
1037	52	28	38	22
1193	59	23	45	22
Liddell			Morwell	
718	8	5	28	15
773	16	11	38	22
863	30	21	48	26
923	36	23	52	26
1037	40	22	56	26
1193	45	21	63	26

Table 1.2.2. Product yields (wt % daf) from pyrolysis of Liddell coal, as measured by Xu and Tomita.²³

T(K)	H ₂	CH ₄	CO
718	0.0	0.1	0.2
773	0.0	0.3	0.3
863	0.1	1.5	0.8
923	0.2	2.8	1.5
1037	0.5	3.6	2.8
1193	1.3	5.5	5.3

1.3 Pyrolysis of Volatiles

As volatiles exit the surface of a coal particle, they are pyrolysed to soot, light oils, and gases. This pyrolysis step controls soot formation, and defines the fuel species which enter the volatile flame surrounding the particle during combustion.

Volatiles pyrolysis research is related to several practical applications, including coal combustion, gasification, and liquefaction. In the liquefaction studies, the volatiles are often pyrolysed at high pressures (10 to 50 atmospheres) under hydrogen to increase the yields of desirable light oils. The studies of volatiles pyrolysis motivated by combustion are of course conducted at atmospheric pressure in an inert gas.

Reviews have been written by Fynes et al.²⁶ and Furfari et al.²⁷ which detail the various approaches taken to the hydrolysis of volatiles and the yields achieved. The observed trends in yields from hydrolysis²⁸ have many similarities to the trends of the inert gas experiments discussed below. But the use of high pressure hydrogen has been shown to significantly increase the yields of CH₄ and light oils.^{2,8,17} And, hydrolysis consumes hydrogen, while pyrolysis in an inert gas produces hydrogen. Thus any application of hydrolysis results to research in coal combustion must somehow exclude the influence of high pressure hydrogen.

Most of the inert gas studies of volatiles pyrolysis have been conducted by three groups of researchers. Tyler and coworkers have pyrolysed a brown and 10 bituminous coals from America and Australia in a fluidized bed.^{13,14,24,29,30,31} Xu and Tomita have studied Liddell bituminous coal in a 2-stage reactor.^{21,25} And Serio et al. have implemented a 2-stage reactor to study the pyrolysis of a Pittsburgh bituminous coal.²²

Of these 3 groups, Tyler and coworkers have reported the most extensive characterizations of the products of secondary pyrolysis. They have measured total weight loss, tar yields, and light hydrocarbon gas yields,^{29,30} and have more recently reported yields of CO, CO₂, and the derivatives of 1-, 2-, 3-, and 4-ring aromatics (H₂ and H₂O yields were not reported).²⁴ They have also examined tars after secondary pyrolysis with ¹H nmr and ¹³C nmr spectroscopy.^{13,14,15} Their observed product yields are generally similar to those of other research groups.

Tyler and coworkers reported that extensive secondary pyrolysis caused the production of large amounts of CH₄, CO, benzene, and naphthalene.²⁴ The C₂ and C₃ hydrocarbons and alkyl substituted aromatic species were also produced at lower

temperatures, and then eliminated at higher temperatures. The yields of tars decreased with increasing temperature,^{29,30} presumably due to their conversion to soot and light gases. However, soot yields were not measured. Finally, ¹H nmr studies showed that the aromaticity of the tars increased with increasing temperature.¹³

Unfortunately, all of the pyrolysis experiments reported by Tyler and coworkers were conducted in a fluidized bed pyrolyser. Since the fluidized bed heats the coal particles with a hot gas, devolatilization of the particles and secondary pyrolysis of the volatiles occur simultaneously. Thus, it is impossible to separate the effects of these two processes on the reported yields. The residence time in the fluidized bed is also uncertain, due to the tortuosity of the flow paths through the bed. These ambiguities cause difficulty in differentiating the species formed by secondary pyrolysis from those formed during devolatilization, and in resolving the time dependence of the pyrolysis reactions.

Xu and Tomita avoided the problems associated with fluidized beds by implementing a two-stage reactor.²¹ A fixed bed of coal was devolatilized in the first stage of the reactor and an inert carrier gas swept the volatiles into the second stage, where they were pyrolysed (at temperatures from 675 to 1175 K and residence times from 1 to 7 seconds). Xu and Tomita measured the yields of light hydrocarbon gases, CO, CO₂, H₂, and light oils.²⁵ Most of their reported trends in yields had previously been observed by Tyler and coworkers. However, since Xu and Tomita clearly separated the processes of devolatilization and secondary pyrolysis, they were able to show that variations in the yields of light aliphatics which Tyler and coworkers had attributed to devolatilization were actually the result of secondary pyrolysis. They also reported yields of H₂ and H₂O, which showed the production of large amounts of H₂ during secondary pyrolysis. But they did not measure the yields of tars and soot; thus it is impossible to determine from their work to what extent tars were converted to soot and other products.

In contrast, Serio et al. reported measurements of tar conversion,²² but did not discuss yields of gas and light oil, beyond mentioning that significant cracking of gases and light oils was not observed. Nor did they measure the production of soot. Since their experiments were conducted with a two-stage reactor similar to that used by Xu and Tomita, which they operated over approximately the same temperature ranges and residence times (900 to 1200 K and 0.6 to 1.1 sec.), they should have observed significant changes in the yields of gases and light oils. Their measurements of over 50 % tar conversion at their maximum temperatures also indicate that large amounts of soot, gases, and light oils were produced.

Each group of researchers has added valuable information to our knowledge of volatiles pyrolysis. Tyler and coworkers have reported the yields of tars, and a number of gases and light oils from simultaneous devolatilization and secondary pyrolysis. Xu and Tomita have shown that many of the trends in yields which had been attributed to devolatilization were the result of secondary pyrolysis. And Serio et al. have shown that extensive tar decomposition occurred in the temperature range and residence times of these measurements. But all of the reported measurements were made at lower temperatures and longer residence times than are typical of coal combustion. No single study has yet unambiguously separated devolatilization and secondary pyrolysis, and measured the yields of all of the products from secondary pyrolysis, including soot.

1.4 Pyrolysis of Model Compounds

When applied in connection with coal volatiles, the term "model compound" generally refers to higher molecular weight hydrocarbons, especially aromatic species, which are representative of the compounds in light oils and tars. As mentioned above, volatiles also contain large amounts of hydrogen, carbon monoxide, and the smaller aliphatic hydrocarbons, but the chemistry of these species is fairly well understood, as witnessed by the large detailed reaction schemes compiled by Westbrook et al.³² and others. Little is known about the chemistry of the larger hydrocarbons.

Model compounds have been studied to determine the temperatures at which characteristic chemical structures in the compounds decompose, and their rates of decomposition. In principle, measurements with model compounds can be utilized to infer decomposition temperatures and rates for similar chemical structures in the light oils and tars. For instance, a thorough study of aliphatic side chains on benzene, naphthalene, anthracene, and larger aromatic ring structures might lead to a general rule which could be applied to predict the decomposition of side chains in tars.

While it should be possible in principle to understand the pyrolysis of tars and light oils by pyrolysing model compounds, the practical difficulties to this approach will be challenging. Of the model compounds discussed below, the largest has a molecular weight of 178 g/mole, while tar molecular weights range from 100 to 2000 g/mole. The possible chemical structures for this range of molecular weights must be very large, and can probably only be represented by a set of model compounds with a large range of molecular weights. Additional complications can be expected from the interaction of neighboring chemical structures. Furthermore, naphthalene (molecular

weight = 128 g/mole) and species larger than naphthalene are solids at room temperature, and it is not clear that the largest of these solid model compounds can be melted and evaporated without causing extensive reactions in their liquid phases (i.e. coking). From these two considerations, a complete understanding of tar pyrolysis based on model compounds appears to be a distant goal.

Nonetheless, research has already established several trends which are useful to a qualitative understanding of the decomposition of light oils and tars. Garcia and Huttinger³³ have observed large amounts of hydrogen from the pyrolysis of naphthalene at 1200 K for 20 seconds. (For other naphthalene pyrolysis experiments see Lahaye et al.³⁴) Similar H₂ yields have been reported by Cypres and Bettens³⁵ for the pyrolysis of phenanthrene and anthracene at 1200 K for several seconds. (Anthracene and phenanthrene pyrolysis have also been studied by Badger et al.^{36,37}) Both experimenters report observing 4- and higher-ring aromatics, and a charry, soot-like substance, which they suggest indicates that the aromatic compounds are condensing to form larger species with 4 and more aromatic rings. Cypres and Bettens and Garcia and Huttinger also observe small amounts of CH₄, and only trace amounts of other hydrocarbon gases. These observations indicate that ring rupture is occurring. Unfortunately, it is not clear from these experiments to what extent hydrocarbon gases are reincorporated into larger aromatic species and soot. However, it is interesting to note that H₂, CH₄, and soot are major products from the pyrolysis of model compounds.

Frazer and Anderson³⁸ have observed that aromatic species are effective promoters of soot when used as additives during C₂H₂ pyrolysis. They have determined that the effectiveness of the aromatic compounds increases in this order: benzene < naphthalene < toluene < alpha-methylnaphthalene < anthracene < beta-methylantracene. Though the order is basically correlated with molecular weight, toluene is more effective than naphthalene. This suggests the importance of aliphatic side chains to soot growth. Emdee et al.³⁹ have also emphasized side chains in their oxidation study of o-xylene. To explain observed yields of naphthalene and indene, they have proposed a reaction mechanism in which aliphatic groups are added to the methyl side chains of o-xylene to form new rings. This recognition of the effectiveness of aromatic species, and especially large aromatic species with aliphatic side chains, in promoting soot is especially relevant to the decomposition mechanisms of tar.

Hausmann et al.⁴⁰ have observed that 20 to 30 % of the nitrogen released in coal volatiles is incorporated in soot. The nitrogen in soot could originate in either

gas-phase volatiles (especially HCN) or tar. Cerny et al.⁴¹ have observed that the nitrogen in tars is bound in carbazoles and their benzo derivatives. The relative rates of decomposition and condensation to soot of these multi-ring, nonaromatic chemical structures could be important to determining the mechanisms by which nitrogen is incorporated in soot.

Garcia and Huttinger³³ have observed large amounts of CO from the pyrolysis of naphthol. Further evidence is offered for the phenolic origin of CO by the ¹H nmr measurements of Collin et al.,¹⁴ who observed that as tars are pyrolysed, the concentrations of hydroxyl protons decrease. Of course phenolic hydroxyls are not the only possible source of CO. Schlosberg et al.^{42,43} have observed CO from the pyrolysis of dibenzyl ether, while Cronauer et al. have produced CO by pyrolysing aldehydes.⁴⁴ CO is also an important product of secondary pyrolysis.

Bruinsma et al.⁴⁵ have observed that aliphatic side chains on benzene decay at pyrolysis temperatures between 800 and 1200 K (at residence times of 5 seconds), and that the decomposition temperature decreases with increasing chain length. They also have observed that this process is a source of alkenes and alkynes. Another source of light aliphatics has been discovered by Cypres and Bettens,³⁵ who have noted that perhydrophenanthrene undergoes ring rupture at temperatures from 1000 to 1200 K (and a residence time of 2.5 seconds), to produce large amounts of CH₄, C₂H₄, and other C₂ and C₃ hydrocarbons. Surprisingly, they have found that large hydrocarbon yields are unique to the pyrolysis of perhydrophenanthrene, and that other hydrogenated 3-ring structures tend to undergo dehydrogenation to form stable anthracene and phenanthrene, and condense to soot.

All of the studies mentioned above display the common drawback of having been performed at lower temperatures and longer residence times than is characteristic of coal combustion. At the higher temperatures of coal combustion, the competing pyrolysis processes will occur much faster, and different processes may be favored. While these studies focus on certain chemical structures in the model compounds, there is very little information about the concentrations of chemical structures in tars and light oils.

However, taken together these studies clearly emphasize the importance of soot formation during the pyrolysis of large aromatic hydrocarbons. They also indicate that the soot formation processes can produce large amounts of H₂, CO, and lesser amounts of light hydrocarbons. As observed in Section 1.3, H₂, CO, and soot are major products from the secondary pyrolysis of coal volatiles. Finally, it is apparent

that fuel nitrogen is incorporated into soot, and this incorporation could prove very important to the nitrogen chemistry of the coal. Studies of model compounds containing nitrogen might lead to a better understanding of the relation between nitrogen chemistry and soot formation.

1.5 Combustion of Volatiles

Volatiles combustion governs many of the important physical and chemical phenomena which occur during pulverized coal combustion. The heat release from the combustion of volatiles has a strong influence on the heating rate of the coal particles, and consequently, on devolatilization. The tars released during devolatilization form soot, and this soot either survives, or is consumed in, the volatile flame. And the volatiles burn in the initial stage of the pulverized coal flame, and thus govern the ignitability and flammability of the particles.

One study has been published which focuses on volatiles combustion.⁴⁶ But it offers little insight on the burning of volatiles. Most of the useful information which can be found on this subject has appeared in studies of the combustion of particles,^{18,47,48} and in research on coal dust explosions.^{6,49,50} Some predictions may also be made based on measurements of devolatilization yields.

For instance, Howard² has assumed heating values for tar and light hydrocarbons (other than ethylene and methane) of 10.9 and 8.9 kcal/g, respectively, to estimate the heat release for combustion of the volatiles from a Lignite coal (as measured by Suuberg⁸). The total heat release of the original coal was calculated from the formula of Mott and Spooner.⁵¹ Howard estimates that the light gas volatiles contribute about 15 % of the total heat release from combustion of the coal, while the tars contribute 8 %. Since the volatiles from a lignite coal have relatively small amounts of tar, oils, and light hydrocarbons, we can anticipate that the heat release for bituminous volatiles will be even higher than these estimates. Clearly volatiles combustion contributes significantly to the heat release of the coal. However, it should be noted that these estimates also assume that the volatiles are burned completely.

But there is no reason to believe that the volatiles are completely burned in the volatile flame which surrounds the coal particle. Timothy et al.⁵² estimate that for free stream oxygen concentrations less than 100 %, the soot formed from tar will not be completely consumed in the volatile flame. They suggest that the soot which

survives the flame is swept into the soot contrails which have been observed in particle combustion experiments.

The volatiles are both released and burned during the initial stages of coal combustion. Chars burn more slowly in the combustion gases heated by the volatiles. From these observations, it seems reasonable that the ignitability of the volatiles must govern the ignition of the flame. This has been established in coal dust suspensions,^{6,49,50} where Hertzberg et al.⁶ have observed that the flammability limits of the dusts are inversely proportional to their volatile contents.

Since only volatiles burn in the initial stage of the flame, it also seems reasonable to assume that their combustion governs the stoichiometry of that initial stage. While this conjecture may not have any intuitive appeal for the complex recirculating flames encountered in practical applications, it is at least sensible for the laminar, premixed flames of coal dust studied by Milne and Beachey.^{47,48} These researchers detected the peak burning velocities in their flames for very fuel-rich mixtures, whereas peak burning velocities should ordinarily occur for mixtures with equivalence ratios near 1. However, when their equivalence ratios were recalculated with only the volatiles included as fuel, their peak velocities did correlate with an equivalence ratio near 1. Thus the stoichiometry of the flat flame was completely determined by the volatiles.

Each of the combustion studies discussed in this section adds useful information to our knowledge of volatiles combustion. Howard has indicated that the volatiles contribute significantly to the heat release of the coal. (Howard's estimates were for a Lignite; higher rank coals can be expected to release an even higher portion of their heat by combustion of the volatiles.) Timothy et al. have shown that soot can survive the volatile flame. And Hertzberg et al. and others have demonstrated that volatiles are important to the ignition and flammability of coal. All of these studies emphasize the importance of a more fundamental understanding of volatiles combustion.

1.6 Oxidation of Model Compounds

As with the pyrolysis of model compounds, oxidation studies have been conducted to establish the rates at which heavier aromatic compounds are destroyed, and to determine the new species generated; it is then hoped that inferences can be drawn from this information about the oxidation of tars and light oils. It should also

be mentioned that much of the model compound research to date has been motivated by an interest in the combustion of petroleum products such as gasoline.

Brezinsky⁵³ has written a review of research on the high temperature oxidation of aromatics. Most of the research which he discusses is conducted at very dilute fuel concentrations, to reduce the ambiguities associated with heat and mass transfer. The research is also limited to the oxidation of benzene and its derivatives. Brezinsky reports that the derivatives of benzene first lose their side chains by oxidation, and are reduced to benzene, or a phenyl radical. The aromatic ring is then broken by the direct attack of oxygen. While these studies are important to understanding the mechanism by which aromatic rings are oxidized, the very dilute fuel concentrations of the experiments suppress the mechanisms by which PAH and soot are formed.

To study soot formation in an oxidizing environment, researchers have conducted experiments with flames. Toquan et al.⁵⁴ have compared soot formation rates in a natural gas diffusion flame, and in the diffusion flame formed by a coal derived liquid, which was 30 % aromatic by weight. They have observed that the coal liquid flame produces several orders of magnitude more soot than the natural gas flame, and that a fraction of the aromatic species in the fuel go directly to soot, without decomposing. Bittner and Howard⁵⁵ have also observed the formation of soot in a premixed flame of benzene. They suggest that the benzene provides a structure upon which aliphatics are added to form PAH, which eventually condenses to soot. From these studies, it is apparent that aromatics are important promoters of soot formation in oxidizing systems, as well as pyrolysing systems.

1.7 Flame Studies of Multiple-Fuel Mixtures

Volatiles are complex multiple-fuel mixtures. They contain tars, light oils, H_2 , CO, CH_4 , C_2H_2 , and several other light alkanes and alkenes. For the experiments discussed in subsequent chapters, tars and light oils have been removed, so that only the combustion of light gases is considered. Even so, the mixture of light gas fuels is very complex in comparison to fuel mixtures which have been examined before.

The most complex light gas mixtures for which we can find published results are the ternary-fuel mixtures of Levy et al.⁵⁶ They have considered combinations of H_2 , CO, and CH_4 or natural gas. The substitution of natural gas for CH_4 was found to have no measurable effect on combustion. Levy et al. report measurements for 20 different mixtures, all of which had an equivalence ratio of 1.

The fuel proportions of many of the mixtures considered by Levy et al. were carefully set, so that these mixtures would have the same products and flame temperatures (though they had widely varying levels of CO, CH₄, and H₂). Levy et al. adjusted the fuel concentrations in this way to test the importance of flame temperature to the burning velocity of a mixture. Since burning velocities and flame temperatures are known to be closely correlated, it seems reasonable to hypothesize that burning velocities might be predicted by simply calculating a mixture's flame temperature. Unfortunately, though, Levy et al. observed that mixtures with the same flame temperatures had widely varying burning velocities.

Yu et al.⁵⁷ studied binary fuel mixtures of CH₄-air and C₃H₈-air with small amounts of added H₂. They report that the burning velocity for these binary-fuel mixtures is linearly proportional to the amount of added H₂. As they point out, this result is not surprising for the small concentrations of H₂ considered, and could not be expected to hold for larger H₂ additions.

Finally, Iijima and Takeno⁵⁸ and Milton and Keck⁵⁹ studied hydrocarbon-hydrogen mixtures in combustion bombs. Their mixtures were essentially the same as those studied by Yu et al., but the use of the bomb allowed the extension of the measurements to account for variations in reactant temperature and pressure. The measurements of Milton and Keck were limited to equivalence ratios of 1, and while Iijima and Takeno did study off-stoichiometric mixtures, neither group offers any valuable insights into multi-fuel combustion.

As evidenced by the research of Levy et al., the combustion of multiple-fuel mixtures is a very complex subject. While researchers have made important contributions to this subject, the predictive capability required for the combustion of coal volatiles will probably require many more experiments.

1.8 Motivation

The devolatilization of coal and the secondary chemistry of the volatiles are closely interrelated by their associated heat transfer and mass transport. Devolatilization rates and yields depend strongly on the heating rate and final temperature of the coal. Heating rates and particle temperatures are, in turn, influenced by volatiles combustion. And mass transport and secondary pyrolysis of the volatiles control the reactants entering the volatile flame. In order to develop a full understanding of the combustion of a pulverized coal particle, it is necessary to understand the secondary chemistry of the volatiles.

These questions may be asked about the secondary chemistry of volatiles:

1. To what extent are volatiles pyrolysed as they are transported from the surface of the particle to the volatile flame, and what are the concentrations of the species which finally enter the flame?
2. What are the relative rates of the condensation of tars to soot and tar decomposition to form gases and light oils?
3. To what extent are nitrogen species in the tars incorporated in soot, and what fraction of tar nitrogen is released to the gas phase?
4. What fractions of the gases and light oils become bound in the soot?
5. What are the mechanisms by which tars burn in the volatile flame, and to what extent is soot formation from tar favored in the presence of oxygen?
6. What fraction of the soot survives the volatile flame?
7. What is the heat release of the volatile flame and the distance of the flame from the particle?

The processes of soot formation and combustion, and the mechanisms by which nitrogen is incorporated into soot may play an important role in the chemistry of NO_x formation. The fate of the soot in the volatile flame may also be an important factor in particulate emissions from coal combustion. The extent of secondary pyrolysis and the species formed may govern the ignitability and flammability of the coal particles. And the heat release from the volatile flame and the distance of the flame from the particle may well influence the devolatilization time, and the heat generated in the initial stage of the pulverized coal flame.

The answers to the questions above will also be of interest to workers in other areas of research. For instance, the secondary pyrolysis of volatiles is very similar to volatiles cracking, as it occurs in the gasification of coal; thus the reported yields from volatiles pyrolysis should prove useful to coal gasification research. The combustion of tars is essentially the combustion of high molecular weight aromatic fuels; aromatic fuel combustion is being studied in connection with the recent increases in the aromaticity of the gasolines burned in automobiles. Researchers have found that the flammability limits of coal dust suspensions are correlated with the volatile contents of coals; thus the study of volatiles combustion may prove useful to research on the prevention of coal dust explosions. Finally, the volatiles are

composed of many fuels, and their combustion adds valuable information about the combustion of multiple-fuel mixtures.

1.9 Scope of the Study

Both the secondary pyrolysis and combustion of the volatiles from a bituminous coal will be studied. Devolatilization and secondary pyrolysis experiments will be conducted in a novel flow reactor (to be constructed for this study) in which secondary pyrolysis of the volatiles occurs after devolatilization is complete. This allows unambiguous measurements of the yields from both processes. Measurements will be made for reactor temperatures from 1500 to 1700 K, and a nominal residence time of 200 msec. These conditions are typical of coal combustion. Yields of tar, soot, H_2 , CO, CH_4 , and C_2 and C_3 hydrocarbons will be determined as a function of reactor temperature. These measurements will indicate the extent of tar conversion, and the major products formed from secondary pyrolysis of the volatiles.

The actual temperature histories of the particles and gas will not be measured for this study. The yields will instead be reported as a function of the temperature of the reactor. The instrumentation for temperature measurements will be developed during future studies. The yields of CO_2 , H_2O , and the light oils will also not be measured, though these species are expected to be present in significant amounts. CO_2 and H_2O measurement capabilities will be developed for future studies.

Combustion studies will be conducted in a constant volume bomb, which will be designed and constructed for this study. Tar and soot will be removed before introducing the volatiles to the bomb, so that only the combustion of the light gas volatiles will be considered. The burning velocities of light gas volatiles will be determined both as functions of mixture stoichiometry and the temperature at which the volatiles are pyrolysed.

The burning velocities of the light gas volatiles may be converted to overall reaction rates, though these computations will not be completed for this study. These reaction rates will allow approximation of heat release rates, and the distance of the volatile flame from the particle. Of course the accuracy of these approximations will depend on the impact of the removal of tar and soot.

2. Experimental Facility

2.1 Introduction

A schematic diagram of the experimental facility is shown in Figure 2.1.1. The radiant coal flow reactor at the left of the figure consists mainly of a feeder, which entrains coal particles in a gas flow, and a radiant furnace, which heats the particle suspension as it passes downward. By properly controlling the flowrates of both coal and carrier gas (as discussed in Section 2.3.6), the extents of primary devolatilization and secondary pyrolysis can be independently adjusted. The constant volume combustion bomb is shown to the right in Figure 2.1.1. The bomb is a spherical pressure vessel, into which premixed gases are introduced, and then ignited to create a flame, which propagates from the ignition point to the vessel walls. The bomb is well suited for studying premixed flames, and for determining the products of combustion. Volatiles are transported from the reactor to the bomb through a small copper tube.

This chapter discusses the design and construction of the constant volume bomb and the radiant flow reactor in detail. The effects of variations in the important parameters of these facilities are also discussed.

2.2 The Constant Volume Combustion Bomb

2.2.1 Background

We can measure the heat release, sooting thresholds, and laminar burning velocities of the volatiles with the bomb. The heat release and sooting thresholds are determined by analysing the products of combustion (see Section 3.4.4), and are of course useful to modeling heat transfer and soot formation during the combustion of coal. Laminar burning velocities are determined by studying the propagation of the flame. As mentioned earlier, laminar burning velocities are directly applicable to the study of coal dust mixtures. But burning velocities can also be converted to global reaction rates. Though the volatile flame surrounding the particle is probably strongly influenced by diffusion, the thickness of that flame and its distance from the particle are controlled by these global rates.^{52,60} While burning velocity measurements will not provide detailed information about the chemical mechanisms governing volatiles combustion, they could prove useful in approximate models of the combustion of a pulverized particle.

Figure 2.1.1 Schematic representation of the constant volume combustion bomb, the radiant coal pyrolyser, and the method for transporting volatiles.

The constant volume bomb has several advantages which recommend it over other combustion experiments. Among these, a small gas sample is required instead of a continuous flow, as with burner methods. Thus, the batch mode of the bomb requires the devolatilization of less coal than steady flow experiments. Also, gases are mixed by measuring their partial pressures, which provides more accurate mixture concentrations than flow measurements with rotameters. The combustion products remain in the bomb, and are easily collected for subsequent analysis. And the reactants in the bomb are compressed isentropically during combustion, so that their temperatures and pressures rise as the mixture burns; in a single experiment, burning velocities are determined for a range of temperatures and pressures.

Constant volume bombs have been used since the 1920's for the measurement of burning velocities, and they remain a popular technique. A sample of the fuels for which burning velocities have been measured is given in Table 2.2.1.1. The higher molecular weight fuels have been examined more recently in connection with internal combustion engine studies. As discussed in Section 1.7, binary fuel mixtures of hydrogen and methane have also been combusted in bombs.

Table 2.2.1.1. Burning velocity measurements by bomb technique.

Species	Reference	Species	Reference
methane	61-64	propane	63, 64, 66
acetylene	64, 65	ethylene	64, 67
methanol	68, 69	butane	70
2-methylpentane	67	n-heptane	63, 71
benzene	71	toluene	67
iso-octane	63, 69, 71	indolene	69, 72
hydrogen	61	carbon monoxide	73
ozone	74		

Of course the constant volume bomb is only one of many different methods for measuring burning velocities. These include flame propagation in soap bubbles, cylindrical and slot bunsen burners, open tubes, counterflow flames, and flat flames. Andrews and Bradley⁷⁵ have compared the reported measurements from these different methods for the maximum burning velocity of methane in air at 298 K and 1 atm. If the collected measurements for each technique are averaged, then bombs give 35.8 cm/sec (7 sources, standard deviation = $s = 1.95$ cm/sec); burners, 37.7 cm/sec

(8 sources, $s = 2.1$ cm/sec); tubes, 36.4 cm/sec (3 sources, $s = 2.2$ cm/sec); soap bubbles, 34 cm/sec (1 source); flame kernels, 36.5 cm/sec (1 source); and, nozzle burners with schlieren and particle tracking, 44.8 cm/sec (2 sources, $s = 0.07$ cm/sec). The measurements from these techniques vary by over 30 %.

Andrews and Bradley⁷⁵ have developed correction factors to reduce the variation between measurements. They have compensated for errors inherent in the techniques, such as the effects of wall quenching and flame thickness. They conclude that the maximum burning velocity of methane in air is 45 ± 2 cm/sec. More recently, Dixon-Lewis and Islam⁷⁶ have corrected burning velocity measurements for the effects of lateral flow expansion, and report that the maximum burning velocity is 39 or 40 cm/sec. Finally, Yu et al.⁵⁷ have determined burning velocities in an adiabatic, counterflow flame, and extrapolated to zero flame stretch to find that the maximum burning velocity is about 42 cm/sec. The scatter in the corrected values is only slightly smaller than the scatter in the original measurements. Of course, a comparison such as this should also consider the chronology and "quality" of the measurements, but the scatter in reported measurements has not been reduced with time (compare references 58 and 63), and the subjective judgement of "quality" is a difficult task. However, a refinement in the accuracy of burning velocity measurements was not one of the objectives of this study. We have accepted possible, small inaccuracies in the bomb measurement technique so that we may exploit the bomb's advantages.

2.2.2 Overview of the Facility

The main components of the constant volume bomb are shown in Figure 2.1.1. They include a spherical pressure vessel in which gases are burned, a mixing manifold for preparing gas mixtures, a spark triggering circuit for igniting mixtures, diagnostics and computerized data acquisition for recording the combustion transient, and an oven for heating the facility. Typically the bomb is operated in this manner: volatiles are bled into the spherical pressure vessel; a mixture of oxygen and nitrogen is prepared in the mixing manifold, and added to the volatiles in the vessel; and the volatile/O₂/N₂ mixture is then ignited by an electric spark. As a flame spreads outward from the ignition point in the center of the bomb to the vessel wall, the hot combustion gases behind the flame expand, and the pressure in the bomb rises. This pressure rise is monitored by a piezoelectric pressure transducer. The arrival of the flamefront at the vessel wall is recorded by ionization gages. The design of each of

the elements of the bomb apparatus is discussed in detail in the following sections. The effects of variations in the parameters are also discussed.

2.2.3 The Combustion Vessel and Heating Facility

The spherical pressure vessel was fabricated from a cylinder of 316 stainless steel (Figure 2.2.3.1), and certified by hydrotesting for a maximum working pressure of 550 psi at 820 K (Melco Steel Corp., Azusa, CA). To produce the 6 in. diameter spherical chamber in the cylinder, the cylinder was cut in half, hemispheres were machined in the cylinder ends, and then the two half sections were bolted back together. The seal between the sections was made with a metal and glass fiber o-ring (Flexatalic Corp.). Access to the spherical chamber is provided by 10 ports which project radially into the chamber (see Figure 2.2.3.1). These ports have been fitted with gas inlet and exhaust connections, a piezoelectric pressure transducer, three ionization gages, two spark electrodes and a rupture disk. The gas flow connections, diagnostics, and spark electrodes will be discussed in following sections.

But the rupture disk is essentially part of the pressure vessel, since its only purpose is to protect the vessel from damage. The disk is rated to break at 770 psi (approximately 1.5 times the working pressure of the vessel) and 820 K, and to vent the chamber rapidly upon rupture. Since the rupture disk is only designed to withstand a pressure differential in the outward direction (i.e. higher than atmospheric pressure in the vessel), it was necessary to add a vacuum support to the disk to avoid its implosion when the bomb is evacuated.

The facility is also equipped with an oven to heat the bomb from room temperature to 820 K. The bomb and an oven door are mounted on a welded tubular platform (see Figure 2.1.1); the oven body (3.6 kW, Cress Mfg. Co.) is mounted on casters to allow it to enclose the bomb, or be rolled away for easier access.

2.2.4 Gas Mixing and Handling

The gas handling system consists of two mixing tanks, three pressure gages, a vacuum pump, and a manifold which connects all of these elements (Figure 2.2.4.1). The manifold is constructed of stainless steel Swagelok flow elements and 1/8 in. stainless steel tubing. The mixing tanks are also made from stainless steel, and will withstand pressures in excess of 1800 psi. Since stainless steel is nonmagnetic, the tanks (approximately 2 liter capacity for each tank) are equipped with magnetic stirrers for accelerating the mixing of the added gases.

Figure 2.2.3.1 Diagram of the spherical pressure vessel. The vessel was constructed of 316 stainless steel by Melco Steel Corp., Azusa, CA.

Figure 2.2.4.1 The gas mixing and handling manifold.

The system is fed by pressurized gas cylinders of O_2 , N_2 , CO_2 and various noncondensable fuels (CH_4 , C_2H_2 , C_2H_4 , C_3H_8 , CO , and H_2 are currently available). The vapors from liquid fuels can also be added by evaporation from a test tube attached to the manifold. Since the manifold is not currently heated, some caution must be exercised when adding fuel vapors. If the partial pressure of the fuel at room temperature approaches its vapor pressure in the manifold or the storage tanks, then the fuel vapor will begin to condense, and the partial pressure of fuel vapor will become unpredictable. We have found by trial and error that consistent fuel concentrations can be maintained if the partial pressure of a condensible fuel is kept below about half of its vapor pressure, and we infer from this that negligible adsorption or condensation occurs at this pressure level (note that the margin of safety in pressures also ensures that the fuel will not condense during the cold morning hours).

The mixture concentrations are set by the measurement of partial pressures; differential (Drucker), absolute (Omega Eng. part # PX304-050A5V), and vacuum (Kurt J. Lesker Co.) pressure gages are mounted on the manifold for this purpose. The function of the vacuum gage is to insure that the manifold is adequately evacuated. The absolute gage is used to monitor the addition of major components of the mixture, while the differential gage has been added to measure the partial pressures of sparse components. Since the accuracy of the differential gage is ± 0.01 psi (± 0.1 % of full scale), and the accuracy of the absolute gage is ± 0.25 psi (± 0.5 % of full scale), the differential gage greatly improves the accuracy of the concentrations of sparse components. (Major components usually exceed the 10 psi measurement range of the differential gage.)

As an illustration of the use of the differential and absolute gages, the procedure for mixing CH_4 with O_2 and N_2 is as follows: (1) the system is pumped down to approximately 0.1 torr as confirmed by the vacuum gage; (2) a valve is closed to isolate one side of the differential gage, and provide a reference pressure; (3) CH_4 is injected into the mixing tank until the differential gage indicates that the correct amount has been injected (usually 2 to 4 psi); (4) the valve to the reference side of the differential pressure gage is opened so that both sides of the pressure gage are at the manifold pressure; (5) N_2 is fed into the mixing tank, and the quantity injected is measured with the absolute pressure gage (usually 20 to 30 psi); (6) the valve for the reference side of the differential gage is again closed to isolate the reference side of the gage at a new reference pressure; (7) the differential gage is used to determine the amount of O_2 injected into the storage tank (usually 4 to 8 psi); and (8) the mixing tank is isolated for 20 to 30 minutes to allow the magnetic stirrer to

mix the gases thoroughly. The chief advantage of the differential pressure gage is that it allows us to accurately measure the small changes in pressure associated with the addition of sparse components both before and after major components have been added (i.e. at any initial manifold pressure). After a gas mixture is composed, it can be stored in the mixing tanks, and then bled into the bomb through a sidearm of the gas mixing manifold.

2.2.5 Ignition System

After the spherical chamber of the bomb is filled with mixed gases, the motion of the gases is first allowed to die out (we typically allow 5 minutes for the gases to settle, though this is probably far more than necessary), and then the gases are ignited with an electrical spark. The spark is produced between two copper electrodes (1/8 in. diameter) which form a gap at the center of the vessel. To ensure consistent firing, the ignition system is designed to deliver several times the minimum ignition energy of the gases, and to deliver that energy consistently. Since minimum ignition energy is usually defined as the energy at which the gas ignites 10 % of the time, and is thus not an exact quantity, it is necessary to allow a large margin between the spark energy and the minimum ignition energy of the mixture. But it is also necessary to keep the ignition energy as low as possible, so that the energy input from the spark does not appreciably affect the propagation of the flame. Tests to confirm a negligible influence of the spark energy on the flame are discussed in Section 4.3 (see Figure 4.3.5).

To obtain consistent energy delivery, Metghalchi⁶² has recommended a circuit with a capacitor as its central element. We constructed several preliminary capacitor-based designs which were unable to deliver enough energy, before finally completing a successful circuit. The preliminary designs are discussed in Appendix A, and their inadequacies are explained in detail. Appendix A also discusses the modifications made to overcome these problems.

The final ignition circuit is shown in Figure 2.2.5.1. The design consists of high and low voltage loops, and a transistor-transistor logic (TTL) circuit. The TTL circuit provides a synchronizing pulse to the computer and the low voltage loop. Upon receiving the TTL signal, the low voltage loop creates a voltage pulse which is sent through the pulse transformer to break down the spark gap in the high voltage loop.

Figure 2.2.5.1 The final ignition circuit. The TTL trigger circuit is shown at the bottom of the figure, and the spark gap appears at the right above.

The TTL circuit is shown at the bottom of Figure 2.2.5.1. The trigger button provides a 5 volt pulse which "bounces", as shown in the figure. The transistors and capacitors shown in the figure have been added to remove this "bounce", which would otherwise cause inconsistent firing of the ignition circuit, and unreliable triggering of the computer.

The low voltage loop is shown to the left of the pulse transformer in Figure 2.2.5.1. The loop consists mainly of a capacitor, and a silicon controlled rectifier (SCR). Initially the rectifier is an open circuit, and the voltage from the power supply charges the capacitor (typically to 500 V). When the SCR receives a 5 volt pulse from the TTL circuit, it becomes a conductor, and the charge in the capacitor drains through the SCR to ground. This induces a current in the low voltage side of the pulse transformer (since it is in series with the SCR and the gap), and creates a high voltage pulse in the high voltage loop, which breaks down the gap.

The high voltage loop is shown to the right of the pulse transformer in Figure 2.2.5.1. This loop contains the spark gap and a large capacitor, which is charged (to between 200 and 1000 V) before the ignition circuit is fired. When the gap breaks down, it becomes a conductor, and the energy stored in the capacitor is dissipated in the gap. Almost all of the energy delivered to the gap comes from this capacitor.

To monitor the performance of the final ignition circuit, we measured the energy dissipated in the spark gap. These measurements were quite difficult, and are discussed in detail in Appendix A. Of course, the energy dissipated in the gap depends on the initial energy stored in the capacitor, and this dependence is shown in Table 2.2.5.1. If we compare the measured energies in the table with the minimum ignition energies⁷⁴ of some typical fuels in Figure 2.2.5.2, it is apparent that the ignition circuit delivers ample energy.

Table 2.2.5.1. Spark energies for various initial capacitor charge voltages.

Charge Voltage (V)	Spark Energy (mJ)
275	14
400	19
450	24
475	26

Figure 2.2.5.2 Minimum ignition energies for various hydrocarbons as functions of their equivalence ratios.⁷⁴

2.2.6 Piezoelectric Pressure Transducer

As the flame spreads outward from the spark gap to the vessel walls, the hot combustion gases behind the flame expand, and the pressure in the vessel rises. This pressure rise occurs very rapidly (typically 100 psi in 50 msec), and is our primary diagnostic during combustion. It is from this pressure measurement that we infer laminar burning velocities for the volatiles.

Pressure transients of this nature are routinely measured with piezoelectric pressure transducers. We have installed a transducer (Kistler Instrument Corp., Part #603B1) with a water-cooled sensor housing (also supplied by Kistler) in one of the 10 ports of the bomb. The water-cooled housing maintains the sensor temperature below 320 K for oven temperatures to 920 K. This is well below the temperature rating of the transducer, which is 470 K. The electrical leads to the transducer must also be cooled, and we have achieved this by wrapping the leads around the water lines to the housing, and then wrapping Fibrefrax cloth insulation around the leads.

The charge signal from the transducer is sent to a charge amplifier (Kistler Model 5004), which creates a voltage signal to be recorded by the computer. The charge amplifier is accurate to less than $\pm 1\%$ of the pressure signal (i.e. a pressure of 10 psi is measured to an accuracy of 0.1 psi). The influence of the accuracy of the pressure measurement on the accuracy of inferred burning velocities is discussed in Section 3.3.

2.2.7 Ionization Gages

One of the assumptions of our analysis is that the propagating flame is spherical, as discussed in Section 3.2.2. While this assumption is reasonable for the combustion of many mixtures, slow-burning flames may be distorted by buoyancy. Buoyancy causes the flames to rise, and contact the top of the chamber wall before they contact the bottom of the wall. To check for distortions, we have constructed ionization gages which detect the arrival of the flame at the wall.

Three ionization gages have been located at ports near the top and the bottom of the bomb. The gages consist of two wires which form a gap (1 mm wide) near the wall (about 2 mm from the wall) of the bomb (see Figure 2.2.7.1). A large voltage is applied across the gap by the circuitry shown in the figure, so that as the ion-rich region of a flame passes over the gap, a current is induced. Though the gages were manufactured with thermocouple wires, the performance of the gages does not rely at

Figure 2.2.7.1 Schematic representation of an ionization gage and its associated circuitry.

all upon the thermoelectric properties of the wires. These wires were chosen because of their convenient diameter and stiffness.

The major purposes of the circuitry shown in Figure 2.2.7.1 are to apply a large voltage (about 150 V) to the gap, and to measure the current through the gap. The 10 kOhm resistor shown converts the current through the gap to a voltage signal to be sent to the computer, and the 10 nF capacitor filters DC signals before they enter the computer. The performance of the ionization gages, and an example of their detection of buoyancy are shown and discussed in Section 4.5.

2.2.8 Data Acquisition and Storage

The signals from the pressure gages in the mixing manifold, the ionization gages, and the piezoelectric pressure transducer are all sent to an AT-style microcomputer (12 MHz 286), where they are either displayed on the monitor screen or stored on the hard disk. A trigger signal is also sent from the ignition system to the computer to synchronize ignition and the acquisition of the signals from the bomb. Since the ignition system contains large voltages, and the computer contains sensitive circuitry, we have taken the precaution of sending all signals through an over-voltage protector. We have also filtered all of the signals with a low pass filter, to avoid noise from the radio frequency power supply (see Figure 2.1.1). The over-voltage protection and low pass filter circuits were designed, constructed, and tested in-house, and their operation will be discussed in detail in this section.

Since the signals from the transducers are analog, and the computer operates digitally, it was necessary to install an analog to digital (A/D) convertor board. The A/D board (Data Translation 2801) will convert up to 8 analog signals, and handles signal magnitudes of 0 to 10 volts. The digitized signals have 12 bit resolution (i.e. the board can resolve voltage changes of $1/4096$ of the full scale voltage). The board also contains a trigger channel which receives a trigger signal from the ignition system, and then sends a command to the computer to begin recording signals from the A/D channels. Because the combustion transient is very rapid, and occurs for a short time, we operate the board in the direct memory access (DMA) mode, in which the computer records the signals every 0.3 msec, or at a sampling rate of 13.7 kHz (this is the maximum sampling rate for this board). This sampling rate defines a Nyquist frequency of 6.8 kHz ($13.7 \text{ kHz}/2$). To avoid distortion (aliasing, etc.) of the signals from the transducers, it is important that the transducer signals have a bandwidth with a maximum frequency below the Nyquist frequency. We have Fourier transformed the signals from the transducers to determine their frequency

spectra, and found that their maximum frequencies are well below the Nyquist frequency. Thus, this sampling method will provide accurate measurements of our signals.

However, we have also found that when the combustion bomb and the radiant coal flow reactor are operated simultaneously, the radio frequency power supply adds noise to our transducer signals. Fortunately, though, this noise has a frequency of 450 kHz, and is easily filtered. To eliminate this noise, we have constructed a low pass filter with a cutoff frequency of 65 kHz (Figure 2.2.8.1). The filter is a simple series resistor and parallel capacitor, as shown in the figure. The 65 kHz cutoff frequency has been chosen so that frequencies less than 13.7 kHz are diminished by less than 1 %, while the noise at 450 kHz is almost completely eliminated.

In theory, the low pass filter should also stop any stray high-voltage, high-frequency signal from the ignition system. However, for safety, we have added an over-voltage protection circuit. The over-voltage circuit (shown in Figure 2.2.8.2) only allows signals of magnitude less than 12 volts to pass to the computer. As shown in the figure, the circuit consists of reference points of +12 and -12 volts which are connected to the input signal line through diodes. As long as the magnitude of the signal remains below 12 volts, the diodes are back-biased, and they act as open circuits. But if the signal rises above +12 or drops below -12 volts, one of the diodes turns on and sinks current to the reference point, so that the input signal to the circuit is held at the reference point voltage. When the magnitude of the input again drops below 12 volts, the diode turns on, and the signal is passed without distortion. However, if the signal voltage remains above 75 volts, the 1/16 amp fuse in the circuit will blow.

The over-voltage protection circuit was tested for a worst case situation by firing the spark pulse of the ignition circuit (which is ordinarily sent to the pressure vessel) directly into the protection circuit. Despite the large voltage (> 20 kV) and rapidity ($< 1/2$ microsecond) of the pulse, no signal was observed at the output of the protection circuit. We also tested for protection from DC signals by applying a DC voltage to the input of the over-voltage circuit; the voltage was increased until the fuse blew without observing a signal at the circuit output. To test mid-range frequencies, we fed the sine wave output from a signal generator into the protection circuit. The circuit clipped the sine wave neatly at ± 12 V, without distorting the wave between these two extremes. Example signals from the gages and transducer are shown in Chapter 4, and their interpretation and computational reduction are explained.

Figure 2.2.8.1. Low pass filter for the data acquisition system.

Figure 2.2.8.2. Over-voltage protection circuit for the data acquisition system.

2.2.9 Parametric Study of the Constant Volume Bomb

The pressure rise in the bomb as the flame moves outward compresses the unburned gases isentropically, causing both the unburned gas temperature and pressure to rise. Thus a single combustion experiment provides measurements of burning velocity for a range of reactant gas temperatures and pressures.

Figure 2.2.9.1 shows a typical pressure-temperature line along which burning velocities are measured for a single combustion experiment. This line is defined by the relation between pressure and temperature at constant entropy ($P/P_0 = (T/T_0)^{C_p/R}$), which gives a straight line in log-log coordinates, with a slope of C_p/R . To make measurements for a wider range of temperatures and pressures, we can adjust the initial temperature and pressure (T_0 and P_0) of the mixture, and thus move the straight line up and down and left and right as shown on the plot in Figure 2.2.9.1.

The pressure and temperature limitations of our measurements are set by the apparatus. Since we do not have provisions for cooling the bomb, the low temperature boundary is room temperature. While the oven will heat the bomb to about 1100 K, the bomb itself is rated for a maximum temperature of about 800 K. However, since the gas temperature typically rises by 200 K during the compression of the reactants, the high temperature boundary is about 1000 K. The upper pressure boundary is limited by the maximum working pressure of the bomb, which is 500 psi. The low pressure boundary is dependent upon the mixture, since the heat release is a function of the pressure, and a minimum heat release is required to sustain the flame.

As seen in Figure 2.2.9.1, if enough experiments are conducted, we can back out the independent variations with temperature and pressure of the laminar burning velocity. This information is related directly to the global reaction rate. The pressure variation provides the order of the global reaction, while the temperature variation provides the temperature dependence of the global reaction rate constant.

2.3 The Radiant Coal Flow Reactor

2.3.1 Overview

The radiant coal flow reactor was originally designed and built for primary devolatilization experiments.^{7,77,78} As implied by its name, the reactor suspends pulverized coal particles in an inert flow and heats those particles primarily with radiation. Since the carrier gas in which the coal is suspended is transparent to

Figure 2.2.9.1 Pressure-temperature relation of the reactant gases for individual combustion transients in the bomb. By adjusting the initial pressure and temperature in the bomb, the burning velocity is measured for a wide range of temperatures and pressures, and temperature and pressure dependencies can be determined.

radiation, the gas remains relatively cool. Thus, as volatiles leave the coal particles, they are quenched rapidly in the cool gas, so that their secondary chemistry is minimized. The radiant reactor is ideal for primary devolatilization experiments, since it avoids the tendency of other apparatus to obscure the products of primary devolatilization by secondary chemistry.

However, we have found that at higher coal loadings and longer particle residence times, the suspended coal particles begin to heat the gas. With proper adjustment of the coal loadings and residence times it is possible to completely devolatilize the coal, and then have secondary chemistry begin. This allows us to study both primary devolatilization and secondary pyrolysis in the same heating section of the reactor.

For this study, a radiant coal flow reactor has been built which is almost identical to the reactor originally constructed for primary devolatilization experiments (except that the furnace section is 12.5 cm long, instead of 5 cm long).^{7,77,78} The reactor consists of 4 major parts (see Figure 2.1.1): a coal feeder which suspends the coal particles in the gas flow; a furnace which heats the particles radiantly; a sampling arm which draws the volatiles off at the furnace exit and transports them to the bomb; and a virtual impactor which separates and collects the char and tar products. Both the coal and gas flowrates are adjustable in the feeder, and the temperature of the furnace can be varied from 1000 K to 1850 K.

The operation of each major part of the reactor and the impact of varying the reactor's important parameters will be discussed in the following sections.

2.3.2 The Coal Feeder

The purpose of the coal feeder is to entrain a steady flow of coal particles in a downflowing stream of inert gas (N_2 for this study). The particles are pushed from a tube by a rod, and fall into the downflowing gas stream. Unlike the fluidized bed-type feeders which are common in the literature,^{24,29,30,31} this feeder design is sure to give a steady flow of particles with no time-variation in size distribution.

A schematic of the feeder is shown in Figure 2.3.2.1. The brass tube in the center of the feeder contains the coal, which is pushed out its top by the teflon rod. The speed of the motor at the top of the housing is varied to adjust the rate at which coal is pushed above the top of the tube. A wedge scrapes the coal particles from the top of the brass tube, and they slide down the ramp and fall into the flow tube to the

Figure 2.3.2.1. The coal feeder.

furnace. N_2 is introduced at the bottom of the feeder housing, and it flows out of the housing through the flow tube. N_2 also flows through an annular passage surrounding the flow tube. Near the top of the furnace, the annular and center flows meet, and the annular flow acts as a sheath to keep the coal particles in the center flow away from the furnace walls.

For this study, the coal and gas flowrates in the center tube are 4.4 gm/min and 3 slpm respectively. The annular flowrate is 1 slpm. With an average diameter of 90 microns for the coal used (the coal is described in detail in Section 6.2), the flowrates in the center tube translate to a particle number density in the flow of 2400 #/cc (particles per cubic cm). (Particle number density is computed as the coal mass flowrate divided by the product of the gas flowrate and the mass per particle.) Note that only the flowrate in the center tube is used because the sheath does not contain coal particles. Though our particle number density is high in comparison with the number densities of other researchers (who typically operate at 200 to 400 #/cc),^{7,24} it compares quite favorably with the number densities estimated for the feedpipe of a typical coal-fired burner (1000 to 5000 #/cc).⁷⁹ However, while number densities are important to certain aspects of the heat transfer in the suspension, we must consider the weight ratio of the coal and gas to characterize the stoichiometry and dilution in the suspension. For this study, the weight ratio is 0.95 gm coal/gm N_2 (including the N_2 flows in both the center and annular tubes), which compares favorably with the 1 lb coal/lb air rule of thumb which is commonly stated for industrial boilers. The nominal residence time is about 500 msec, based on a cold gas flowrate in the center tube of 3 slpm. However when the slip velocity of the particles and the expansion of the gas due to its heating are taken into account, we estimate that the actual residence time is about 200 msec.

The feeder was designed to allow wide variations in the flowrates of both the gas and the coal. The flow of coal can be varied from 0.1 to 7 gm/min while the gas flowrate is adjustable from 1 to 8 slpm. These flows translate to the range of number densities from 20 to 10000 #/cc. The range of possible gas flowrates provides a range of nominal residence times based on cold gas flowrate of from 275 msec to 2 sec, which gives good resolution of the time dependence of pyrolysis.

The copper tube which carries the coal suspension from the exit of the coal feeder to the furnace inlet is approximately 40 cm long. As the suspension passes downward through the tube, the particles are mixed with the gas, so that at the furnace inlet, they are well dispersed. Several centimeters above the inlet, the copper tube connects with a quartz tube, which carries the suspension through the furnace.

2.3.3 The Radiant Furnace

A schematic of the furnace section is shown in Figure 2.3.3.1. The furnace consists of a well-insulated graphite cylinder which is heated inductively by a radio-frequency power supply. As particles fall through the quartz tube at the center of the furnace, they absorb radiation from the graphite. The inert gas which carries the particles is transparent to radiation, and it remains relatively cool.

However, the heat transfer in the furnace is complicated by the fact that the quartz tube is not perfectly transparent, and we estimate that radiation from the graphite typically raises its temperature to above 1000 K. Both the tube and the particles heat the N_2 carrier gas convectively. Typically, for low particle number densities the temperature of the gas lags that of the coal particles by about three hundred degrees. But at high number densities, the gas and the coal particles will have approximately the same temperature histories. The estimation of these temperature histories and their variation with varying number density are discussed in section 2.3.6.

For this study, the graphite cylinder was heated to temperatures of from 1000 to 1700 K. The temperature of the cylinder was determined by optical pyrometry, and will be referred to throughout this document as the furnace temperature. The furnace is capable of attaining temperatures up to 1850 K. At furnace temperatures higher than 1850 K, the quartz tube softens and implodes.

2.3.4 The Sampling Arm

Several centimeters below the exit of the furnace, we have added a sampling arm to draw a fraction of the volatile gas from the flow and transport it to the bomb. Since only a fraction of the total gas flow is drawn off, the coal particles (which are near the center of the tube) are not drawn into the arm. They continue downward and are trapped at the bottom of the reactor. No particles have been observed in the sampling arm; thus the arm is efficient at removing only volatile gas and soot from the stream. The sampling arm is located close to the furnace exit in order to collect the volatiles before they cool, and the tars in the sampled flow remain in the vapor phase. In the future, tar vapors will be transported to the combustion bomb by heating the line between the sampling arm and the bomb. For this study, the flow was quenched and the tars were removed on a filter as discussed in Section 2.4.

Figure 2.3.3.1. Inductively-heated furnace. The radiant section of the furnace is 12.5 cm long.

2.3.5 The Virtual Impactor

The coal flow reactor is operated in two different configurations. For volatiles transport to the bomb, the sampling arm is added, and a glass wool filter is installed in the main flow to trap the char particles and tar before the flow is exhausted (see Figure 2.1.1). For weight loss and tar yield measurements, the sampling arm and quartz filter are removed, and the virtual impactor is added to separate and collect the tar and char.

Before the flow enters the impactor, it is cooled by a quench gas added at the furnace exit. Typically the tar condenses upon cooling to form droplets of 1 to 10 microns in diameter, which are considerably smaller than the chars (greater than 50 microns). This size disparity is exploited to separate and collect the chars and the tars in the impactor.

The virtual impactor is shown in Figure 2.3.5.1. As gases enter the impactor, they form a stagnation point at the top of the tube. Most of the flow is redirected into the annulus surrounding the tube. But the char particles cannot follow the flow, and they fall into the tube, where they are collected in the char collector. Since the tar droplets have a smaller diameter, they follow the gas, and are collected on the annular filters (Whatman EPM 2000; collection efficiency 99.9% at 0.3 microns). For the high number densities of this study, soot is also formed in the reactor, and because of its small size, it collects with the tars on the annular filters. The proportions of tar and soot are determined by first weighing the amount of tar and soot on the filters, and then washing the filters in a solvent, and filtering the solvent to collect the soot. The filters are then reweighed to determine the amount of soot collected, and the amount of tar is taken as the difference in these two weight measurements. Weight loss and tar yield measurements made with the virtual impactor are shown and discussed in section 6.2.

2.3.6 Parametric Study of the Radiant Coal Flow Reactor

Because the parametric dependence of the radiant coal flow reactor is very complicated, we have constructed a computer model of the reactor to study the effects of variations in the parameters (furnace temperature, gas flowrate, and coal particle number density) on the residence time and gas and coal particle temperature histories in the furnace.

Figure 2.3.5.1. The virtual impactor.

The model considers both momentum and energy transfer. We have accounted for radiation from the graphite cylinder to the coal particles and the quartz tube. This is the dominant mode of heat transfer in the furnace. We have also considered convection from the hot quartz and coal to the gas. The quartz tube will carry heat out of the ends of the furnace by conduction, and this has been accounted for by applying finite differencing to the tube.

To simplify the model, many of the heat transfer phenomena are neglected. For instance, the thermal boundary layers on the tube and around the coal particles are ignored, and only the mixed mean temperature of the gas is considered. The size distribution of the particles is also neglected, with the assumption that the weight-averaged size is representative of the particles.

To model momentum transfer, we have assumed that the gases in the furnace have a plug flow. Both the particle and gas velocities must be computed, since the particles are pulled downward by gravity, and will have some slip velocity in the flow. The major complicating factor to the momentum transfer computations is the changing temperature of the gas. As the gas temperature increases, the gas expands and accelerates, and we have accounted for this by conservation of mass.

In addition to ignoring the radial velocity profile of the gas, we have neglected the momentum addition from the particles to the gas. However, since this momentum addition will tend to "flatten out" the velocity profile in the center of the tube, the effects of the particles and the radial profile tend to cancel. Though the model ignores many important heat and momentum transfer phenomena occurring in the furnace, its main purpose is to help develop an understanding of the trends in the dependent variables with variations in the parameters. For this purpose, the model is adequate.

Three predictions of particle and gas temperature histories are shown in Figure 2.3.6.1 for a gas flowrate of 3 slpm, and a furnace temperature of 1600 K. As we decrease the number density of the particles, while maintaining a constant gas flowrate and furnace temperature, the temperatures of the particles and gas decrease, and the residence time increases slightly. Also the disparity between particle and gas temperatures increases, with the gas temperature ultimately falling more than 100 degrees below the particle temperature. (This disparity should become even more pronounced with increasing particle diameter.) Though not shown in the figure, the effect of varying the gas velocity and furnace temperature is to raise and lower the particle and gas temperature curves, or lengthen and shorten them without changing

Figure 2.3.6.1 Model predictions of the particle and gas temperature histories in the radiant flow reactor. The furnace temperature and the gas flowrate are maintained constant for these predictions at 3 slpm and 1600 K. The number density is increased by increasing the mass flowrate of coal.

their relative magnitudes. Even at the highest number densities, the final particle temperature remains well below the temperature of the furnace.

The number density of the coal suspension can be varied from 20 to 10000 #/cc, and the gas flowrate from the feeder can be adjusted between 1 and 8 slpm. Also, the furnace temperature can be varied from 1000 to 1850 K. However, the possible combinations of these values are limited, since high number densities and furnace temperatures cause the gas flow to become extremely hot. If, at the same time, the flowrate of gas is too low, then buoyancy will cause the flow to reverse, and blow coal particles back into the feeder. For the flowrate and number density conditions of this study, this buoyant recirculation starts at about 1800 K.

From the discussion above, it is apparent that the adjustability of the furnace temperature and gas flowrate allow us to vary both the maximum particle temperature and the residence time. The third parameter, number density, gives us a method to independently adjust the gas temperature. For instance, at number densities of about 100 #/cc, the convective heating of the gas by the particles is low, and the gas temperature remains fairly low over most of its residence time in the furnace. This condition is excellent for studying primary devolatilization, since the secondary chemistry of the volatiles is slow at these low temperatures, and the residence time in the furnace is too short for significant secondary pyrolysis to occur. As the particle number density is increased, the convective heating of the gas increases, and the maximum gas temperature rises. At some number density, secondary chemistry of the volatiles becomes significant. Since the gas temperature always lags the particle temperature, it is possible to choose a number density at which primary devolatilization is complete before secondary chemistry begins. This condition is ideal for studying the secondary chemistry of the volatiles, because the variations in the product yields after primary devolatilization is complete are directly attributable to secondary chemistry. We have found that this ideal condition is achieved at a number density of about 2400 #/cc.

2.4 Volatiles Transport from the Reactor to the Bomb

Volatiles are transported from the reactor to the combustion bomb through a 1/4 in. copper tube. For this study, the tube remained unheated. However, in future studies the tube will be heated to 520 K to maintain tars in the vapor phase, and transport them to the bomb to study their combustion. Methods for handling the tars are discussed in detail in Section 4.8.

As shown in Figure 2.1.1, the volatiles are quenched rapidly to room temperature by a water-cooled heat exchanger after their removal in the sampling arm. The tars present in the vapor condense to form an aerosol which is collected (along with soot) on a filter at the exit of the heat exchanger. The remaining light gas volatiles then flow into the combustion bomb.

Before an experiment, the bomb is first evacuated. Then as the bomb fills with volatiles, the pressure rises, and the flowrate (monitored by a rotameter) begins to decrease. This decrease in flowrate should affect the flow upstream of the bomb, so that the flowrate through the furnace section of the reactor should also decrease. However, the flow to the bomb is a small fraction of the total flow through the reactor, so that the residence time of the gas and particles in the furnace is not appreciably altered.

2.5 Chemical Analysis of the Volatile Products

The tools available for chemical analysis in the lab include a high performance liquid chromatograph, a gas chromatograph, and an elemental analyser. The elemental analyser gives carbon, hydrogen, and nitrogen weight percents for solids collected from the filters. Gases are withdrawn by gas tight syringe, and analysed by gas chromatography. The H_2 and CO concentrations are determined with a thermal conductivity detector (TCD) after separation with Molecular Sieve 5A. The C_6H_6 and C_1 through C_4 hydrocarbon concentrations are measured with a silicalite column and a flame ionization detector (FID). Though CO_2 and H_2O are also present in significant amounts, we do not have the capability to measure their concentrations at this time. Finally, the liquid chromatograph provides molecular weight distributions of tars. Though the chromatograph is not implemented in this study, it will prove useful in future experiments with the tars.

3. Analysis for Flame Propagation in the Constant Volume Combustion Bomb

3.1 Introduction

We have implemented a computer program (listed in Appendix B) which closely follows the theoretical analysis of Metghalchi and Keck⁶⁶ to infer laminar burning velocities from the experimental pressure measurements. The program is based entirely on simple thermodynamic relations, and requires thermodynamic and combustion properties for the reactants, including their heats of formation, specific heats, the stoichiometry, and the diluent ratio. The only required instantaneous measurement is the pressure rise during combustion. The formulation of the model, design calculations for single-fuel mixtures, and the influence of tar properties are discussed in this chapter.

This same analysis was also used as a design tool to gage the sensitivity of the computed burning velocities to uncertainties in the pressure and the input parameters. The sensitivity calculations were first completed for single-fuel mixtures, since their properties are well known. The resolution for changes in mixture stoichiometry and burning velocity was quite good. However, sensitivity to uncertainty in the specific heat of the reactants was also significant, and this has important implications for the estimation of tar properties. We were unable to find values of the thermodynamic properties of high temperature coal tars. Furthermore the measurement of these properties for the relevant range of tar production conditions (including devolatilization temperature, heating rate, etc.) is a research project in itself. Instead the properties were estimated using group additivity. Fortunately, burning velocities are very insensitive to tar properties, so that, for very wide ranges of estimates, the uncertainty in the inferred burning velocities is only about 5 %.

3.2 Elements of the Model

3.2.1 General Features

The spherical flame which expands outward from the center of the bomb is physically very complex, involving heat and mass transfer, and the chemical reactions among dozens of species. But the flame can also be considered in terms of its overall stoichiometry, heat release, and total mass flowrate, without complicated calculations of species and temperature profiles. The model implemented in this

study takes this approach, by ignoring species and temperature gradients, neglecting radiation heat transfer, and only considering combustion reaction rates implicitly.

The model considers three main physical influences. Two of these, namely the heat release from combustion and the compression caused by the expansion of the hot combustion gases, are expressed by conservation of volume and conservation of energy. The third influence, the flowrate of the reactant mixture into the flame, is represented by a mass conservation equation invoked at the flame surfaces. Though no combustion reaction rate appears explicitly in the model, the reaction rate will determine the mass flowrate into the flame, and its influence is included implicitly through the laminar burning velocity in the mass flowrate equation. The two conservation equations and the mass flowrate equation comprise the core of the model, and the only other important element is an approximate equilibrium code for calculating the thermodynamic parameters in these equations. Formulation of the conservation relations and the approximate equilibrium code are discussed in detail in the following sections.

3.2.2 Assumptions

The combustion of volatile mixtures in the bomb is idealized as the radial propagation of a smooth, spherical flame sheet. If we neglect the thickness of the flame, the contents of the bomb can be divided into burned gases in thermochemical equilibrium and unburned gases which are chemically frozen (i.e. the species concentrations are fixed). As unburned gas passes through the flame, its temperature changes, causing it to expand greatly, and isentropically compress the rest of the gas in the bomb. Flame movement is slow compared to the mechanisms for pressure equalization, so that the pressure is assumed uniform throughout the bomb. These are the major assumptions involved in the analysis, though other important assumptions are made in connection with the simplification of the conservation equations as discussed below.

3.2.3 Conservation Equations

The following mathematical treatment closely follows that of the combustion bomb simulator of Metghalchi and Keck.⁶⁶ The most fundamental constraints on the transient behavior are conservation of volume, which stipulates that the volumes

occupied by the burned and unburned gases must equal that of the bomb, and conservation of energy, which relates the instantaneous internal energies of the burned gases, unburned gases and original combustible mixture.

For Volume: Bomb Vol. = Unburned Gas Vol. + Burned Gas Vol.

$$V = \int dV_u + \int dV_b \quad (3.2.3.1)$$

Energy: Total Int. E. = Unburned Gas Int. E. + Burned Gas Int. E.

$$E = \int dE_u + \int dE_b \quad (3.2.3.2)$$

For negligible heat loss to the vessel wall, the total internal energy is constant.

Rewriting the equations in terms of intensive properties and dividing by the total mass of combustible mixture, M,

$$\frac{V}{M} = \int v_u \frac{dm_u}{M} + \int v_b \frac{dm_b}{M} \quad (3.2.3.3)$$

$$\frac{E}{M} = \int e_u \frac{dm_u}{M} + \int e_b \frac{dm_b}{M} \quad (3.2.3.4)$$

In actuality the fractions of unburned and burned gas are not independent of each other, so that if we define $x = m_b/M$, then $1 - x = m_u/M$. After integrating, the final forms of the conservation relations are

$$\frac{V}{M} = (1-x)v_u + x v_b \quad (3.2.3.5)$$

$$\frac{E}{M} = (1-x)e_u + x e_b \quad (3.2.3.6)$$

where c_u and v_u are functions of T_u and P and c_b and v_b are functions of the average burned gas temperature, T_b , and P . Note that the burned gas properties are assumed to be uniform throughout the vessel, and that an average temperature, T_b , is deemed adequate for specifying their values. Takeno and Iijima have modeled the actual temperature gradient in the burned gases by assuming isentropic compression of the burned gases and ignoring heat conduction.⁶¹ But the error associated with ignoring the gradient has been found by Metghalchi and Keck to be small.⁶⁶

The pressure and unburned gas temperature are related by the law of isentropic compression (which is based on ideal gas behavior, reversible compression, and no heat losses):

$$\frac{P}{P_i} = \left(\frac{T_u}{T_i} \right)^{\frac{\gamma}{\gamma-1}} \quad (3.2.3.7)$$

where the subscript, i , signifies the initial state, and γ is the ratio of specific heats of the unburned gas.

At this point, the conservation relations are formulated as functions of T_u , P , T_b , and x . The time dependence is not explicit; rather, a value for x or P can be specified, and the remaining three unknowns can be determined from the three available equations (Eq. 3.2.3.5, 3.2.3.6, and 3.2.3.7).

The rate of flame propagation establishes the transient behavior, as seen explicitly in the mass balance around the flamefront. Since the flame is modeled as a thin spherical shell, there is no appreciable storage of mass in the flame itself, and the pertinent form of mass conservation is

Mass Entering Flame = Change In Burned Gas Mass

$$\rho_u S_u A_f = M \frac{dx}{dt} \quad (3.2.3.8)$$

where S_u is the burning velocity of the mixture, A_f is the flame area, and ρ_u is the unburned gas density. The unburned gas density (or reciprocal specific volume, v_u) is specified by the volume and energy conservation relations defined above. With a simple geometric relation, the area of the spherical flame, A_f , can also be expressed as a function of x and v_b , and we find that

$$A_f = (36\pi)^{1/3} (Mxv_b)^{2/3} \quad (3.2.3.9)$$

When Eq. 3.2.3.9 is applied to Eq. 3.2.3.8, the burning velocity, S_u , is expressed in terms of known variables.

For the unburned gases, the specific internal energy, e_u , and specific volume, v_u , are related to T_u and P by the ideal gas law and the specific heat at constant pressure, c_p . Analogous relations for the burned gases are based on species concentrations at equilibrium, as discussed in the next section.

3.2.4 Approximate Equilibrium Model

For the burned gases, the specific internal energy, e_b , and specific volume, v_b , are related to P and T_b by an equation of state and the heat capacity, as for the unburned gases, but here the influence of chemical dissociation must be accounted for. The primary consequences of dissociation are reduced mean molecular weights, and increased heat capacities. In principle, the species concentrations and associated heat capacities can be determined by minimizing the Gibbs free energy of the system, but the computational effort required is prohibitive.

Martin and Heywood⁸⁰ have developed an accurate and computationally simple method to determine the thermodynamic state at equilibrium. Their approach is especially suited to our application, in so far as the enthalpy and density of combustion products are defined from the pressure, temperature, equivalence ratio, elemental C:H ratio of the fuel, and the elemental N:O ratio of the oxidizer. The savings in computational effort is brought about by the fact that Martin and Heywood's method does not calculate the concentrations of the many possible species, but instead lumps them into monatomic, diatomic, and triatomic components. The Martin and Heywood model is less informative than a Gibbs free energy-based solver, which gives the concentrations of all of the chemical species; but it is simpler, faster, easier to use, and it provides the equilibrium thermodynamic state of the combustion products, which is all that we require.

Martin and Heywood model hydrocarbon combustion with the reaction

for $\phi < 1$,

for $\phi > 1$,

where

$$\varepsilon = 4d/(1+4d),$$

d = the ratio of carbon to hydrogen atoms in the fuel,

ϕ = moles of fuel per mole of O_2 ,

ψ = moles of N_2 per mole of O_2 ,

U = extra number of monatomic molecules due to the dissociation of diatomic molecules,

Y = extra number of diatomic molecules due to the dissociation of triatomic molecules,

and M_3 , M_2 , and M_1 represent all possible triatomic, diatomic, and monatomic species, respectively, which are involved in the dissociation chemistry.

The equilibrium chemistry is reduced to two relations among M_3 , M_2 , and M_1 : triatomics dissociating to diatomics, and diatomics dissociating to monatomics.

At equilibrium these concentrations are related by the equilibrium constants for the reactions, K_1 and K_2 :

$$\frac{[M_3]^2}{[M_2]^3} = K_1 \quad (3.2.4.5)$$

$$\frac{[M_2]}{[M_1]^2} = K_2 \quad (3.2.4.6)$$

Stoichiometric coefficients for the moles of M_1 , M_2 , and M_3 per mole of O_2 appear in the generic hydrocarbon combustion reactions given above (Eq. 3.2.4.1 and 3.2.4.2). Substituting these coefficients into the equilibrium constants yields definitions for U and Y in terms of the mixture characteristics and the values, K_1 and K_2 , and we find that

$$U = \frac{(\epsilon\phi - 2Y)[\phi(1 - \epsilon) + 1 + Y + \psi]}{4PK_1K_2Y - (\epsilon\phi - 2Y)} \quad (3.2.4.7)$$

$$U = \frac{K_1Y(1 - \phi + Y)}{K_2(\epsilon\phi - 2Y) + K_1Y} \quad (3.2.4.8)$$

Equations 3.2.4.7 and 3.2.4.8 must be solved iteratively for U and Y . The equilibrium constants expressed in terms of T_b and ϵ are:

$$\begin{aligned} K_1 &= 5.819(10^{-6}) \exp \left(0.9674\epsilon + \frac{35810}{T_b} \right) \\ K_2 &= 2.961(10^{-5}) \exp \left(2.5930\epsilon + \frac{28980}{T_b} \right) \end{aligned} \quad (3.2.4.9)$$

Martin and Heywood obtained these constants by matching the predictions of their approximate equilibrium model with detailed equilibrium calculations involving more than 40 species.

Specifying the temperature and pressure of the combustion products and the fuel characteristics now determines the relative concentrations of monatomics, diatomics, and triatomics in the burned gases. In terms of P and T_b , the specific volume of the burned gases (which is one of the primary dependent variables) follows from the ideal gas law.

The model for the specific internal energy of the burned gases, e_b , based upon statistical mechanics, is also given by Martin and Heywood; pertinent relations are

$$\begin{aligned} m_{cp} e_b &= \frac{R}{2} (6[M_3] + 5[M_2] + 3[M_1]) T_b \\ &+ R(3[M_3] + [M_2]) \left(\frac{T_v}{\exp(T_v/T) - 1} \right) \\ &+ m_{cp} h_f \end{aligned} \quad (3.2.4.10)$$

where

m_{cp} = the mass of product per mole of O_2 ,

T_v = a characteristic vibrational temperature,

R = the universal gas constant,

and h_f = the heat of formation of the products at a reference temperature of 0 K for gaseous O_2 , N_2 , and H_2 , and solid graphitic carbon.

Again, correlations for T_v and h_f are taken from Martin and Heywood as follows:

$$T_v = \frac{3256 - 2400\varepsilon + 300\psi}{1 - 0.5\varepsilon + 0.09\psi} \quad (3.2.4.11)$$

for $\phi < 1$,

$$m_{cp} h_f = 10^3 \frac{R}{2} \left[\varepsilon \phi (-94.570) + 2 (1 - \varepsilon) \phi (-57.471) \right. \\ \left. + (121.5 + 29.59\varepsilon) Y + 117.5 U \right] \quad (3.2.4.12)$$

for $\phi > 1$,

$$m_{cp} h_f = 10^3 \frac{R}{2} \left[(2 - (2 - \varepsilon)\phi) (-94.570) + 2 (1 - \varepsilon) \phi (-57.471) \right. \\ \left. + 2(\phi - 1)(-27.375) + (121.5 + 29.59\varepsilon) Y \right. \\ \left. + 117.5 U - \frac{6.5 (\phi - 1)}{\varepsilon} \right] \quad (3.2.4.13)$$

Based on the approximate Martin and Heywood dissociation equilibrium model, e_b and v_b have been expressed in terms of P , T_b , and the combustible mixture characteristics. Interrelations among the primary dependent variables (v_u , v_b , P , and x) are now in closed form, and the model is complete.

3.2.5 Calculation of Pressures and Burning Velocities

The model has been implemented in two forms. As a design program, it generates simulated pressure records from the burning velocity measurements of other researchers. In this form, the program predicts the influence of various parameter changes on the pressure history during combustion. As a data reduction program, the model transforms actual measured pressure records to burning velocities. For both of these tasks, most of the model remains identical. In fact all of the necessary change occurs in one equation, Eq. 3.2.3.8.

In the design program, Eq. 3.2.3.8 establishes the transient behavior of the pressure rise. The equation is implemented to determine the time, t , as a function of extent of combustion, x , and takes the form,

$$t = \int_0^x \frac{M}{\rho_u S_u A_f} dx = \int_0^x \frac{v_u}{S_u} \left(\frac{36\pi}{M} x^2 v_b^2 \right)^{-1/3} dx \quad (3.2.5.1)$$

where A_f has been replaced with its expression from Eq. 3.2.3.9. The relationship between x , v_u , v_b , and P is established by the conservation relations (Eq. 3.2.3.5 - 3.2.3.7) prior to evaluating Eq. 3.2.5.1, and S_u is given by a correlation from the combustion literature. The quadrature is based on the trapezoidal rule, which is ideally suited to stiff problems, such as this one, in which the integration step size must be varied over several orders of magnitude to achieve an accurate result.

It is worth noting here that for $x = 0$ the integrand of Eq. 3.2.5.1 is indeterminate, and that this poses a problem with evaluating the integral. However, for small x the integral can be approximated by

$$t = \int_0^x \frac{v_u}{S_u} \left(\frac{36\pi}{M} x^2 v_b^2 \right)^{-1/3} dx = 3 \left(\frac{36\pi}{M} \right)^{-1/3} \left[\frac{v_u}{S_u v_b^{2/3}} \right]_{t=0} x^{1/3} \quad (3.2.5.2)$$

which is then summed with the rest of the integration as determined by the trapezoidal rule.

For the data reduction program, the implementation of Eq. 3.2.3.8 is much simpler. The purpose of the equation in this case is to establish the laminar burning velocity,

$$S_u = \left(\frac{36\pi x^2 v_b^2}{M} \right)^{-1/3} v_u \frac{dx}{dt} \quad (3.2.5.3)$$

where dx/dt is evaluated numerically. Again the conservation equations relate v_u , v_b , and x to the experimentally determined pressure. Though the data reduction is algebraically simple, the evaluation of Eq. 3.2.5.3 poses problems.

A typical evaluation of the mass fraction of burned gases, x , versus pressure along the isentrope appears in Figure 3.2.5.1. As seen in Figure 3.2.5.1, and substantiated by Lewis and von Elbe using analysis, x is nearly linearly proportional to the change in pressure from its initial value.⁷⁴

The linear relationship between x and P is only approximate, and for our calculations we always relate these two variables through the conservation equations (Eq. 3.2.3.5 - 3.2.3.7). However, this simplified relationship is useful for clarifying the problems posed in evaluating Eq. 3.2.5.3. In mathematical terms,

$$x = \frac{P - P_i}{K} \quad (3.2.5.4)$$

where P is the instantaneous pressure, P_i is the initial pressure, and K is approximately the difference between the initial and final pressure. Substituting for x ,

$$S_u = \left(\frac{36\pi (P - P_i)^2 v_b^2}{MK^2} \right)^{-1/3} v_u \frac{dP}{dt} \quad (3.2.5.5)$$

The equation can be further reduced by noting that

$$v = \frac{1}{\rho} = \frac{RT}{MP}$$

which, when substituted, gives a final expression for burning velocity,

$$S_u = \frac{RT_u \frac{dP}{dt}}{M_b P} \left(\frac{36\pi (1 - P_i/P)^2 R^2 T_b^2}{MK^2 M_u^2} \right)^{-1/3} \quad (3.2.5.6)$$

Thus burning velocities are evaluated from the initial mixture characteristics and the variables T_u , T_b , M_b , and P . A value for T_u is specified by the law of isentropic

Figure 3.2.5.1 Mass of burned gases, normalized by the mass of the mixture, as a function of pressure for isentropic combustion of CH_4/air .

compression; values for T_b and M_b are assigned from thermochemical equilibrium stipulations; and the pressure is measured.

While the problem is clearly well-posed, we must also consider sensitivity aspects. For example, the definition of S_u will not be reliable at very early times, where the pressure change is small; the equations indicate this constraint, since for short times

$$\frac{dP}{dt} \rightarrow 0$$

$$(1 - P/P_b) \rightarrow 0$$

Due to the reciprocal scaling on $(1 - P/P_b)$ in the formula, S_u is indeterminate under such circumstances.

Most importantly, the modeling shows that burning velocities can be inferred from the pressure trace, but that the evaluation of burning velocity requires taking the time-derivative of the transient pressure record. In fact this differentiation is a necessary step of all bomb studies based on pressure measurements. The differentiation of experimental data is often problematic since it tends to greatly amplify the inherent noise.

We avoided noise problems by fitting a smoothing spline to the data, and then evaluating the derivative of the spline. Thus, we removed the noise before evaluating the derivative. Of course, when smoothing experimental data it is necessary to use caution in order not to remove important information with the noise. A feature of our software package⁸¹ allowed us to adjust the amount of smoothing, and we tested various levels of smoothing to validate our procedure. Figure 3.2.5.2 shows a noisy curve for which no smoothing is used. A second curve has been added with smoothing, and it is apparent from the figure that the noise has been removed from the smoothed curve while retaining good agreement with the unsmoothed curve. The sudden drops in burning velocity at high pressures are caused by heat loss to the bomb walls, which becomes significant toward the end of the experiment. The impact of heat loss will be discussed in the next section. Figure 3.2.5.2 also shows a third curve which was generated by fitting a low order polynomial to the data. Obviously, this fitting method is not successful.

Effect of the fitting method on the inferred burning velocities for the combustion of a stoichiometric CH_4/air mixture. For an exact fit of the data, the calculated velocities are very noisy. For a suitable amount of smoothing, the resulting curve still agrees well with the noisy curve, except that the noise is eliminated. The line shown which deviates significantly from the noisy curve was determined by using a low order polynomial to fit the data. Clearly, polynomial fits are not suitable.

Figure 3.2.5.2

3.2.6 Procedure for Determining Bounds of Valid Portions of Pressure Trace

Only the intermediate part of the pressure trace from each run can be used to determine burning velocities. As explained in the last section, the resolution of our pressure measurement is a factor during the first moments of flame propagation, and heat losses come into play during the last half of each run. Consequently the set of valid isentropic conditions actually accepted for each run is substantially smaller than the range of conditions for a run. But preheating and pressurization can overcome these limitations.

A series of runs can generate burning velocities along isentropic conditions which are much broader than those accepted for any particular run, provided that the initial conditions of a succeeding experiment lie on the isentrope of a previous one. The first run in the series uses the lowest temperature and pressure; the next run starts with a mixture near the highest temperature and pressure accepted from the previous run. Hence, the second run is a continuation of the first, in so far as the same isentropic relation is maintained throughout the sequence of experiments. The number of segments used to map out any particular isentrope is limited only by the pressure and temperature limits of the apparatus.

An illustration of this procedure is seen in Figure 3.2.6.1 for a stoichiometric mixture of methane and air. Here three runs were used to cover the isentrope which begins at room temperature and 0.7 atm.; the pair of symbols on each curve delineate the range of valid data for each run as explained below. The large oscillations at the beginning of each run are due to inadequate resolution in our pressure measurement, while burning velocities rapidly decay to zero at the end of each run because of heat losses to the wall.

The initial conditions for the second and third runs were set to maintain the same isentrope by preheating the entire bomb in an oven, and increasing the initial pressure. The initial conditions for the third run were deliberately kept close to those for the second, to illustrate the reproducibility. The agreement is acceptable, in that the maximum deviation is only about 4% of the measured values. Most importantly, even with the large overlap in this study, only three runs are needed to span a pressure range of 10 atm and a temperature range of 300 K.

The beginning of the valid region of each curve is based on the resolution of the pressure transducer, albeit indirectly. As seen in Figure 3.2.6.1, the least value of pressure in the acceptable data is at least half an atmosphere above the initial

Figure 3.2.6.1 A series of runs to determine the laminar burning velocity at constant entropy for a wide range of temperature and pressure. A stoichiometric mixture of CH_4 and air was combusted at initial conditions of 0.7 atm and 298 K (dotted line); 1.74 atm and 383 K (solid line); and 2.5 atm and 424 K (dotted line). The valid data for the dashed line lie between the circles. The squares and triangles delineate the valid data from the second and third experiments.

pressure. Yet the minimum resolution in our pressure measurement, as imposed by the 12 bit A/D convertor, is only 0.00664 atm. Rejection of higher pressure data is tied to the fact that the burning velocity is proportional to the first derivative of pressure, and this criterion is far more demanding than the absolute measurement uncertainty. The minimum resolution in the first derivative imposed by the A/D convertor is the minimum resolution in the pressure divided by the time between samples. We have chosen the positions of the symbols in Figure 3.2.6.1 to represent the points at which the pressure change between samples exceeds 5 times the minimum resolution of the pressure measurement. This choice results in a first derivative which is within 1 in 5, or 20 %, of its correct value. Thus the error range is ± 10 %, resulting in a maximum 10 % error in burning velocity.

The high end of the range of valid data is assigned to eliminate the effects of heat losses. The theory of flame propagation in a closed vessel under isentropic conditions predicts that the burning velocity should increase continuously throughout a run, due largely to the compression heating of the unburned gases. The measurements in Figure 3.2.6.1, however, demonstrate that heat losses drastically decrease the burning velocities during the later stages. The maximum burning velocity occurs where these two competing effects are balanced, and should in fact be a reasonable indicator of when heat loss becomes important. However, analysis also shows that the rate at which the burning velocity increases (i.e. the slope of the burning velocity-time curve) should also increase during the entire experiment. Of course the slope of a smooth curve must reach a maximum and begin to decrease well before that curve passes through its maximum. Consequently, a more accurate estimate of the onset of heat losses is where the first derivative of burning velocity reaches a maximum. The symbols in Figure 3.2.6.1 were defined in this way, and therefore do not coincide with the maximum burning velocities.

3.3 Sensitivity Calculations

The sensitivity calculations discussed here were made for single-fuel mixtures, since the properties of these mixtures are well known.

3.3.1 Changes in Mixture Stoichiometry

Due to the concentration dependence in the heat release rates, rise times for the pressure trace vary widely over the relevant range of the equivalence ratios. Computed pressure traces for equivalence ratios of 0.8, 1, and 1.3 for methane-air mixtures are shown in Figure 3.3.1.1. The minimum rise time is 40 msec for a stoichiometric mixture, while the pressure transient extends over 80 msec for the rich mixture. The ultimate pressure in the vessel is also a maximum for the stoichiometric mixture. This behavior is not a direct influence of the combustion kinetics; rather, the maximum flame temperature for the stoichiometric mixture results in the greatest compression.

This interpretation is based on the results in Figure 3.3.1.2, where the speed of the propagating flame (dR/dt) is compared to the burning velocity of the mixture (S_u). For the equivalence ratios considered, the flame propagates at a much higher speed than its associated burning velocity. In the laboratory reference frame, the flame speed is the sum of the burning velocity (i.e., the speed at which a flame moves in a quiescent gas, indicative of the balance between the heat release rate and heat conduction) and the radial velocity due to the compression of the unburned gases (which is a convective velocity). We were initially surprised at the disparate magnitudes of these two terms, and concerned that the transient pressure is insensitive to the burning velocity.

But the convective velocity due to the compression is also proportional to the burning velocity, because heat release is driving the compression. Formally, we found that the propagation speed is directly proportional to the burning velocity, according to

$$\frac{dR}{dt} = \left(\frac{S_u}{v_u} \right) \left(v_b + x \frac{dv_b}{dx} \right) \quad (3.3.1.1)$$

This relation is further demonstrated by the results in the next section.

Figure 3.3.1.1 Simulated pressure traces for CH₄/air mixtures with equivalence ratios of 0.8, 1.0, and 1.3.

Figure 3.3.1.2 Flame propagation speeds (dR/dt) and burning velocities (S_u) for the three CH_4/air mixtures of Figure 3.3.1.1.

3.3.2 Effect of Varying Burning Velocity

To further investigate the sensitivity of the pressure traces to burning velocity, we simulated stoichiometric methane/air combustion for three independent burning velocity correlations. As shown in Figure 3.3.2.1, in two of the correlations, the burning velocities at 1 atm are similar but the velocities at elevated pressures diverge, while in two others, the burning velocities at 1 atm are appreciably different, but the burning velocities converge for higher pressure.

The simulated pressure traces for each burning velocity correlation appear in Figure 3.3.2.2. The pressure trace is indeed sensitive to the burning velocity. It appears that the induction time is most sensitive to the burning velocity at 1 atm, and this influence displaces the rising pressure trace over a time interval which can be measured accurately. Comparing the results for the correlations of Perlee et al.⁶⁸ and Bradley and Mitcheson⁸², the effect of their disparate burning velocities at 1 atm outweighs their comparable burning velocities at higher pressure. Conversely, for the results for the correlations of Garforth and Rallis⁸³ and Bradley and Mitcheson⁸², the computed pressure traces are similar because the burning velocities at 1 atm are similar, but the disparate velocities at higher pressures are not apparent in the pressure traces. These results are in accord with a well-known guideline for measuring burning velocity in combustion bombs: The initial portion of the pressure trace is most sensitive to burning velocity.⁷⁴

3.3.3 Comparison of the Simulation of Two Different Fuels

The previous simulations of methane combustion illustrate the behavior of a relatively slow-burning hydrocarbon. We also simulated benzene combustion to ensure adequate time resolution for faster burning fuels. These simulations are based on a burning velocity correlation reported by Babkin et al.⁷¹ Figure 3.3.3.1 compares the pressure traces for stoichiometric benzene-air and methane-air mixtures. The corresponding burning velocity correlations are shown in Figure 3.3.3.2. Both the greater combustion exotherm and the faster burning velocities for benzene combustion account for the higher ultimate pressure and the shorter rise time in the benzene pressure trace. Notwithstanding, resolving such traces in the laboratory is feasible.

Figure 3.3.2.1 Burning velocity correlations for stoichiometric CH_4/air mixtures, as determined experimentally by three groups of researchers.

Figure 3.3.2.2 Simulated pressure traces for the burning velocity correlations given in Figure 3.3.2.1.

Figure 3.3.3.1 Comparison of simulated pressure traces for stoichiometric mixtures of C_6H_6 and CH_4 with air.

Figure 3.3.2.2 Burning velocity correlations for the pressure traces of Figure 3.3.3.1.

3.3.4 Effect of Varying Diluent

The results given above illustrate the intrinsic rise times and ultimate pressures for various fuel-air mixtures. While hydrocarbon-air combustion is clearly compatible with our instrumentation, changing the diluent concentration is the most expedient way to tailor the pressure traces to the instrumentation (since the bomb size and equivalence ratios are fixed).

Simulations were prepared for $\text{CH}_4/\text{O}_2/\text{N}_2$ in which the methane and oxygen were held in stoichiometric proportions while the proportions of nitrogen and oxygen varied; results shown are for $\text{N}_2:\text{O}_2$ of 3.76 (value for air), 5, and 7. Pressure traces appear in Figure 3.3.4.1; propagation speed in Figure 3.3.4.2; and burning velocities in Figure 3.3.4.3. Increasing the amount of diluent decreases the reaction rate, resulting in dramatically reduced rise times but similar ultimate pressures (Figure 3.3.4.1). As seen in Figures 3.3.4.2 and 3.3.4.3, the flame propagation speeds and burning velocities fall by 80 % for this range of diluent concentrations.

The addition of diluent clearly extends the time resolution in the pressure measurement. However, there is a limitation to this strategy. Buoyancy effects, which tend to elevate the propagating flame and distort its shape, become more pronounced as the burning velocity decreases; its influence is documented for CO combustion.⁷⁴ Using flame ionization detectors on the bomb walls to monitor the sphericity of the flame, we identified the maximum allowable diluent during the characterization of our experiments, as discussed in Section 4.4.

3.3.5 Effect of the Specific Heat at Constant Pressure of the Mixture

The sensitivity of the pressure traces to the burning velocity has already been illustrated above. However, since the impetus for flame propagation is heat release, thermophysical properties as well as reaction rates are important. The internal energy of the combustion products is adequately evaluated from the approximate thermodynamic equilibrium model discussed in Section 3.2.4. But the internal energy of the unburned gases is sensitive to the specific heat and heat of formation, and these values are not well known for coal tar.

Simulations for methane-air combustion with very large variations in values of c_p (best estimate, 100% increase, and 1000% increase) appear in Figures 3.3.5.1, 3.3.5.2, and 3.3.5.3. Even for such large variations, the pressure traces are insensitive

Figure 3.3.4.1 Simulated pressure traces for stoichiometric CH_4/air mixtures with various levels of dilution. $\text{N}_2/\text{O}_2 = r$.

Figure 3.3.4.2 Propagation speeds (dR/dt) for the simulations of Figure 3.3.4.1.

Figure 3.3.4.3 Burning velocities for (S_u) for the simulations of Figure 3.3.4.1.

Figure 3.3.5.1 Simulated pressure traces for stoichiometric CH_4/air combustion with parametric variations in the specific heat of the unburned gas.

to the specific heat (Figure 3.3.5.1). However the final burning velocity changes by 10 and 30 % for the 100 and 1000 % increases in c_p , respectively (Figure 3.3.5.2). This influence is due entirely to the impact of specific heat on the unburned gas temperature, shown in Figure 3.3.5.3, which is rooted in the law of isentropic compression. While such large variations in the specific heat of methane might at first seem unwarranted for this sensitivity study, it should be pointed out both that the specific heats (on a molar basis) of the high molecular weight tars are as much as one to two orders of magnitude larger than that of methane (see section 3.4.2), and that the specific heats of tars have never been measured, and are thus very uncertain. A closer examination of the influence of the specific heats of tars is warranted, and the next sections discuss the assignment of heats of formation and specific heats for tars, and explore the influence of uncertainties in those assigned values on computed burning velocities.

3.4 Adaptation of the Computer Analysis for Inclusion of Tars

Tars are obviously difficult to handle in the laboratory, and their ill-defined chemical constitution and broad molecular weight distribution also present problems in the inference of laminar burning velocity from the transient pressure measurement during flame propagation. In particular, the analysis requires the enthalpy of the fuel mixture, expressed in terms of the heat capacity at constant pressure and the standard heat of formation of the fuel components. Of course, the elemental composition of the fuel mixture and the fuel equivalence ratio are also required to assign the heat release.

The thermochemical data are readily available for noncondensable gases, and we have developed the chromatographic procedures to identify the compositions of such gases. In contrast, we have not found the required thermochemical data for pyrolysis tars in the literature, although studies of synthetic coal liquids have appeared recently.¹⁶ Furthermore, tars comprise so many different compounds that it is impossible to classify them in terms of the concentrations of individual species. We do, however, have the facilities to measure molecular weight distributions in this laboratory.

We resolved these ambiguities with sensitivity studies to establish the impact of the uncertain thermophysical properties on the inferred burning rates, as explained in the three sections which follow. Then a strategy to assign the fuel equivalence ratio with chromatographic analysis of the combustion products is discussed.

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3.4.1 Heats of Formation and Specific Heats of Tars

The heat of formation and specific heat of the tars produced by flash pyrolysis have never been determined. Even though we can generate pure pyrolysis tar in this laboratory, the time to experimentally assign the properties in a bomb calorimeter, even if limited to a single coal and a small range of the parameter space for pyrolysis (i.e. heating rate, final temperature, and residence time) would be considerable. So we adopted an analytical tact. Limits on the property values were estimated from group additivity methods, and the simulations based on the extreme values were evaluated for sensitivity.

We used the simplest form of group additivity developed by Benson et al.⁸⁴ As its name suggests, the method develops the properties of complex molecules in terms of additive contributions from the characteristics of its constituent functional groups. The contributions to specific heat or heat of formation for each group are then summed to determine these quantities for the molecule. Then small correction factors are added when certain functional groups are in close proximity. The contributing factors have been determined and tabulated for a large number of groups as a function of temperature.

As an example, benzene is composed of six carbon atoms located in an aromatic ring, each of which is attached to a hydrogen atom. Thus the functional group notation for benzene is $6(\text{C}_\text{B}(\text{H}))$, where C_B denotes an aromatic carbon, and the estimated specific heat at 300 K is $6(3.24) = 19.44$ cal/moleK. This compares favorably with the experimental value of 19.65 cal/moleK.

We proceed toward larger molecules by estimating the specific heats of anthracene and phenanthrene. They should be the same since both molecules contain $8(\text{C}_\text{B}(\text{H}))$'s and $4(\text{C}_\text{B}(\text{C}_\text{B}))$'s, and the estimated value is 52.84 cal/mole-K. The experimental specific heats are 49.46 cal/mole-K for phenanthrene and 55.17 cal/mole-K for anthracene. Again group additivity provides a fairly accurate estimate, but it fails to distinguish between the different molecules. Obviously the different conformation of these molecules could be resolved with more refined corrections.

Extensions of group additivity from a single species to complex mixtures such as tar requires the functional group concentrations in the tar. Average functional group concentrations can be assigned from elemental analysis, proton nuclear magnetic resonance, low voltage high resolution mass spectroscopy, infrared

spectroscopy, and open column preparative liquid chromatography.¹⁶ While several researchers are characterizing the products of coal liquefaction, we have been unable to find similar results for the tars from flash pyrolysis. We therefore studied only broad classes of hydrocarbons, to assign limiting values to the physical properties.

3.4.2 Influence of Uncertainty in Specific Heat Estimation on Calculated Burning Velocities

At any particular temperature and molecular weight, the range of plausible values for the specific heats is bounded. The upper bound is based on straight-chain alkanes, while the lower bound is based on fully condensed aromatics. No hydrocarbon molecule will have a specific heat outside of these bounds. Specific heat estimates for these broad classes based on group additivity appear in Figure 3.4.2.1. We estimated that the tar produced for our studies has a number average molecular weight of about 300 to 400 g/mole, and the bounds shown in Figure 3.4.2.1 indicate a maximum uncertainty in specific heat of $\pm 20\%$.

While this predictive capability would ordinarily seem troublesome, it suffices for our purposes because the laminar burning velocities are relatively insensitive to c_p of the tar. In the sensitivity studies, we reprocessed experimental pressure histories reported in Ch. 5 for synthetic mixtures representing the volatiles from Montana lignite and Pittsburgh #8 bituminous coals. In these mixtures, various amounts of CO, CO₂, CH₄, H₂, H₂O, and C₃H₈ were added for light gases, while C₆H₆ was substituted for tar. The Pittsburgh #8 mixture was an especially good case for testing the sensitivity to tar properties because of its large proportions of tar in comparison to other coals. In this sensitivity study, the properties of benzene are replaced by the estimates for tar; since tar is highly aromatic with substantial aliphatic components, two limits are considered: paraffinic alkanes and fully-condensed aromatics. The molecular weight is also changed, from benzene's to our estimate for the mean molecular weight of tar. While the H/C ratio would also require adjustment, it turns out that the ratio for benzene is very close to the expected value for pyrolysis tar.

The laminar burning velocities for the Pittsburgh #8 volatiles inferred for the limiting values of c_p appear in Figure 3.4.2.2. Note that the maximum variation in the calculated laminar burning velocity is only 2 %. Consequently, any value for c_p within the predicted range is satisfactory, because the variation is within the variations due to other experimental uncertainties.

Figure 3.4.2.1 Bounds on the specific heat of hydrocarbons, as estimated by functional group additivity at 300 K.

Figure 3.4.2.2

Effect of uncertainty in the specific heat of tar on laminar burning velocity for a mixture of simulated bituminous volatiles in air. The burning velocity is plotted as a function of pressure for isentropic combustion of the volatiles. Note that the maximum deviation is 2 %.

Actually, the insensitivity to c_p is easy to rationalize. From a physical standpoint, c_p is a measure of the energy required to raise a mole of tar by one degree. Since c_p for tar is relatively large, it would seem that a large amount of energy is required to raise the temperatures of mixtures which include tar. Due to tar's high molecular weight, however, the molar concentrations of tar in the reactant mixture are very small, and its contribution to the thermal capacitance of the mixture is diminished considerably.

3.4.3 Influence of Uncertainty in Heat of Formation Estimation on Calculated Burning Velocities

Just as limiting values of the specific heat of coal tar were based on straight-chain alkanes and pure aromatics, these two molecular classes bound the possible values of the heat of formation of tar. In contrast to the narrow range for specific heat, however, the limiting values of the heat of formation are not tightly bounded. As seen in Figure 3.4.3.1, at the average molecular weight of the tar (which we approximated as about 350 g/mole), the limiting values are +140 and -140 kcal/mole, a range which is considerably wider than the entire range of values expected for all other pyrolysis and combustion products.

Nevertheless, the impact of this range on the burning velocities is marginal. As in the sensitivity study of specific heats, we substituted the upper and lower bounds of the heat of formation for that of benzene, and again reprocessed the experimental pressure transient for the simulated pyrolysis gases from the Pittsburgh #8 coal. The limiting burning velocities appear in Figure 3.4.3.2, and show a maximum variation in calculated burning velocity no greater than 4 %. Thus while the heat of formation is highly sensitive to the composition of the tars, the calculations for laminar burning velocity are almost independent of the tar heat of formation.

Here again, the proportions of sensible and chemical energy rationalize the insensitivity. The burning velocities are sensitive to the temperature of the products, which is much more sensitive to the heat of combustion than the heats of formation of the reactants. This is especially true of coal tar because the mole change in the global combustion reaction is very large. At first this statement may appear deceptive, since the heat of combustion for a fuel is defined as the difference between the heats of formation of the products and reactants at complete combustion. However, by our estimates every mole of tar burned produces 24 moles of CO_2 and 12 moles of H_2O , so that the total heat of formation of the products is about 2800 kcal/mole at 300 K.

Figure 3.4.3.1 Bounds on the heat of formation of hydrocarbons, as estimated by functional group additivity at 300 K.

Figure 3.4.3.2

Effect of uncertainty in the heat of formation of tar on laminar burning velocity for a mixture of simulated bituminous volatiles in air. The burning velocity is plotted as a function of pressure for isentropic combustion of the volatiles. Note that the maximum deviation is 4 %.

Subtracting ± 140 kcal/mole for the reactants from 2800 kcal/mole for the products yields a variation in the heat of combustion of only $\pm 5\%$. Consequently, the heat of combustion of coal tar is almost independent of its heat of formation. Incidentally, this argument implies that experimental determinations of the heat of formation of coal tar based on the heat of combustion are subject to very large uncertainties.

3.4.4 Gas Chromatography of the Combustion Products as a Method for Determining the Required Tar Information

The inference of burning velocities from measured pressure histories also requires values of the fuel equivalence ratio of the mixtures. We determine the concentrations of noncondensibles in the mixture with gas chromatography. The elemental compositions of tar are now routinely measured in our laboratory, and the method to assign tar MWD's is in the final stages of development. However, since the chemical constitution of the volatiles mixture is so complex, the mixture composition will always be subject to considerable uncertainty. In this section a strategy based on the much simpler chromatographic analysis of the combustion products is developed to assign the equivalence ratio of the mixture.

The strategy simply recognizes that the elemental proportions of products and reactants are necessarily the same, and the product distribution is especially simple when oxygen is abundant. We will first characterize the products of fuel lean combustion, for which the major products are CO_2 , H_2O , O_2 , and NO . The chemical analysis of a specific product mixture defines the stoichiometry for that run.

While the strategy is straightforward there are of course complications in its implementation. Only the proportions of the product species, not the absolute amounts, are assigned from the chromatographic analysis. We must therefore develop a sampling procedure, and a relation among the proportions and the total amounts of all species.

The combustible mixture is doped with a known amount of an inert tracer, such as Krypton. After combustion, a small sample of the gases will be recovered in a multiport sampling valve which is heated to avoid condensation of H_2O . The sample can then be injected into the GC to assign the relative concentrations of H_2O , CO_2 , O_2 , NO , and Kr . Since a known amount of Kr was added to the reactants, and since Kr is inert, the amounts of all product species can be determined. Once these are known, the atom populations of C, H, and O in the reactant mixture are also specified.

An important proviso for this procedure is that all of the major combustion products must be analyzed. Of course, for fuel lean combustion to temperatures below about 2200K, the products listed above are the only major species. But the ultimate temperatures in the bomb studies are much higher, and dissociation is an important consideration. Immediately after combustion the products will typically be at approximately 3500 K and 10 atm. The temperature is unusually high because of the isentropic compression of the products at constant volume. At this temperature and pressure, dissociation overrides the influence of equivalence ratio, so that H_2 , CO, and many of the radicals will be present in substantial amounts. Representative compositions based on thermochemical equilibrium calculations appear in Table 3.4.4.1.

Table 3.4.4.1. Mole Fractions at 3500 K and 10 atm for species in chemical equilibrium. Atom populations are approximately those for combustion of the pyrolysis gases from a Bituminous coal in air. Due to STANJAN, a chemical equilibrium solver developed by Professor Reynolds of Stanford University.

Species	Mole Fraction
CO	9.99e-2
CO ₂	3.80E-2
H	1.96E-2
OH	2.80E-2
H ₂	1.12E-2
H ₂ O	3.40E-2
NO	3.13E-2
N ₂	6.74E-1
O ₂	3.48E-2

Immediately after combustion, the gas cools rapidly by heat transfer to the bomb walls and H_2 , CO, and the radicals recombine into stable species, primarily H_2O and CO_2 . If the cooling occurs too rapidly, though, the high concentrations of CO and H_2 will "freeze out" (i.e. the recombination rate will become so low that the concentrations will remain at their superequilibrium values). Clearly chemical kinetics factor into the ultimate product compositions.

To identify the ultimate species for the GC analysis, we conducted kinetic simulations for a mixture of gases with approximately the same C:H:O:N ratios as coal volatiles in air (based on Suuberg's data).⁸ The kinetic mechanism consisted of the 39 chemical reactions and 18 chemical species given in Table 3.4.4.2. It was simulated using the CHEMKIN kinetics package developed at Sandia National

Laboratory.⁸⁵ The cooling process was modeled as constant volume using an exponential decay in temperature from 3500 K to 550 K. The time constant for cooling was estimated from the measured pressure decrease after combustion in our experiment; its base value is 0.12 s and, to be conservative, we also conducted calculations for a cooling time constant of 0.01 seconds. The initial concentrations were assigned from chemical equilibrium at 3500 K and 10 atm. Spatial variations were neglected.

Figure 3.4.4.1 shows the transient variation in concentration associated with the longer time constant. The equilibrium values at two instants in the cooling cycle also appear along the two vertical dashed lines. Note by comparing the transient and equilibrium values that NO, CO, and H₂ are frozen at superequilibrium values, especially near the end of the cooling cycle. Notwithstanding, for both cases the frozen levels of CO and H₂ are 2 to 4 orders of magnitude lower than those of the major species. We conclude that the elemental proportions of the reactant mixture can be based on the straightforward analysis of the products of lean combustion, and that only the amounts of CO₂, H₂O, O₂, NO, and Kr must be considered.

Table 3.4.4.2. Reactions and Species considered for rapid cooling of the products of combustion. Products are initially in equilibrium at 3500 K and 10 atm.

SPECIES	
CO CO ₂	
H ₂ H OH H ₂ O HO ₂ H ₂ O ₂	
O ₂ O	
N ₂ N NO NO ₂ N ₂ O HNO HONO HNO ₃	
REACTIONS	
H ₂ +O ₂ =2OH	N+O ₂ =NO+O
OH+O=H+O ₂	N+OH=NO+H
O+H ₂ =OH+H	NO+N=N ₂ +O
OH+H ₂ =H ₂ O+H	NO+OH+M=HONO+M
OH+OH=O+H ₂ O	NO+HO ₂ =NO ₂ +OH
H+OH+M=H ₂ O+M	NO ₂ +H=NO+OH
H+O ₂ +M=HO ₂ +M	NO ₂ +O=NO+O ₂
HO ₂ +OH=H ₂ O+O ₂	NO ₂ +OH+M=HNO ₃ +M
HO ₂ +H=2OH	NO ₂ +H ₂ =HONO+H
HO ₂ +H=H ₂ +O ₂	NO ₂ +M=NO+O+M
HO ₂ +O=O ₂ +OH	NO ₂ +NO ₂ =NO+NO+O ₂
HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	N ₂ O+H=N ₂ +OH
H ₂ O ₂ +M=OH+OH+M	HNO+M=H+NO+M
H ₂ O ₂ +H=HO ₂ +H ₂	HNO+OH=NO+H ₂ O
H ₂ O ₂ +H=H ₂ O+OH	HNO+H=H ₂ +NO
H ₂ O ₂ +OH=H ₂ O+HO ₂	CO+O+M=CO ₂ +M
H ₂ O ₂ +O=HO ₂ +OH	CO+OH=CO ₂ +H
H ₂ +M=H+H+M	CO+O ₂ =CO ₂ +O
O ₂ +M=O+O+M	HO ₂ +CO=CO ₂ +OH
H+O+M=OH+M

Figure 3.4.4.1 Constant volume cooling of a well-stirred mixture. Initial conditions are equilibrium at 3500 K and 10 atm. The temperature follows a negative exponential from 3500 to 550 K with a time constant of 0.12 seconds.

4. Characterization Experiments for the Constant Volume Combustion Bomb

4.1 Introduction

We have performed extensive characterization experiments with single-fuel mixtures to confirm our implementation of the apparatus, as discussed in Chapter 2, and the analysis, as discussed in Chapter 3.

The simplest test of the apparatus is a direct comparison of raw pressure measurements with reported data. Comparisons were made for 5 different fuel/air mixtures (the fuels were H_2 , CO , C_3H_8 , CH_4 , and C_6H_6), and the agreement was quite good for all fuels. The ability to reproduce pressure traces from several other experimental programs offers strong support for the correctness of our measurements.

The measurements were also tested against theoretical calculations. Ultimate pressures (i.e. pressures just after the completion of combustion) were compared to theoretical estimates for the combustion products in thermochemical equilibrium. The fast-burning mixtures agreed quite well with theoretical estimates; but the deviations in the slower burning mixtures were probably due to a combination of radiative heat loss from the combustion products and buoyant distortion of the flame.

The radiant heat losses only become significant near the end of combustion as discussed in Chapter 3. But buoyancy degrades the entire pressure trace. To verify that the flame remains undistorted by buoyancy, we have constructed and installed ion gages which detect the approach of the flame front. Buoyant levitation of the flame is indicated when the upper gages are activated before the lower one. Tests with methane/air confirmed this detection method.

After confirming our pressure measurements, we proceeded to evaluate the analytical scheme which reduces pressures to laminar burning velocities. Again, the most simple test was a direct comparison between the burning velocities from the analysis and reported burning velocity correlations. The overall agreement was very good, and the analysis is sound. We also tested the sensitivity model discussed in Chapter 3, by comparing simulated pressure traces generated from burning velocity correlations with actual measurements. These tests show that the sensitivity model predicts the pressure traces quite well.

A unique feature of the combustion bomb is its capability for measuring burning velocities over wide ranges of temperature and pressure. We tested our abilities in this respect by producing burning velocity correlations for CH_4/air and $\text{C}_6\text{H}_6/\text{air}$ combustion. While we were unable to find C_6H_6 correlations to compare our results with, the CH_4 correlation agreed very well with that of Metghalchi and Keck.

The presence of light oils and condensible tars in the volatiles greatly complicates the fuel handling tasks in our apparatus. If the constant volume bomb and the transport lines for the volatiles are not maintained at a high enough temperature, the tars will condense. On the other hand, if the temperature of the bomb is too high, the tars, which are thermally less stable than the permanent gases in the volatiles, will tend to pyrolyse. We tested our tar handling abilities by transporting volatiles containing tar vapors to the heated bomb, and monitoring the pressure in the bomb over a long period of time to assure that no secondary pyrolysis was occurring. These studies confirmed that it is possible to transport tar vapors without significant condensation or pyrolytic cracking.

The following sections discuss our characterization experiments in detail.

4.2 Physical Characteristics of the Experimental Pressure Traces

Pressure traces for hydrogen, benzene, and methane combustion appear in Figure 4.2.1, illustrating features common to all mixtures. The rate of pressure increase is extremely slow during the initial stages. Although this feature resembles an ignition delay, in this system it is a consequence of the spherical geometry alone. Midway through the process, the pressure begins to rise exponentially, then reaches its ultimate value. The rapid pressure oscillations which occur when combustion is nearly complete, which are especially noticeable in the case of H_2 combustion, are routinely observed with fast-burning mixtures. Although they have been discussed, no satisfactory explanation for them is yet available.⁷⁴ The slowly decreasing pressure after quenching at the walls indicates cooling of the burned gases.

Both the time scale for flame propagation and the ultimate pressure vary significantly with the burning velocity. The maximum burning velocities in air for H_2 , C_6H_6 , and CH_4 are 291, 45, and 37 cm/s, respectively. So the longer times to achieve the ultimate pressures from these fuels, from 14 to 36 to 48 ms, respectively, are a clear indication of progressively lower burning velocities. However, the variation in time constants for the transient pressure is clearly not directly

Figure 4.2.1 Transient pressure measurements for the combustion of stoichiometric CH_4/air (dotted line), $\text{C}_6\text{H}_6/\text{air}$ (solid line), and a fuel-lean mixture of 20% H_2/air (dashed line).

proportional to variations in the burning velocities. In particular, the high burning velocity of hydrogen is not manifest in the pressure trace by a proportionate reduction in the duration of the experiment.

The time scale in the pressure trace represents two factors: the speed of laminar flame propagation and the outward movement of the unburned gases due to the isentropic compression. As discussed in the previous chapter, both factors are proportional to the burning velocity because the heat release is driving the compression. Consequently the heat release of a mixture affects this time scale. The relatively low energy release from hydrogen mixtures accounts, in part, for the relatively long time scale in this pressure trace.

The isentropic compression affects the time scale in two additional ways, by increasing the temperature and pressure of the unburned gases throughout an experiment. For all fuels, gas preheating increases the burning velocity; this influence is pronounced for mixtures with relatively low adiabatic flame temperatures. But the effect of pressurizing the reactants varies widely for different fuels and, generally speaking, increased pressure may increase or decrease the burning velocity. The burning velocities of hydrogen increase substantially with increasing pressure, while those for methane decrease slightly.

We were surprised to find that the ignition energy can also alter the time scale for flame propagation. As demonstrated in the following section, above a threshold energy level, the time scale decreases monotonically with increasing ignition energy. In so far as this effect is unrelated to normal flame propagation, it is a potential artifact of combustion bomb studies. But it is easy to eliminate, by using moderate ignition energies.

In summary, all of the information pertaining to the combustion rate is conveyed by the evolution of the pressure in time. Since the unburned gases are compressed throughout, burning velocity correlations as functions of instantaneous temperature and pressure can, in principle, be inferred from each pressure trace. In other words, the durations of the experiment for different fuels will reflect variations in the burning velocities at atmospheric pressure, as well as the responses to variations in the pressure and temperature of the unburned mixture. Consequently, the apparent time scale is not directly proportional to the burning velocity.

4.3 Direct Comparisons of Transient Pressure Measurements

Although combustion bombs have been used for decades, only a handful of actual transient pressure records have been reported. Most reported data have already been reduced to burning velocities. We duplicated several of these cases to validate the accuracy of our pressure measurement, and present these comparisons in this section.

Of course bombs of various sizes have been studied, and the radius of the bomb factors into the apparent time scale for flame propagation. Fortunately the results from bombs of different sizes are self similar, and can be rescaled for comparison on the basis of a prescribed size as follows:

$$t_{\text{rescaled}} = t_{\text{apparent}}(r_{\text{comparative}}/r_{\text{actual}}) \quad (4.3.1)$$

where r_{actual} and t_{apparent} are the reported radius and time history, respectively, and $r_{\text{comparative}}$ and t_{rescaled} are the corresponding quantities for comparison with our results. For example, the results from a 12 in. bomb should be identical with those from our 6 in. bomb if the measured time history from the 12 in. bomb is reduced by a factor of one-half.

Rescaled pressure measurements for combustion of 20% H_2 in air in a 12 in. diameter bomb appear in Figure 4.3.1.⁷⁴ Based on the rescaling to our 6 in. bomb, these results indicate that the ultimate pressure of 97 psi is achieved in about 12 msec. Our record for this case, which is included in Figure 4.3.1, indicates that the ultimate pressure of 97 psi is reached in about 14 ms.

Garforth reported transient pressure data for the combustion of stoichiometric CH_4/air in a 6.3 in. bomb.⁸⁶ His rescaled data appear with the results of this study in Figure 4.3.2. Although these traces are in general agreement throughout, two aspects may be regarded as irregularities. First, Garforth's time scale is roughly 3 ms longer during the later stages of combustion. Second, Garforth's ultimate pressure is 135 psi, versus 124 psi in this study. However, 135 psi is also higher than that predicted for adiabatic, constant volume combustion after the mixture has achieved thermodynamic equilibrium, which is impossible. As discussed below, the slower rise time and lower ultimate pressure are probably due to an uncertain mixture composition. Bear in mind that these discrepancies are not large; the percentage deviations in final pressure and time history are only 4 and 6%, respectively.

Figure 4.3.1 Pressure measurements for the combustion of 20 % H₂/air. Our measurements appear as the solid line, while the measurements of Lewis and von Elbe⁷⁴ are indicated by the circles.

Figure 4.3.2 Comparison of our pressure measurement (curve) for stoichiometric CH_4/air combustion with the measurement of Garforth (circles).⁸⁶

Flock et al.⁷³ reported a partial transient pressure measurement for combustion of benzene in a 10 in. bomb, which has been rescaled for comparison with our results in Figure 4.3.3. The agreement in this case is especially satisfying because the time scale for flame propagation is under 10 msec. The time scale is much shorter than in all previous cases, and the ultimate pressure is also relatively high, because the oxidizer contained less diluent than air.

Flock et al.⁷³ have also reported a pressure trace for the combustion of wet CO, which has been rescaled and compared with our results in Figure 4.3.4. The agreement is exceptional. Again, the time scale is very short because of low diluent levels, even though CO is relatively slow-burning. Incidentally, Flock et al. studied mixtures with low levels of diluent to produce bright flames and improve their photographs.

The influence of ignition energy on the time scale for flame propagation is seen in Figure 4.3.5, for a stoichiometric propane/air mixture. The data were reported by Metghalchi and Keck⁶⁶; the solid and dashed lines are our measurements for cases which differ only in their spark ignition energies. For the results in Figure 4.3.5, the ignition energies were about 20 and 120 mJ for the dashed and solid lines, respectively.

Clearly variations in ignition energy alter the time scale for flame propagation, although we have not seen any previous characterizations of this influence in the literature. These effects are always reproducible. Moreover, the traces for several ignition energies described a continuous variation in the time scales, provided that the ignition energy was higher than a threshold value. Below the threshold ignition energy, changes in the ignition energy did not affect the pressure trace. The dashed pressure record in Figure 4.3.5 depicts the time scale for cases in which ignition energy is no longer important.

We suspect that Metghalchi and Keck's results are affected by the energy input during ignition, and that our dashed pressure record is the most accurate one in Figure 4.3.5. Actually, small variations in the mixture composition would account for the small deviations in this comparison as well. In any case, the ignition energy must be kept below the threshold energy level at which its affect becomes important to avoid this artifact.

Figure 4.3.3 Comparison of pressure measurements for combustion of 4.7 % C_6H_6 in 35 % O_2 and 60.3 % N_2 . Our measurement appears as the curve, while the measurements of Fiock et al.⁷⁰ are indicated by circles.

Figure 4.3.4 Comparison of pressure measurements for combustion of 64.9 % CO in 32.4 % O₂ and 2.7 % H₂O. Our measurement appears as the curve, while the measurements of Fiock et al.⁷⁰ are indicated by circles.

Figure 4.3.5

Comparison of our pressure measurements for stoichiometric C_3H_8 /air combustion with the measurement of Metghalchi and Keck (circles).⁶³ The dashed and solid lines are for spark ignition energies of 20 and 120 mJ, respectively.

4.4 Comparison of Ultimate Pressures

We next consider comparisons among measured ultimate pressures and the pressures computed for thermochemical equilibrium of the burned gases. In actuality, the combustion products in the laboratory never reach equilibrium because there is a radial temperature gradient in the system which reduces the actual ultimate pressure below the value associated with thermochemical equilibrium. However, extensive calculations by Lewis and von Elbe for a variety of fuels indicate that the error in final pressure introduced by neglecting the temperature gradient is never greater than 1%.⁷⁴ Consequently, values of the equilibrium pressure are upper bounds on the observed values, and the deviations should be very small. The equilibrium pressures in the following comparisons were determined with STANJAN; more than 20 species are considered in each calculation.

The observed and calculated ultimate pressures for a variety of fuels appear in Table 4.4.1. At this point we focus on the equilibrium pressures determined with STANJAN, and will return to the second set of calculation results later in this section. Note that the measured pressures reliably convey the influence of fuel type throughout. And for the fuel mixtures which burn rapidly, the agreement is within one percent, as expected. But the observed pressures for the relatively slow-burning mixtures of CH_4 and C_3H_8 are 4 to 5% lower than the equilibrium values, which is too large to attribute to temperature gradients. In fact, Lewis and von Elbe tabulated these deviations for mixtures which exhibit a wide range of combustion time scales, and showed that, indeed, they become larger for mixtures which burn slowly.

Deviations of 4 to 5% are probably due to heat losses, which become more pronounced for relatively slow-burning mixtures. We expressed the deviation in pressure in terms of an enthalpy deficit, and found that it is consistent with the estimated enthalpy loss associated with the radiant flux to the walls from the hot combustion products. And for the fast-burning mixtures, the estimated heat losses are actually negligible, thereby accounting for the close agreement between the observed and equilibrium pressures. We also investigated the heat loss to the copper electrodes, by adding two additional electrodes, but observed no appreciable change.

The comparison between observed and calculated ultimate pressures also clarifies the evaluation given in Figure 4.3.2, for stoichiometric methane/air combustion. The ultimate pressure reported by Garforth is hard to rationalize, being higher than the equilibrium pressure. To stretch the point, perhaps superequilibrium concentrations of dissociated species would yield pressures higher than the

equilibrium values. It seems more likely that a mixing error, or unusual diluent or moisture concentrations account for their observation.

Table 4.4.1. Ultimate temperatures (K) and pressures (psia) for stoichiometric combustion of a variety of fuels in air, including observed and equilibrium values.

		Calculated			
	Measured	STANJAN		Design Model	
	P_{final}	P_{final}	T_{final}	P_{final}	T_{final}
CH ₄	125	129.5	2588.0	129.2	2583.0
C ₃ H ₈	131	137.3	2631.7	137.1	2626.5
C ₆ H ₆	137	138.3	2705.4	138.0	2699.7
H ₂ ^a	97	97.6	2196.9		
CO [*]	43	44.1	3154.3		

^aThe H₂ data are for a fuel-lean mixture of 20 % H₂/air.

^{*}The CO data are for a mixture of 64.87 mole % CO, 32.44 mole % O₂, 2.69 mole % H₂O.

Returning to Table 4.4.1, the third column gives the ultimate equilibrium pressures and temperatures as estimated by our design model. The comparison of these numbers with those from STANJAN is a direct test of the accuracy of Martin and Heywood's approximate equilibrium model. When we consider the simplicity of the Martin and Heywood model, and the complexity of STANJAN, the agreement seems quite extraordinary.

The impact of variations in stoichiometry on the ultimate pressures appears in Table 4.4.2. Although the measurements are in accord with the general tendencies, the quantitative discrepancies with the calculated values are larger than those for stoichiometric mixtures in Table 4.4.1. Since the burning velocity generally decreases for off-stoichiometric mixtures, the larger deviations are due to the impact of buoyancy. Buoyancy levitates the fireball and, in extreme cases, causes it to contact the upper chamber wall before the mixture is completely consumed. Such contact enhances the heat transfer from the gas, which lowers the observed final pressure. Conclusive evidence for buoyancy effects is discussed in the next section.

Table 4.4.2. Variation in ultimate pressures (psia) with stoichiometry for CH₄/air mixtures.

Equivalence Ratio	Experimental P_{final}	STANJAN P_{final}
0.7	102.0	109.3
0.8	110.0	117.7
0.9	117.5	124.6
1.0	125.5	129.5
1.1	127.0	131.7
1.3	121.5	129.7
1.4	104.0	127.5

4.5 The Sphericity of the Flamefront

Buoyancy effects reduce the ultimate pressure and, more importantly, undermine an inherent assumption in the inference of burning velocity from the pressure trace; viz., that the flamefront is spherical throughout. To identify distorted flamefronts, three ionization gages are mounted at different circumferential locations through the bomb walls. A voltage pulse is detected as the flamefront approaches the gage, and all signals are synchronized with the spark ignition signal on the microcomputer. When all gages are mounted at the same radial position, coincident signals verify a spherical flame. Conversely, the buoyant levitation of the fireball is evident when the upper gages fire before the lower one.

The gage signals and the associated pressure traces for spherical and distorted flamefronts appear in Figures 4.5.1 and 4.5.2, respectively. In these cases the gages were mounted flush with the chamber walls. The record for the stoichiometric methane/air mixture, shown in Figure 4.5.1, shows coincident signals from the ionization gages, verifying that the flamefront is indeed spherical. But buoyancy effects are observed for lower burning velocities as, for example, in the record for a rich methane/air mixture ($\phi = 1.4$) in Figure 4.5.2. Note that the duration of flame propagation in the rich mixture is nearly three times longer than for the stoichiometric mixture. And the two gages located in the upper hemisphere of the bomb fire about 30 msec before the signal from the lower gage is recorded. Clearly, the ionization signals reliably indicate distorted flamefronts.

Figure 4.5.1 An example of the ionization gage signals for CH_4/air combustion where buoyancy effects are negligible. All gages are located flush with the bomb wall. The dotted and dashed lines are signals from gages located in the upper hemisphere of the bomb, while the solid line is from a gage located in the lower hemisphere. The signal from the pressure transducer has been superposed for comparison.

Figure 4.5.2

An example of the ionization gage signals for CH_4/air combustion at an equivalence ratio of 1.4, where buoyancy effects are important. As in Figure 4.5.1, the dotted and dashed lines are signals from gages located in the upper hemisphere of the bomb, while the solid line is from a gage located in the lower hemisphere. Again, the pressure transducer signal has been superposed.

But, since the gages are mounted flush with the walls, the substantial time lags between the ionization signals and the time to reach the ultimate pressures in Figures 4.5.1 and 4.5.2 are disturbing. We found similar observations from independent studies in combustion bombs.^{62,87} We first investigated forced diffusion of ions ahead of the flame front, by changing the bias voltage and polarity of the gauges, but observed no effect. Signals due to cool flames, in the compressed mixture near the walls, were ruled out by observations of similar time delays for hydrogen mixtures. Although we still have no definitive mechanism for the time delays, our characterization studies have clarified this phenomenon.

Using the flame propagation model discussed in Section 3.3.1, the instantaneous flame position was computed from the pressure trace from a stoichiometric CH_4/air mixture. These values are compared with signals from ionization gages mounted at several radial positions in Figure 4.5.3. In the figure, the data points indicate the times when the ionization signals were recorded, while the curve shows the computed flame position. Note that, except at the wall, the flame positions inferred from the pressure trace coincide with the ionization signals, within the expected thicknesses of the flame. It is also important to realize that the time lag at the wall corresponds to a spatial separation of only 7 mm. This scaling suggests that near the wall, the flame is distorted, perhaps as a wrinkled front, rather than a planar sheet; in any case it seems to be thickened. Metghalchi and Keck have proposed that the ion gages are triggered prematurely by light from the flame (they suggest that the ion gages behave like photo diodes). While their arguments in support of this suggestion seem reasonable, they don't offer an explanation for our observation that the ion gage signals agree everywhere except at the wall. However, we will not pursue this further, because the ionization gages do reliably indicate the minimum burning velocity for which the flamefront remains spherical.

4.6 Comparison with Simulated Pressure Histories and Burning Velocity Correlations

The comparisons shown so far indicate that our pressure measurements are in general agreement with the results of previous studies, and also with constraints tied to thermochemical equilibrium. The scheme to monitor the sphericity of the flamefront is also satisfactory. In the remaining sections, we examine the laminar burning velocities assigned from the transient pressure measurements.

At first glance, the burning velocities seem to be a direct measure of the uncertainty of this experiment, in so far as laminar flame speeds for simple fuels are

Figure 4.5.3 Comparison of the instantaneous flame position determined from the measured pressure history with the firing times of the ionization gages when mounted at several radial positions in the bomb (circles). These measurements are for stoichiometric CH_4/air combustion.

well known. But as seen in Figure 4.6.1, the burning velocities assigned from combustion bomb studies are somewhat lower than those from other experimental methods. Flame stretch, preferential diffusion, and the variations in the state of the unburned gases throughout each run could account for these differences. But we have not attempted to resolve these long-standing inconsistencies between experimental methods. Instead, we have compared our measurements directly to others reported for combustion bombs.

Among the various combustion bomb studies reported in the literature, two are especially well-suited for evaluating the absolute uncertainties in our burning velocity correlations. The results of Metgalchi and Keck⁶² (M&K) and of Takeno and Iijima⁶¹ (T&I) include burning velocity correlations along isentropes which originate at STP, and a limited number of pressure measurements. Our results are evaluated first, by directly comparing the burning velocities and, second, by using reported correlations and our design computer model to simulate the pressure traces for comparison with our measurements. We focus on methane/air combustion in this report, although these investigators also studied various other simple hydrocarbon fuels.

At the outset, it is worth noting the calculation procedures used by these investigators. Metgalchi and Keck computed the pressure derivative by finite difference, calculated burning velocity with virtually the same model we use, but reported a least-squares fit of the burning velocity correlation. (We prefer to smooth the pressure trace rather than the burning velocity correlation.) Takeno and Iijima do not discuss their procedure for computing derivatives. Their model is also similar in many respects, although their energy balance is a collapsed form of the hydrodynamic equation and an energy balance (the Hugoniot equation). The explicit assumptions in their analysis are the same as the others, but we really have no way to definitively evaluate all of the potential differences.

It is also worth noting that the results of both independent studies represent correlations for large numbers of experiments. As described in Section 2.2.9, a single experiment gives burning velocities for varying temperature and pressure along a line of constant entropy. To make measurements for a wider range of temperatures and pressures, we can adjust the initial temperature and pressure in the bomb to either move to a different line of constant entropy, or move to a different starting point on the same constant entropy line. By varying their initial conditions, M&K and T&I were able to measure burning velocities for a wide range of temperatures and pressures. They then developed correlations for these measurements as functions of temperature and pressure. In the figures below, our burning velocities are the results

Figure 4.6.1

Effects of equivalence ratio on burning velocity for CH₄/air mixtures.⁵⁸ The letters indicate the method used to obtain particular curves: S, spherical bomb; B, burner; D, double kernel; and N, numerical calculation. The spherical bomb method consistently predicts the lowest burning velocities.

of single experiments, and are thus plotted along lines of constant entropy. The results shown for M&K and T&I are computed from their correlations for the pressure and temperature conditions along the same constant entropy lines.

The burning velocity comparisons for an equivalence ratio of 0.9 appear in Figure 4.6.2. For this mixture composition, the agreement among all three studies is within ten percent throughout. To pursue the comparison further, pressure traces were computed for both reported burning velocity correlations using our design model. They are compared to our measured pressure trace in Figure 4.6.3. The simulated pressure transients are somewhat faster than the measurement, but not significantly. For this mixture, both burning velocities and pressure histories are probably within the experimental and analytical uncertainties throughout.

A similar comparison for an equivalence ratio of 1.1 appears in Figures 4.6.4 and 4.6.5. In the comparison of burning velocities in Fig. 4.6.4, our results are consistent with M&K's, but about twenty percent lower than T&I's. The comparison of pressure traces for $\phi = 1.1$, in Fig. 4.6.5, shows the variations in the pressure measurements associated with the variations in burning velocity in Fig. 4.6.4. The time scale for flame propagation for T&I's results is about ten percent shorter than the other two, and the discrepancy is well beyond the experimental uncertainty.

The discrepancies with T&I's results become more systematic with the comparisons for equivalence ratios of 1.0 and 1.3, in Figs. 4.6.6 and 4.6.7. These three studies are consistent for near-stoichiometric mixtures, but T&I's results deviate substantially for the very rich mixture. Actually the discrepancies become progressively larger as the mixture composition is varied away from the stoichiometric point. Note in Fig. 4.6.7 that T&I's time scale for flame propagation is now 33% shorter than the others at $\phi = 1.3$ (cf. 10% shorter for $\phi = 1.1$ in Fig. 4.6.5). Similarly, the discrepancies in the burning velocities becomes larger for mixtures away from stoichiometric.

Of course, the validation of our results against the studies of M&K is encouraging. But since our procedures and analysis are virtually identical to theirs, we pursued the discrepancies with T&I further, by evaluating our burning velocities at nominally atmospheric pressure and temperature for various equivalence ratios against the accepted values. Our burning velocity correlations for four mixtures are collected in Fig. 4.6.8, while reported values from bomb studies for the range of flammable methane/air mixtures appear in Fig. 4.6.9. Note that the maximum burning velocity in Fig. 4.6.9 is for $\phi = 1.06$, which explains our identical results for

Figure 4.6.2 Comparison of our burning velocity measurements (triangles) to the correlations of Metghalchi and ⁵⁸ for the isentropic compression of CH₄/air at an

Comparison of our pressure measurements (triangles) to the simulated pressure traces produced by the burning velocity correlations of Metghalchi and Keck (squares)⁵⁹ and Takeno and Iijima (circles)⁵⁸ for the isentropic compression of C11/air at an equivalence ratio of 0.9.

Figure 4.6.3

Figure 4.6.4 Comparison of our burning velocity measurements (triangles) to the correlations of Metghalchi and Keck (squares)⁵⁹ and Takeno and Iijima (circles)⁵⁸ for the isentropic compression of CH₄/air at an equivalence ratio of 1.1.

Comparison of our pressure measurements (triangles) to the simulated pressure traces produced by the burning velocity correlations of Metghalchi and Keck (squares)⁵⁹ and Takao and Iijima (circles)⁵⁸ for the isentropic compression of C11/air at an equivalence ratio of 1.1.

Figure 4.6.5

Figure 4.6.6 Comparison of our burning velocity measurements (triangles) to the correlations of Metghalchi and Keck (squares)⁵⁹ and Takeda and Iijima (circles)⁵⁸ for the isentropic compression of CH₄/air at equivalence ratios of 1.0 (solid lines) and 1.3 (dashed lines).

Comparison of our pressure measurements (triangles) to the simulated pressure traces produced by the burning velocity correlations of Metghalchi and Keck (squares)⁵⁹ and Takeno and Iijima (circles)⁵⁸ for the isentropic compression of C11.4/air at equivalence ratios of 1.0 (solid lines) and 1.3 (dashed lines).

Figure 4.6.7

Figure 4.6.8 Variation in burning velocity with stoichiometry for the isentropic compression of CH_4/air mixtures. The results are produced from our experimental data using a smoothed spline fit to evaluate the pressure derivative.

Figure 4.6.9

Reported burning velocities⁵⁶ for CH_4/air combustion in a combustion bomb.

equivalence ratios of 1.0 and 1.1. Moreover, the extrapolated values of our results for standard conditions are about 36 cm/s at $\phi = 1.0$ and 21 cm/s at $\phi = 1.3$. These values are slightly lower than the values in Fig. 4.6.8, but seem to be within the scatter in that data nevertheless. T&I's burning velocities are too high for rich mixtures, when compared to the data in Fig. 4.6.9 but, unfortunately, they lie within the range of reasonable values in Fig. 4.6.1. Note also that T&I's results at $\phi = 1.3$ are lower than the values from other experimental methods. In the midst of all of this scattered data, we cannot conclude that T&I's values are unreasonably high for rich mixtures.

An examination of their procedures was also inconclusive. Among the various factors which might pinpoint the source of the discrepancies with T&I's results, stretch effects, the submodel for thermochemical equilibrium, gas mixing times, and the uncertainty in the pressure measurement can be ruled out. One aspect of their experimental procedure seemed especially suspicious, at first. They studied mixtures saturated with water vapor, while ours are dry. Flame speeds in bunsen burners are sensitive to water vapor concentrations, but tend to decrease monotonically with the saturation level.⁹⁰ Similarly, if they omitted the water vapor in the analysis of their pressure traces, the values would be too low (not too high). Differences in the analysis do remain, however, but we will not pursue these further.

4.7 Burning Velocity Correlations for Wide Ranges of Temperature and Pressure

4.7.1 CH₄/air Combustion

Fifteen separate experiments with stoichiometric methane/air mixtures yielded the burning velocities shown in Figure 4.7.1.1. There are three families of points, designated by separate symbols, which comprise variations in initial temperature at fixed pressures of 2, 3, and 4 atm. For each family, burning velocity increases linearly with increasing temperature on a log-log plot. This behavior would be well correlated with a power law based on the ratio $T_i/300K$.

Two correlations appear for each family of points. For each pressure, the solid lines are the linear regressions based on our measurements, while the dashed lines were computed from the burning velocity correlation reported by Metghalchi and Keck from their combustion bomb studies.⁶² As seen in the figure, our results are in very good agreement with their correlation. The lines based on their correlation do have slightly smaller slopes than ours, probably because their correlation is based on

Figure 4.7.1.1 The variation of burning velocity with reactant temperature and pressure for C_6H_6 mixed with air at an equivalence ratio of 1. The dotted, solid, and dashed lines resulted from linear regression analyses of the data.

data which cover a broader range of pressure than ours. In any case the discrepancies are acceptably small.

4.7.2 C₆H₆/air Combustion

Laminar burning velocity correlations have been reported for propane,⁶³ hydrogen,⁶¹ methane,^{61,62} iso-octane,^{63,71} n-heptane,^{63,71} methanol,^{68,69} and indolene^{69,72} but, surprisingly, none are available for benzene in the temperature and pressure ranges of our measurements. As a model aromatic hydrocarbon with proportions of hydrogen and carbon similar to those in coal tar, benzene combustion may become an important reference system for interpreting the burning velocities of actual coal volatiles. Surely, if coal tar and benzene, or any model compound, are observed to burn at similar rates, then we would have an important simplification to report.

Experiments with benzene mixtures also provide an opportunity to develop handling procedures for a condensible fuel, although benzene is certainly much easier to work with than coal tar. To prepare the mixture for these experiments, benzene vapor is evaporated from a test tube of the liquid into an evacuated mixing vessel. Then O₂ and N₂ are added and allowed to mix thoroughly before transferring the combustible mixture from the mixing vessel to the bomb. The benzene concentration will only change when its partial pressure is comparable to its saturated vapor pressure; consequently, condensation of the fuel is not normally a problem.

The burning velocities for stoichiometric benzene/air mixtures at three initial pressures and a range of initial temperatures appear in Figure 4.7.2.1. As for methane/air, the values suggest a power law form for the dependence on temperature, because they are again linearly correlated in logarithmic coordinates. Also, as for methane/air, burning velocities decrease for increasing pressure.

These measurements seem to be the only data available for C₆H₆/air combustion in the stated pressure and temperature ranges. Any correlation of tar burning velocity using benzene measurements would require more data to cover a broader region in the temperature-pressure domain.

4.8 Handling of Multicomponent Mixtures

As discussed in Section 2.3.4, volatiles are drawn from the radiant coal flow reactor in a sampling arm located just below the exit of the reactor furnace, and

Figure 4.7.2.1

The variation of burning velocity with reactant temperature and pressure for CH₄ mixed with air at an equivalence ratio of 1. The solid lines resulted from linear regression analyses of the data. The dashed lines are based on the correlation of Metghalchi and Keck.⁵⁹

transported through a 1/4 in. copper tube to the bomb. The sampling arm is located close to the furnace exit in order to collect the volatiles before they cool, and the tars in the sampled flow remain in the vapor phase. For this study, volatiles were immediately quenched after being drawn into the arm, and the soot and condensed tars were removed in a filter. However, in future studies, the copper tube will be heated so that tar vapors may be transported to the bomb for combustion studies.

The presence of light oils and condensible tars in the volatiles greatly complicates the fuel handling tasks. If the constant volume bomb and the transport lines for the volatiles are not maintained at a high enough temperature, the tars will condense. On the other hand, if the temperature of the bomb is too high, the tars, which are thermally less stable than the permanent gases in the volatiles, will tend to pyrolyse.

We have conducted preliminary experiments with tars from an Illinois #6 coal to assure that no pyrolytic cracking or condensation occurs in our apparatus. For these tests, both the transport line and the bomb were maintained at a temperature of 520 K. Other researchers^{22,25} have observed that no condensation and very little pyrolytic cracking of the tars occurs at this temperature. Volatiles containing tar vapor were introduced from the radiant flow reactor to the bomb, and the mixture was allowed to sit in the bomb for about half an hour. The pressure was continuously monitored during this time. As observed in Ch. 1, if substantial cracking of the tars had occurred, large amounts of H₂ and CO would have been released, and we would have observed a significant increase of the pressure in the bomb. However, no pressure change was observed. Of course, this simple pressure test does not rule out the possibility of significant pyrolytic reactions in which no mole change occurs, and a closer examination of the tars (perhaps with ¹H nmr spectroscopy) may be warranted in future studies. (This concern might be pursued by condensing tars on a filter after transporting them through a long heated line, and examining the condensate.)

We have also conducted experiments to test for slow oxidation of the tars at 520 K. These tests are important because O₂ is introduced to the bomb and allowed to mix with the volatiles before the mixture is ignited. It is not desirable for slow oxidation to significantly alter the composition of the volatiles before they can be burned. These tests were conducted in much the same manner as the pyrolytic cracking experiments. Volatiles containing tar vapors were introduced to the heated bomb, and O₂ was added. The mixture was allowed to sit several hours, during which time the pressure was monitored. Since the complete oxidation of an average tar

molecule should produce 24 CO₂ molecules and 12 H₂O molecules, as discussed in Section 3.4.3, we would expect a significant pressure rise if slow oxidation of the tars were occurring. Again, no pressure rise was observed. These preliminary experiments suggest strongly that tar vapors can be transported at 520 K, without significantly altering their compositions.

5. Burning Velocities of Simulated Coal Volatiles

5.1 Introduction

In preparation for our studies of actual volatiles, we first experimented with mixtures of synthetic volatiles. These were composed of pure gases, in proportions based on reported product distributions from the devolatilization of two coals, with a few simplifying substitutions to facilitate the mixing. Prepared reactants were burned in the constant volume bomb to determine their laminar burning velocities. By working with pure gases, we were able to perform burning velocity measurements on volatile-like mixtures without the added experimental complications associated with pyrolysis of the coal. (Experiments with actual coal volatiles are discussed in Ch. 6.)

These experiments were designed to gauge the sensitivity of the volatiles burning rates to various coal-related parameters. The importance of coal type was examined by synthesizing the light gas volatiles from a lignite and a bituminous coal. We then included benzene in the mixtures to coarsely model the addition of tar. Lignite and bituminous volatiles, with and without "tar", resulted in four different mixtures; burning velocities were determined for each.

5.2 Simulated Light Gases from Coal Pyrolysis

The synthetic volatiles are composed of CO , CO_2 , CH_4 , C_3H_8 , H_2 , N_2 , and C_6H_6 , in proportions based on the product distributions for pyrolysis reported by Suuberg,⁸ with some modifications to facilitate our studies. Table 5.2.1 lists the measured product distributions of volatiles for Pittsburgh #8 HVA bituminous and a Montana lignite coal, as reported by Suuberg.⁸ Since only the major components are identified as molecular species, some arbitrary assignments are necessary. We assume that "other hydrocarbon gases" are adequately represented by C_3H_8 , and that C_6H_6 coarsely models the pyrolysis tars. Hence, the measured yields of tars and other hydrocarbon gases are simulated by equivalent mass percentages of C_3H_8 and C_6H_6 . The validity of these assumptions is discussed below. Having substituted these two species and converted the mass percentages to concentrations we found that the H_2O concentrations given by Suuberg are much greater than can be maintained in the vapor phase at room temperature. Although our system could be heated to allow greater water vapor concentrations, we opted for a simpler solution for this study.

Table 5.2.1. Product distributions of volatiles measured by Suuberg for a lignite and Pittsburgh #8 HVA bituminous coal.⁸ The coals were heated to 1270 K in 1 atm of He at a heating rate of 1000 K/s. The figures in the table are presented as weight percentages of the total volatile yield.

	Lignite (weight %)	Bituminous (weight %)
H ₂ O	31.9	9.9
CO ₂	23.3	3.0
CO	23.1	5.9
CH ₄	3.2	6.2
H ₂	1.2	2.5
Other HC gases	3.9	9.7
Tar	13.3	62.9

Water could conceivably alter the combustion rates in two respects: reduction of the flame temperature by dilution and reduction of the oxy-hydrogen radical pool by chemical interaction. For this study, we assumed that water acts mainly as a thermal diluent, and added more convenient diluents on the basis of similar specific heats. For each mole of H₂O, we added 1/3 mole of N₂ and 2/3 mole of CO₂. These proportions produced approximately the same specific heat at constant pressure as H₂O in both the reactants and the products, and should accurately simulate the dilution effect of H₂O. Consequently, in the synthetic mixtures, the relative amounts of all species are the same as in Suuberg's data, except for N₂ and CO₂. The synthetic mixtures for the atmospheric pyrolysis of a lignite and an HVA bituminous coal are tabulated on a mole basis in Table 5.2.2.

While the same relative amounts of C₆H₆ and C₃H₈ as would be present in the original volatiles are substituted for tar and other hydrocarbon gases, respectively, it is not immediately clear that these substituted species will have the same influence on combustion as the original tar and hydrocarbon gases. However, the H/C ratio of tar typically varies from 1.2 to 1 or lower (see Section 1.2), and is thus reasonably well simulated by the C/H ratio for C₆H₆ of 1. Also, tar is highly aromatic, and will probably be better represented by an aromatic molecule, such as C₆H₆. The "other hydrocarbon gases" must indicate a mixture of C₂ through C₄ hydrocarbons which, in the absence of more detailed information, are appropriately simulated by the C₃ alkane, C₃H₈. Of course, while matching C/H ratios does not guarantee matched burning velocities, it does assure similar amounts of heat release from combustion, as discussed in Section 3.4. And the choice of species with similar structural properties

to those of the original materials should increase the likelihood of simulating the combustion of the volatiles accurately.

Table 5.2.2. Light gas mixtures which simulate the volatiles from lignite and bituminous coals.

	Lignite (mole %)	Bituminous (mole %)
N ₂ (for H ₂ O)	14.1	5.3
CO ₂	40.7	12.4
CO	19.6	6.1
CH ₄	4.8	11.1
H ₂	14.6	35.6
C ₃ H ₈	2.1	6.3
C ₆ H ₆	4.1	23.2

5.3 Simulated Bituminous Mixtures with and without Benzene

The burning velocities measured for the bituminous mixtures without simulated tar (C₆H₆) appear in Figure 5.3.1. The relative proportions of the fuel components are the same as those listed in Table 5.2.2, omitting C₆H₆. Each curve represents the burning velocity along a line of constant entropy. Since isentropic compression causes both the temperature and the pressure of the reactants to rise, the curves shown in Figure 5.3.1 are functions of both reactant temperature and pressure.

The measured burning velocities are relatively high in comparison to light hydrocarbons such as CH₄ and C₃H₈ at all equivalence ratios, because the bituminous mixtures contain so much H₂. However, the burning velocities are also considerably lower than expected for H₂ combustion in air at the same stoichiometries (e.g. for H₂ combustion in air at an equivalence ratio of 1 the laminar burning velocity is about 200 cm/sec); thus the simulated bituminous volatiles are not adequately represented by any single fuel. Note also that the burning velocities for lean and stoichiometric mixtures increase rapidly during the second half of the isentrope. We have no explanation for this tendency at present. The maximum flame speed is near the stoichiometric point, although the data do not indicate if slightly richer mixtures would yield higher velocities, as expected for most other hydrocarbons.

The impact of simulated tar addition is seen in the burning velocities for the bituminous mixtures with C₆H₆ in Figure 5.3.2. Since benzene burns slower than hydrogen, the reduction in overall flame speed for these mixtures, compared to the values in Figure 5.3.1, is expected.

The variation of burning velocity with pressure along lines of constant entropy for simulated mixtures of bituminous volatiles in air without C_6H_6 . The equivalence ratio was varied between 0.7 (fuel lean) and 1.45.

Figure 5.3.1

The variation of burning velocity with pressure along lines of constant entropy for simulated mixtures of bituminous volatiles in air with C_6H_6 substituted for tar. The equivalence ratio was varied between 0.7 (fuel lean) and 1.45.

Figure 5.3.2

5.4 Simulated Lignite Mixtures without Benzene

The burning velocities measured for the lignite mixtures were much lower than those for the bituminous mixtures. In fact, for the mixtures without C_6H_6 , the off-stoichiometric runs (which typically produce lower burning velocities) were invalidated due to the effects of buoyancy. The flames propagated so slowly in these runs that buoyant rise of the hot gases distorted the flame fronts and violated one of the assumptions in the computer analysis; viz. a spherical flame. The only measurements reported for the lignite mixtures without C_6H_6 are for stoichiometric conditions and these are shown and discussed in the next section.

The burning velocities measured for the lignite mixtures with C_6H_6 are shown in Figure 5.4.1. The burning velocities in Figure 5.4.1 are considerably lower than those which might be expected for light hydrocarbons such as CH_4 and C_3H_8 . This may be attributed to the large amounts of the diluents, H_2O and CO_2 , shown in Table 5.2.1, and to the abundance of CO , which is a slow-burning fuel.

Also, Figure 5.4.1 indicates that the peak burning velocities occur for fuel-lean mixtures, instead of for fuel-rich mixtures as is almost always the case. The peak in burning velocity for fuel-rich mixtures is usually explained by the fact that burning velocity is strongly correlated with flame temperature. Because the peak flame temperature occurs for fuel-rich mixtures, burning velocity should also peak on the rich side of stoichiometric. However, laminar burning velocity is also strongly correlated with the dilution level of the mixture.

And for our lignite mixtures, the dilution level varied with varying equivalence ratio. The variations in dilution level were brought about by our desire to study the combustion of simulated volatiles in air, and by our inclusion of the diluents, CO_2 and the CO_2/N_2 added to simulate H_2O , among the volatiles (Table 5.2.2). To decrease the equivalence ratio, we decreased the amount of volatiles. Consequently, the amounts of CO_2 and H_2O were also decreased, and the amount of the total diluent in the mixture (including CO_2 , the CO_2 and N_2 substituted for H_2O , and the N_2 from the air) decreased (see Table 5.4.1).

Figure 5.4.1

The variation of burning velocity with pressure along lines of constant entropy for simulated mixtures of lignite volatiles in air with C_6H_6 substituted for tar. The equivalence ratio was varied between 0.7 (fuel lean) and 1.45.

Table 5.4.1. The actual diluent/O₂ ratios for simulated lignite volatiles combustion without benzene. The diluent is comprised of all of the CO₂ and N₂ present in the mixtures.

Equivalence Ratio	diluent/O ₂ ratio
0.7	4.32
0.85	4.45
1.0	4.57
1.15	4.69
1.3	4.81

A decrease in dilution level causes an increase in both the flame temperature and the reaction rate of the volatiles, and in turn, increases the burning velocity. Since the dilution level decreased with decreasing equivalence ratio, the effect of the decrease was largest at the lowest, or fuel-lean, equivalence ratios. This could account for the higher burning velocities observed for fuel-lean mixtures.

5.5 Comparison of the Burning Velocities for all Simulated Mixtures

Figure 5.5.1 compares burning velocities for lignite and bituminous mixtures with and without C₆H₆; in all cases the equivalence ratio is unity. When we consider the mixtures without C₆H₆, it can be seen that the bituminous mixtures have burning velocities about 3 times higher than the lignite mixtures. Such variations would likely alter the ignition and stabilization regimes of these coal types in a furnace configuration.

The effect of C₆H₆ addition is to lower the burning velocity of the bituminous mixtures while increasing the burning velocity of the lignite mixtures. We anticipate that increases in the concentrations of C₆H₆ would continue this trend until eventually both mixtures exhibited the same burning velocity as the pure C₆H₆ case. This suggestion is supported by the C₆H₆/air data shown in Figure 4.7.2.1.

Finally, it is interesting to note that the impact of varied fuel compositions for the two coal types considered here is roughly the same as the effect of varying equivalence ratio. In Figure 5.3.1 at 1.5 atm, burning velocities range from 30 to 60 cm/sec for equivalence ratios from 0.7 to 1.45, which is comparable to the variation from 20 to 60 cm/sec for the stoichiometric lignite and bituminous mixtures, respectively.

Figure 5.5.1

The variation of burning velocity with pressure along lines of constant entropy for all of the complex simulated mixtures studied. The solid lines represent the simulated bituminous mixtures while the dashed lines represent the simulated lignite mixtures. All curves are for an equivalence ratio of 1.

6. Pyrolysis and Combustion of Actual Volatiles

6.1 Introduction

This chapter discusses our studies of the devolatilization of a high volatile bituminous coal, and the subsequent pyrolysis and combustion of the generated volatiles. Both the primary devolatilization of the coal and the secondary pyrolysis of the volatiles are conducted in the radiant coal flow reactor, as discussed in Ch. 2. The combustion experiments are conducted in the constant volume bomb (discussed in Ch. 2 through 4).

Primary devolatilization was studied as a function of the temperature of the furnace in the flow reactor. We measured both the weight loss of the coal, and the yield of tar. These measurements were intended mainly to establish the products of devolatilization, and to determine the furnace temperature at which primary devolatilization is complete, so that the effects of primary and secondary pyrolysis could be separated.

Secondary pyrolysis was also studied as a function of furnace temperature in the radiant flow reactor. For these studies, we measured the fraction of the solids which were soot, and the yields of $C_1 - C_4$ hydrocarbons, H_2 , CO , and C_6H_6 . These measurements were conducted to observe the pyrolytic cracking of tar to soot and light gases, and to determine the fuels which were to be burned in the combustion experiments.

After the volatiles were pyrolysed, they were transported to the constant volume bomb and burned. For these experiments, the laminar burning velocity was measured, both as a function of the stoichiometry of the mixture, and as a function of the furnace temperature at which the volatiles were pyrolysed. These measurements were intended mainly to gage the effect of secondary pyrolysis on combustion, and to establish the range of laminar burning velocities to be expected for varying stoichiometries.

6.2 Coal Characteristics

The coal used for this study was an HVA bituminous coal (Illinois #6, PSOC 1493D) distributed by the Pittsburgh Energy Technology Center (PETC). Our experiments were for the 75-106 micron aerodynamically-classified size fraction (ultimate and proximate analyses shown in Table 6.2.1). Before use, coals were dried overnight at 330 K under 5 in. Hg. of Ar.

Table 6.2.1. Proximate and Ultimate Analyses for Ill. # 6, PSOC 1493D.

Size (Microns)	Moisture Free Weight Percent						
	Volatile Matter	Ash	C	H	N	O	S
75 - 106	37.5	13.5	64.5	4.6	1.3	14.1	5.6

6.3 Primary Pyrolysis

We have made weight loss and tar yield measurements for the devolatilization of Ill. #6 coal in the radiant flow reactor. These measurements were made for an estimated residence time in the reactor (the estimates account for the slip velocity of the particles and gas heating) of approximately 200 msec, and a coal loading of 2400 #/cc.

Our weight loss and tar yield measurements for the conditions of this study are shown in Figure 6.3.1. As seen in the figure, weight loss is already substantial at the temperature at which tar production begins. This early weight loss is due to the release of light gases, probably CO_2 and H_2O . The ultimate yields are achieved at a temperature between 1500 and 1600 K and correspond to a total weight loss of 62 % and a tar yield of 15 %. Observations very similar to these have been made by Chen et al.,^{7,77,78} though their ultimate tar yield was higher (20 vs. 15 weight % daf) and their total weight loss was lower (57 vs. 62 weight % daf). The larger of these two disparities, that of the tar yield, can probably be explained by the effects of secondary pyrolysis, as discussed in the next section.

From the weight loss and tar yield measurements, it is apparent that about 15 to 20 wt. % of the coal is converted to tar, while about 40 to 45 wt % becomes gases. Most importantly, these measurements show that primary devolatilization is complete at about 1500 to 1600 K.

6.4 Secondary Pyrolysis

To achieve combustible mixtures, we operated at a much higher coal loading than Chen et al. (Their loading was 400 #/cc, while ours was 2400 #/cc.) As explained in detail in Section 2.3.6, higher coal loadings lead to higher gas temperatures, and, thus, to extensive secondary pyrolysis. We have direct support for the occurrence of secondary pyrolysis in the solubility of the tars from our experiment. At the lower furnace temperatures, our tars are completely soluble in tetra-hydrofuran (THF). However, as the furnace temperature approaches 1550 K, we begin to

Weight loss (open circles) and tar yield (solid circles) as a function of furnace wall temperature for the pyrolysis of Illinois #6 coal in the radiant coal flow reactor.

Figure 6.3.1

observe an insoluble fraction, which increases rapidly with increasing temperature (see Figure 6.4.1). We have assumed that this insoluble material is soot. Thus, what we have referred to as tar in Section 6.3 is actually a mixture of tar and soot, and while the yield of tar plus soot has begun to level out at 1600 K, the yield of tar is actually decreasing and the yield of soot is rapidly increasing. This observation suggests that above 1500 K, as shown in Figure 6.4.1, tar is converted by secondary pyrolysis to soot and light gases. In contrast to our measurements, Chen et al.⁷ observe that their tar is completely soluble in THF over the entire temperature range of their measurements. Therefore, the disparity between our measurements and those of Chen et al. must be caused by the loss of tar weight as light gases during the conversion of our tars to soot.

It is interesting to observe that secondary pyrolysis begins near the temperatures at which ultimate yields are achieved. This is fortunate, since it implies that all of the volatiles are released from the coal before the secondary chemistry of the volatiles begins. It is also fortunate for our measurements of the products, since we can assume that trends in the product yields for furnace temperatures above 1500 K are due almost entirely to secondary pyrolysis of the volatiles. To examine the light gases formed and destroyed during the conversion of tar to soot, we used gas chromatography (for details, see Section 2.5) to measure the yields of H_2 , CO, C_1 through C_4 hydrocarbons, and C_6H_6 . The results of these measurements are shown in Figures 6.4.2-6.4.5.

With the exception of C_2H_2 , the C_2 and C_3 hydrocarbons obtain a maximum yield at 1550 K, and decrease continuously thereafter, as seen in Figures 6.4.3 and 6.4.4. This maximum and the subsequent decrease, which were also noted by Nelson and Tyler,²⁴ signal the destruction of the C_2 and C_3 hydrocarbons during secondary pyrolysis. In contrast, the C_2H_2 yield increases continuously with increasing temperature, as seen in Figure 6.4.3.

The CO and H_2 yields also increase continuously (Figures 6.4.2 and 6.4.3), suggesting that CO, H_2 , and C_2H_2 are all created during secondary pyrolysis. The CO and H_2 yields are a large fraction of the light gas products on a molar basis. They also account for a major portion of the hydrogen and oxygen in the original coal. At 1680 K, 45 % of the hydrogen in the original coal becomes H_2 , while 11 % of the original oxygen takes the form of CO.

Methane is the only measured light gas which is apparently not created or destroyed during secondary pyrolysis (Figure 6.4.2). Both the CH_4 yield and the coal weight loss reach their ultimate values at 1600 K, and remain constant thereafter, suggesting that CH_4 is only formed during primary pyrolysis.

Figure 6.4.1 Soot yield (weight fraction of solid volatiles which is not soluble in THF) as a function of furnace temperature for the . pyrolysis of Illinois #6 coal in the radiant coal flow reactor.

H₂ yield as a function of furnace temperature for secondary pyrolysis of the volatiles from Illinois #6 coal in the radiant coal flow reactor.

Figure 6.4.2

Figure 6.4.3
 CH₄ (solid circles) and CO (open circles) yields as a function of furnace temperature for secondary pyrolysis of the volatiles from Illinois #6 coal in the radiant coal flow reactor.

Figure 6.4.4
 C_2 hydrocarbon yields as a function of furnace temperature; C_2H_2 is represented by the open squares, C_2H_4 by solid circles, and C_2H_6 by the solid triangles.

Figure 6.4.5

C_3 hydrocarbon yields as a function of furnace temperature; C_3H_4 is represented by the solid triangles, and C_3H_6 by the open triangles.

Both C_4 hydrocarbons and C_6H_6 were also detected, but only in amounts below about 0.01 wt. %. The C_4 hydrocarbons were present at the lowest measurement temperatures, but decreased rapidly to undetectable levels with increasing temperature. The opposite trend was observed for C_6H_6 , which was only detected at the highest measurement temperatures. Neither the C_4 hydrocarbons nor C_6H_6 occurred in large enough concentrations to influence the interpretation of the combustion studies.

6.5 Influence of Secondary Pyrolysis on Laminar Burning Velocity

After the volatiles exited the furnace section of the radiant coal flow reactor, they were cooled, and the tar and soot were filtered out, as discussed in Section 2.4. Then the remaining light gases were transported to the combustion bomb, and burned. Light gases produced at 1550 K, 1600 K, and 1680 K were studied. The purpose of this set of experiments was to explore the effect on laminar burning velocity of the product variations caused by secondary pyrolysis.

Run-to-run variations in the volatiles concentrations were fairly small, as indicated by the 3 sets of points at 1640 K in Figures 6.4.2-6.4.5. While multiple measurements were made only at this temperature, the observed variations should be indicative of the repeatability of the measurements for the entire temperature range. At 1640 K, the measurements for all of the fuels except CO vary by less than 8 %. The CO variation is about 30 %. However, CO is also the only species for which the gas chromatograph was not calibrated before each run; the use of old calibration data may account for the wider variations. The maximum change in the total yield of fuel, even with the large variations in CO, is only 4 %. This should introduce a maximum error of 4 % in the actual equivalence ratio for the combustion experiments.

When discussing product distributions from coal pyrolysis, yields are customarily stated as a weight % of the original coal. However, this scaling is less satisfactory when considering the combustion of these products, since most of the original coal does not participate in the combustion. We have rescaled the light gas yields on a molar basis (mole % of the light gas fuels) in Figures 6.5.1-6.5.3 to emphasize the abundance of the lighter fuels, and provide a better sense for their importance to the combustion of the mixture.

As seen in Figures 6.5.1-6.5.3, H_2 and CH_4 are the dominant species, with H_2 providing 60 to 80 mole %, and CH_4 providing 10 to 25 mole % of the total fuel. These two fuels contribute most of the heat release during combustion, but CO and C_2H_2 are also important at the higher measurement temperatures, where, as a result of secondary pyrolysis, their yields become significant. The combined effects of the

Figure 6.5.1

Measured fractions of fuels (defined as the ratio of the moles of a particular species to the total moles of measured products) as a function of furnace temperature. The solid triangles represent H_2 , the solid circles represent CH_4 , and the open circles represent CO .

Measured fractions of C_2 fuels (defined as the ratio of the moles of a particular species to the total moles of measured products) as a function of furnace temperature. The solid triangles represent C_2H_6 , the solid circles represent C_2H_4 , and the open squares represent C_2H_2 .

Figure 6.5.2

Measured fractions of C_3 fuels (defined as the ratio of the moles of a particular species to the total moles of measured products) as a function of furnace temperature. The solid triangles represent C_3H_8 and the open triangles represent C_3H_6 .

Figure 6.5.3

remaining fuels (excluding H_2 , CH_4 , CO , and C_2H_2) contribute almost 10 % of the heat release of combustion (even at the highest pyrolysis temperatures), and they cannot be neglected, though no single remaining fuel contributes significantly to the heat release when considered alone.

To emphasize the effect of secondary pyrolysis, the equivalence ratio and dilution level were held constant for all of the combustion experiments in this section. The equivalence ratio is defined as the ratio of the amounts of fuel and O_2 present in the mixture, divided by the ratio of the amounts of fuel and O_2 required for stoichiometric combustion. For the experiments of this chapter, the fuel is defined as all of the species for which measurements are shown in Section 6.4. Since the relative amounts of each fuel species shifted with varying furnace temperature, it is necessary to determine a separate stoichiometric fuel to O_2 ratio for each furnace temperature. Calculations for the dilution level are somewhat less complex. To determine the amount of diluent present, we subtract the measured amounts of fuel from the gas in the bomb before O_2 addition. We then divided the amount of diluent by the amount of added O_2 to obtain the diluent ratio. The desired equivalence ratio and diluent ratio were 0.6 and 5.15 respectively, but run-to-run variations caused these parameters to vary slightly (Table 6.5.1). However, no trend in the pressure traces for these runs (Figure 6.5.4) is attributable to the run-to-run variations, and their influence is probably minor.

Table 6.5.1. Mixture Ratios for the Experiments Testing the Effect of Furnace Wall Temperature on Laminar Burning Velocity.

Furnace Temp. (K)	Equivalence Ratio	Diluent Ratio
1550	0.60	5.19
1600	0.56	5.04
1680	0.61	5.13

The pressure traces for combustion at the three conditions in the table above are all fairly similar (see Figure 6.5.4). The ultimate pressures are approximately the same, suggesting that the heat release is approximately the same for all three cases (see the discussion of ultimate pressures in Section 4.4). The times to reach those ultimate pressures are also fairly similar, though they do decrease slightly with increasing furnace temperature, indicating that the mixtures produced at higher furnace temperatures burn faster. The time scale for the pressure rise is fairly long in all three cases, but buoyancy effects are not important. However, only a small part of each pressure trace is reduced to laminar burning velocities since heat losses and the

Influence of furnace temperature on the transient pressure histories; the dotted line is for a furnace temperature of 1550 K, the dashed line is for 1600 K, and the solid line is for 1680 K. The equivalence ratios and diluent levels for these measurements are shown in Table 6.5.1.

Figure 6.5.4

limitation in the resolution of the measurements invalidate the rest (as explained in Section 3.2.6).

The inferred burning velocities are presented in Figure 6.5.5. The velocities are graphed as functions of both temperature and pressure because of the isentropic compression of the reactants (as discussed in Section 2.2.9). As anticipated above, the burning velocities increase as the measurement temperature increases, ranging from about 20 cm/sec at 1550 K to about 28 cm/sec at 1680 K. This increase in burning velocity is probably due to the rise in the H_2 mole fraction, as shown in Figure 6.5.1, since H_2 has the highest burning velocity of the species in the mixture. However, despite the large percentage of H_2 at 1680 K, the burning velocity for the mixture is still much lower than that for H_2 combustion at the same dilution and equivalence ratio ($S_u = 50$ to 75 cm/sec). Thus, for these cases volatiles combustion cannot be simplified to the study of a dilute hydrogen mixture.

A direct comparison between the results from actual volatiles combustion and the results from combustion of the simulated volatiles (see Ch. 5) is not straightforward. The most serious hindrance to direct comparison is the disparity between dilution levels. The simulated volatiles were burned at the dilution level of air ($N_2/O_2 = 3.76$), while the actual volatiles were burned at diluent/ $O_2 = 5.15$. Additional sources of ambiguity are: the use of different coals (Pitt #8 high volatile bituminous coal for the simulations vs. Ill #6 high volatile bituminous coal for the actual studies), different extents of secondary pyrolysis (little or no secondary pyrolysis for the simulations vs. extensive secondary pyrolysis for the actual studies), and the species substitutions made to simplify the simulation mixtures. While we understand qualitatively how dilution will affect our burning velocity measurements, the effects of these three extra factors are impossible to gauge.

6.6 Burning Velocities as a Function of Stoichiometry

The influence of stoichiometry was studied at a fixed furnace wall temperature of 1640 K. Three cases were run at equivalence ratios of 1.0, 0.8, and 0.7.

The dilution level was held constant at diluent/ $O_2 = 5.4$. In other words the ratio of the total moles of diluent to the moles of O_2 was held constant. However, the mixtures in the bomb contained N_2 , and the H_2O and CO_2 released from the coal, all of which we consider diluents. Though the sum of their amounts remained constant, the relative amounts of each species varied as the amount of volatiles introduced to the bomb was adjusted to vary the equivalence ratio. Since CO_2 and H_2O have higher specific heats than N_2 , the average specific heat of the diluents also varied as the relative amounts of CO_2 , H_2O , and N_2 varied. This variation in specific heat will

Figure 6.5.5 Influence of furnace temperature on the laminar burning velocity for the same conditions as Figure 6.5.4. Again, the dotted line is for a furnace temperature of 1550 K, the dashed line is for 1600 K, and the solid line is for 1680 K.

affect both the flame temperatures and the burning velocities of the mixtures studied in this section, and this effect is discussed below.

Laminar burning velocities for three different equivalence ratios are shown in Figure 6.6.1. The burning velocity curves in the figure exhibit the same basic trends with temperature, pressure, and equivalence ratio as observed for the simulated volatiles in Ch. 5. The burning velocity displays a maximum with varying equivalence ratio. Along an isentrope, the burning velocity increases with increasing temperature and pressure; and, as seen in Figure 6.6.1, the stoichiometric mixture exhibits a less rapid increase in burning velocity along the isentrope than the fuel-lean mixtures. This last characteristic is slightly different than observed for the simulated volatiles in Section 5.3. For the simulations (Figure 5.3.1), the transition from isentropes which increase more rapidly to isentropes which increase less rapidly appears to occur on the fuel-rich side of stoichiometric combustion, instead of on the fuel-lean side, as observed in this set of experiments. We cannot currently offer any explanation for this shift in the transition point.

However, the most outstanding characteristic of our measurements is the occurrence of the peak burning velocity at an equivalence ratio less than 1. No single-fuel mixture exhibits a peak burning velocity for fuel-lean conditions; nor do reported multiple-fuel mixtures.⁸⁹ Without exception, combustion studies report peak burning velocities for fuel-rich conditions.

The occurrence of a fuel-lean peak could be caused by the decrease in the specific heat of the diluents with decreasing equivalence ratio, which was described above. A decrease in the specific heat would cause the flame temperature of the mixture to rise. Laminar burning velocity is strongly correlated with flame temperature, and increasing the flame temperature would cause the burning velocity to rise also. Since the specific heat decreases as the equivalence ratio decreases, the effect of specific heat will be most pronounced for low equivalence ratios. Though we would ordinarily expect the laminar burning velocity at an equivalence ratio of 0.8 to be lower than that at stoichiometric conditions, a significant increase in the burning velocity caused by the decrease in specific heat could reverse this trend.

However, perhaps a more likely explanation for the lean peak is the existence of other undetected fuels; their presence would lead us to report an erroneously low equivalence ratio. But neither C_4 hydrocarbons nor benzene were detected in significant amounts. And high molecular weight hydrocarbons should have condensed and been removed by a filter before the reactants were sent to the bomb (see Ch. 2). Of course, it is possible that the lighter tar species in the product stream remained in the vapor phase, and that these tar species escaped detection by our gas

Figure 6.6.1

Influence of stoichiometry on the laminar burning velocity at a furnace temperature of 1640 K. The solid line represents an equivalence ratio of 1.0, the dotted line represents an equivalence ratio of 0.8, and the dashed line represents an equivalence ratio of 0.7. The diluent/ O_2 ratio is 5.4 ± 0.1 . Note that the highest burning velocity is measured for an equivalence ratio of 0.8.

chromatograph. This speculation is supported by recent gas chromatographic measurements in our lab, which indicate the presence of significant amounts of light oils in the vapor phase in the product stream. Thus, we cannot rule out the presence of unaccounted for fuels at this time.

7. Conclusions

Both devolatilization and secondary pyrolysis experiments were conducted in a radiant flow reactor with an Illinois #6 HVA bituminous coal. The nominal residence time in the furnace section of the reactor was 200 msec for all reported yields, and the temperature of the furnace section was varied between 1500 K and 1680 K for the measurements of secondary pyrolysis.

From the secondary pyrolysis experiments with actual volatiles, we conclude that:

1. The major light gas products of secondary pyrolysis are H_2 , CO, C_2H_2 , and CH_4 . The most abundant of these for the temperature range from 1000 K to about 1700 K is H_2 .
2. A large amount of THF insoluble material, or soot, is also produced, and tar disappears, as the volatiles are pyrolysed. At the maximum reactor temperature of 1680 K, more than 80% of the original tar has been converted to soot and other products.
3. Except for C_2H_2 , the C_2 and C_3 hydrocarbons achieve their maximum yields at a reactor temperature of 1550 K. Above 1550 K, the yields decrease, and only trace amounts are observed at the peak reactor temperature of 1680 K. In contrast, C_2H_2 is a major product, and its yield increases monotonically over the entire temperature range, in tandem with the soot yield.

The volatiles combustion experiments were conducted in a constant volume bomb. After condensing the tars at room temperature, and then removing both the tars and soot on filters, the remaining light gas volatiles were transported to the bomb, where they were mixed with O_2 , and burned. Measurements were made of the laminar burning velocities of the mixtures for varying equivalence ratio and extent of secondary pyrolysis.

From combustion experiments with the noncondensable volatile compounds only, we conclude that:

1. The burning velocity of the light gas volatiles is typically 50 to 60 cm/sec for an equivalence ratio near 1 and a diluent/ O_2 ratio of 5.4 (the diluents are N_2 , CO_2 , and H_2O). Despite the abundance of H_2 in the products, the burning velocity of the volatiles is not dominated by the combustion of a single fuel component.

2. The burning velocity of the light gas volatiles increases slightly with increasing extent of secondary pyrolysis. Light gas volatiles from pyrolysis in the flow reactor at 1550 K have a burning velocity of about 18 cm/sec, while light gas volatiles from pyrolysis at 1680 K have a burning velocity of about 22 cm/sec (for an equivalence ratio of 0.6 and a diluent/O₂ ratio of 5.14). Yet the volatiles change substantially over the same temperature range, as evidenced by the increase in soot yield from 30 % to 80 % of the total solid product yield.
3. The peak burning velocity occurs for an equivalence ratio near 0.8, whereas we would ordinarily expect the peak to be observed for an equivalence ratio near 1. We suspect that this anomaly is caused by undetected fuels (perhaps light oils) which are not accounted for in our equivalence ratio calculations.

Our conclusions have several implications for the combustion of coal. First, it is apparent that secondary pyrolysis converts tars to H₂, CO, CH₄, C₂H₂, soot, and perhaps light oils (unfortunately, we were not equipped to measure oils). The abundance of the relatively fast-reacting H₂ and CH₄ species after secondary pyrolysis might result in a mixture with a higher reaction rate than the mixture which contained the original tar. This could lend credence to the flame sheet model of volatiles combustion.

At the same time, soot production lowers the amount of potential fuel in the system, which could lower the reaction rate of the mixture, and necessitate the use of finite rate chemistry for volatiles combustion. Of course the survival of soot in the combustion zone also lowers the heat release from the flame and raises particulate emissions.

While the measured burning velocities imply a relatively fast-reacting fuel, we cannot state unequivocally that these burning velocities are representative of volatiles combustion, due to our filtering of tar and soot from the reactants. Not only does the removal of these products alter the fuel composition, but it also causes the percentage of the fuel which is transported to the combustion bomb to vary with varying extent of secondary pyrolysis. In other words, since secondary pyrolysis decreases tar concentrations and increases light gas concentrations, less of the total mass of fuel volatiles is removed by the filters as the tars are pyrolysed. Of course, the removal of tar and soot may or may not be important to combustion, depending on the extent of tar decomposition during secondary pyrolysis, and the impact of tar and soot on the heat release and the reaction rate of the volatiles.

The work reported here is a modest beginning at developing a better understanding of secondary volatiles chemistry. Much remains to be done. A high priority of future research should be to determine all of the products from secondary pyrolysis, and thus account for all of the mass of the original volatiles. Complete product distributions are a prerequisite to developing mechanisms for secondary pyrolysis and combustion. The potential importance of unmeasured species is especially evident in this study, since H_2O , CO_2 , and the light oils may have had a significant impact on our combustion results.

But even complete secondary pyrolysis data will be considerably less useful if we do not establish the actual gas and particle temperatures, and residence times in the flow reactor. Times and temperatures are necessary both to define quantitative kinetic rates, and to assess the importance of secondary pyrolysis during pulverized coal combustion. Future secondary pyrolysis yields must be presented not as functions of the reactor temperature, but as functions of actual gas temperatures.

In addition to accounting for all of the mass of the products of secondary pyrolysis, we must more thoroughly examine and characterize those products. For instance, it might be possible to explain the processes of tar condensation into soot and tar decomposition into light gases by examining the aromaticity, H/C ratio, and general structural features of the aerosol products. The process of tar condensation should cause both an increase in tar aromaticity and a decrease in H/C ratio as the aliphatic bridges and side chains of the tars are lost and the cluster sizes become larger. For tar decomposition, the formation of particular gas phase species should correlate with a decrease in the concentrations of certain structural features in the tars.

The nitrogen chemistry of the volatiles should also be more closely examined. There are many processes which might influence nitrogen chemistry, and many methods for studying them. For instance, the nitrogen in tar may either be trapped in soot, or released into the gas phase. The partitioning of tar nitrogen between soot and gas could be studied by measuring nitrogen concentrations in the tar and soot, and determining the gas phase nitrogen species. Hydrocarbon gases and H_2 will also influence gas phase nitrogen chemistry. This influence could be studied by adding extra hydrogen and hydrocarbons to the carrier gas, and observing their effect on the products. The gas phase nitrogen species may also be incorporated in soot. This route for nitrogen could be examined by adding extra amounts of nitrogen-containing species to the carrier gas. Finally, soot and tar may play a major role in the nitrogen chemistry of the flame, and their effect should be explored by burning volatiles with and without soot and tar.

This last experiment could also help to explain the importance of soot and tar to volatiles combustion. The competing processes of tar conversion to soot in the volatile flame and the oxidation of both the soot and tars might be deconvoluted by burning different mixtures for which (1) tar and soot are removed by a cooled filter, (2) only soot is removed by a heated filter, and (3) nothing is removed, so that all of the products of secondary pyrolysis are combusted. Of course it is not yet clear to what extent tars are pyrolysed before they reach the flame, or, in fact, whether tars reach the flame at all, and thus each of these cases must be examined over varying extents of secondary pyrolysis.

Finally, a wide variation of coal ranks must be examined. Surely, one of the most important achievements of this research is a rank-based predictive capability for secondary chemistry.

References

1. Gavallas, G. R., "Coal Pyrolysis," Elsevier (1982).
2. Howard, J. B., "Chemistry of Coal Utilization, Second Supplementary Volume," Ed. M. A. Elliot, p. 665, John Wiley and Sons (1981).
3. Solomon, P. R., Hamblen, D. G., Prog. Energy Combust. Sci., 9:323 (1983).
4. Smith, I. W., Nineteenth Symposium (International) on Combustion/The Combustion Institute, p. 1045 (1982).
5. Wendt, J. O. L., Prog. Energy Combust. Sci., 6:201-222 (1980).
6. Hertzberg, M., Cashdollar, K. L., Lazzara, C. P., Eighteenth Symposium (International) on Combustion/The Combustion Institute, p. 717 (1981).
7. Chen, J. C., Niksa, S., Paper No. 89-11, WSS/CI Spring 1989 Meeting, Pullman, WA March 1989.
8. Suuberg, E. M., "Rapid Pyrolysis and Hydropyrolysis of Coal," Ph. D. Thesis, Department of Chemical Engineering, MIT, Cambridge, MA (1977).
9. Gibbins, J. R., Kandiyoti, R., Fuel, 68:895-903 (1989).
10. Xu, W., Tomita, A., Fuel, 66:627-631 (1987).
11. Freihaut, J. D., Proscia, W. M., Seery, D. J., Energy and Fuels, 3:692-703 (1989).
12. Unger, P. E., Suuberg, E. M., Fuel, 63:606-611 (1984).
13. Collin, P. J., Tyler, R. J., Wilson, M. A., Fuel, 59:479-486 (1980).
14. Collin, P. J., Tyler, R. J., Wilson, M. A., Fuel, 59:819-820 (1980).
15. Calkins, W. H., Tyler, R. J., Fuel, 63:1119-1124 (1984).
16. White, C. M., Perry, M. B., Schmidt, C. E., Behmanesh, N., Allen, D. T., Fuel, 67:119-127 (1988).

17. Bautista, J. R., Russel, W. B., Saville, D. A., Ind. Eng. Chem. Fundam., 25:536-544 (1986).
18. Haussmann, G. J., Kruger, C. H., Twenty-second Symposium (International) on Combustion/The Combustion Institute, p. 223 (1986).
19. Solomon, P. R., Serio, M. A., Carangelo, R. M., Markham, J. R., Fuel, 65:182 (1986).
20. Kobayashi, H., Howard, J. B., Sarofim, A. F., Sixteenth Symposium (International) on Combustion/The Combustion Institute, p. 411 (1976).
21. Xu, W., Tomita, A., 1987 International Conference on Coal Science, Ed. J. A. Moulijn, p. 629, Elsevier (1987).
22. Serio, M. A., Peters, W. A., Howard, J. B., Ind. Eng. Chem. Res., 26:1831-1838 (1987).
23. Xu, W., Tomita, A., Fuel, 66:632-636 (1987).
24. Nelson, P. F., and Tyler, R. J., Twenty-first Symposium (International) on Combustion/The Combustion Institute, p. 427 (1986).
25. Xu, W., Tomita, A., Fuel Processing Technology, 21:25-37 (1989).
26. Fynes, G., Ladner, W. R., Newman, J. O. H., Prog. Energy Combust. Sci., 6:223-232 (1980).
27. Furfari, S., Cypres, R., Fuel, 64:40 (1985).
28. Cypres, R., Furfari, S., Fuel, 64:33-39 (1985).
29. Tyler, R. J., Fuel, 58:680-686 (1979).
30. Tyler, R. J., Fuel, 59:218-226 (1980).
31. Doolan, F. R., Mackie, J. C., Tyler, R. J., Fuel, 66:572-578 (1987).
32. Westbrook, C. K., Dryer, F. L., Schug, K. P., Nineteenth Symposium (International) on Combustion/The Combustion Institute, p. 153 (1982).
33. Garcia, X. A., Huttinger, K. J., Fuel, 68:1300-1310 (1989).

34. Lahaye, J., Palmer, H. B., Sharma, R. K., Carbon, 6:419-420 (1968).
35. Cypres, R., Bettens, B., Fuel, 65:507-514 (1986).
36. Badger, G. M., Donnelly, J. K., Spotswood, T. M., Australian J. Chem., 17:1138 (1964).
37. Badger, G. M., Donnelly, J. K., Spotswood, T. M., Australian J. Chem., 17:1147 (1964).
38. Frazee, J. D., Anderson, R. C., Proc. Third Conf. on Carbon, p. 405, Pergamon (1959).
39. Emdee, J. L., Brezinsky, K., Glassman, I., ESS/CI, Fall 1989 Meeting (1989).
40. Haussmann, G. J., Kruger, C. H., Paper No. 89-77, WSS/CI Fall 1989 Meeting, Livermore, CA, October 1989.
41. Cerny, J., Mitera, J., Vavrecka, P., Fuel, 68:596-600 (1989).
42. Schlosberg, R. H., Dans, Jr., W. H., Ashe, T. R., Fuel, 60:201-204 (1981).
43. Schlosberg, R. H., Ashe, T. R., Pancirov, R. J., Donaldson, M., Fuel, 60:155-157 (1981).
44. Cronauer, D. C., Jewell, D. M., Shah, Y. T., Moll, R. J., Ind. Eng. Chem. Fundam., 18:153-162 (1979).
45. Bruinsma, O. S. L., Geertsma, R. S., Bank, P., Moulign, J. A., Fuel, 67:327-333 (1988).
46. Agarwal, P. K., Pedler, I., Fuel, 65:640-643 (1986).
47. Milne, T. A., Beachey, J. E., Combust. Sci. and Tech., 16:123-138 (1977).
48. Milne, T. A., Beachey, J. E., Combust. Sci. and Tech., 16:139-152 (1977).
49. Smoot, L. D., Horton, M. D., Williams, G., Sixteenth Symposium (International) on Combustion/The Combustion Institute, p. 375 (1977).
50. Howard, J. B., Essenhigh, R. H., Eleventh Symposium (International) on Combustion/The Combustion Institute, p. 399 (1967).

51. Mott, R. A., Spooner, C. E., Fuel, 19:226-242 (1940).
52. Timothy, L. D., Froelich, D., Sarofim, A. F., Beer, J. M., Twenty-first Symposium (International) on Combustion/The Combustion Institute, p. 1141 (1986).
53. Brezinsky, K., Prog. Energy Combust. Sci., 12:1-24 (1986).
54. Toquan, M., Farmayan, W. F., Beer, J. M., Howard, J. B., Teare, J. D., Twentieth Symposium (International) on Combustion/The Combustion Institute, p. 1075 (1984).
55. Bittner, J. D., Howard, J. B., Eighteenth Symposium (International) on Combustion/The Combustion Institute, p. 1105 (1981).
56. Levy, A., Arbib, H. A., Merryman, E. L., ACS Symposium Series No. 217, Ed. W. Barton, p. 113 (1983).
57. Yu, C., Law, C. K., Wu, C. K., Combust. Flame, 63:339-347 (1986).
58. Iijima, T., Takeno, T., WSS/CI, Fall 1987 Meeting, Hawaii (1987).
59. Milton, B. E., Keck, J. C., Combust. Flame, 58:13-22 (1984).
60. Musarra, S. P., Fletcher, T. H., Niksa, S., Dwyer, H. A., Combust. Sci. and Tech., 45:289 (1986).
61. Takeno, T., Iijima, T., Combust. Flame, 65:35-43 (1986).
62. Metghalchi, M., "Laminar Burning Velocity of Isooctane-Air, Methane-Air, and Methanol-Air Mixtures at High Temperature and Pressure," M.S. Thesis, Department of Mechanical Engineering, MIT, Cambridge, MA (1984).
63. Ryan, T. W., Lestz, S. S., Automotive Engineering Congress, Paper 800103, Detroit (1980).
64. Agnew, J. T., Graiff, L. B., Combust. Flame, 19:275 (1972).
65. Rallis, J. C., Garforth, A. M., Steinz, J. A., Combust. Flame, 9:345 (1965).
66. Metghalchi, M., Keck, J. C., Combust. Flame, 38:143-154 (1980).
67. Halstead, M. P., Pye, D. B., Quinn, C. P., Combust. Flame, 22:89 (1974).

68. Perlee, H. E., Fuller, J. N., Saul, C. H., U. S. Dept. of Interior, Bureau of Mines, RI 7839 (1974).
69. Metghalchi, M., Keck, J. C., Combust. Flame, 48:191-210 (1982).
70. Nair, M. R. S., Gupta, M. C., Combust. Flame, 22:219 (1974).
71. Babkin, V. S., V'yun, A. V., Kozachenko, L. S., Combust. Expl. and Shock Waves, 3:221 (1967).
72. Rhodes, D. B., Keck, J. C., SAE Technical Paper No. 850047 (1985).
73. Fiock, E. F., Marvin, Jr., C. F., Caldwell, F. R., Roeder, C. H., "Flame Speeds and Energy Considerations for Explosions in a Spherical Bomb," Report No. 682, National Bureau of Standards (1939).
74. Lewis, B., von Elbe, G., "Combustion, Flames, and Explosion of Gases," Academic Press, New York, NY (1961).
75. Andrews, G. E., Bradley, D., Combust. Flame, 18:133-153 (1972).
76. Dixon-Lewis, G., Islam, S. M., Nineteenth Symposium (International) on Combustion/The Combustion Institute, p. 283 (1982).
77. Chen, J. C., Niksa, S., Paper No. 89-75, WSS/CI Fall 1989 Mtg., Livermore, CA, October 1989.
78. Chen, J., Chang, Y-J. C., Niksa, S., 1989 International Conference on Coal Science, IEA, Tokyo, p. 527 (1989).
79. Mclean, W. J., Hardesty, D. R., Pohl, J. H., Eighteenth Symposium (International) on Combustion/The Combustion Institute, p. 1239 (1981).
80. Martin, M. K., Heywood, J. B., Combust. Sci. and Tech., 15:1-10 (1977).
81. Haskell, K. H., Vandever, W. H., Sandia National Laboratories Report, SAND79-2382 (1980).
82. Bradley, D., Mitcheson, A., Combust. Flame, 26:201-217 (1976).
83. Garforth, A. M., Rallis, C. J., Combust. Flame, 31:53-68 (1978).

84. Benson, S. W., Cruikshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., Walsh, R., Chem. Rev., 69:279-324 (1969).
85. Kee, R. J., Miller, J. A., Jefferson, T. H., Sandia National Laboratories Report, SAND80-8003 (1980).
86. Garforth, A. M., Combust. Flame, 26:343-352 (1976).
87. Gat, N., "The Effect of Exhaust Gas Recirculation and Turbulence on the Burning Velocity, Quenching Distance, and Minimum Ignition Energy in Premixed Methane-Air Combustion," Ph. D. Thesis, Department of Aerospace Engineering and Applied Mechanics, University of Cincinnati (1978).
88. Gibbs, G. J., and Calcote, H. F., Journal of Chemical and Engineering Data, Vol. 4, 3:226-237 (1959).
89. Strehlow, R. A., "Combustion Fundamentals," McGraw-Hill, Inc., New York, NY, p. 262 (1984).
90. Schwab, A. J., "High Voltage Measurement Techniques," The MIT Press, Cambridge, Massachusetts (1972).

Appendix A. Ignition System

A.1 Overview

One preliminary and three improved capacitor-based circuit designs were considered (Figures A.2.1 and A.3.1). The preliminary design was abandoned because it failed to provide the minimum energy required to ignite a typical fuel-air mixture. However, the experience gained with this design was useful to the development of the three improved circuits.

To ensure that the final circuit design would deliver sufficient energy, we measured the transient currents and voltages through the spark gap, and computed the energy delivered to the gap from these measurements. The development of the measurement diagnostics is discussed in detail below.

The preliminary and improved designs are also discussed, and the choice of a final design is explained. Finally, the energies computed from the measurements are cataloged.

A.2 Preliminary Ignition Circuit

The preliminary circuit is shown in Figure A.2.1. The Krytron switch shown is a high-voltage switch. With the switch initially an open circuit, the 1 micro Farad capacitor is energized to a charge voltage of between 0 and 2000 V. Then a trigger pulse is fired into the Krytron switch, and the switch becomes a short circuit, discharging the capacitor through the trigger transformer and into the spark gap.

The components in the circuit are sized to deliver ample energy to ignite all mixtures of interest. For instance, with the storage capacitor energized to 800 mJ (1265 V), and assuming that the transformer behaved ideally, about 80 mJ of energy would have been delivered to the spark gap (based on estimates of the resistance of the spark from subsequent voltage and current measurements across the gap discussed in Section A.4), while the remainder would have been dissipated in the 2 ohm resistor. Though less than 10 mJ should be ample to ignite most fuel-air mixtures (see Figure A.2.2),⁵⁶ this configuration failed to cause ignition of a rich methane/air mixture ($\phi = 1.3$), and the circuit was obviously not functioning as expected.

It seems likely that the failure of this circuit was caused by saturation of the transformer. The magnetic field strength of the transformer cannot be increased

Figure A.2.1
A schematic diagram of the preliminary ignition circuit. The circuit contains a Krytron switch and the energy storage capacitor, which is located on the low voltage side of the transformer, and thus isolated from the gap.

Figure A.2.2 Minimum ignition energies for various hydrocarbons as functions of their equivalence ratios.⁵⁶

above a maximum, or saturation, value, and this limits the flow of energy through the transformer. Most of the energy which should have passed from the capacitor to the gap was stopped by the saturation. This problem was avoided in the final design by putting the energy storage capacitor and the gap on the same side of the transformer.

We also had difficulty with the Krytron switch, which failed frequently. We have hypothesized that the frequent switch failures resulted from excessive currents, and large reverse voltages (i.e. cathode voltage greater than anode voltage). For the final designs, the Krytron was replaced by a silicon controlled rectifier (SCR), which switches more slowly than the Krytron, but is considerably more reliable.

A.3 Improved Ignition Circuits

In the three improved designs (see Figure A.3.1), the energy storage capacitor is mounted on the spark gap side of the transformer, and is charged by a separate power supply. This circumvents the problem caused by saturation of the pulse transformer. Since the charging voltage at the storage capacitor is insufficient to break down the spark gap, the gap is broken down by a high voltage pulse from the transformer. The storage capacitor then discharges into the gap through a pathway to ground.

Of the three improved designs shown in Figure A.3.1, two were abandoned because of difficulties in their implementation. The floating spark gap design required two feedthrough connectors to isolate both electrodes from the grounded bomb. In the preliminary design, one of the electrodes was grounded to the bomb. Unfortunately, the extra feedthrough connector would not fit in the oven. The three-electrode circuit design required an extra port for the third electrode, which carries the high voltage pulse required to break down the gap. All of the ports are currently being used. However, if an extra port existed, this circuit would be favored since the transformer is removed from the spark gap loop, eliminating the large transformer energy losses discussed in the following sections.

We implemented the remaining circuit in Figure A.3.1 in which one of the spark gap electrodes is grounded, and the high voltage pulse propagates through the storage capacitor to break down the gap. This final circuit functions in much the same way as the preliminary design. Initially, the SCR is an open circuit. Before firing the circuit, the capacitors on the spark gap side (the trigger capacitor) and the ignition side (the storage capacitor) of the transformer are charged. Then a trigger is sent to the SCR, and it becomes a closed circuit, discharging the trigger capacitor

Figure A.3.1 The three improved ignition circuits. The three electrode design shown at the top of the figure breaks down the gap with a high voltage pulse from a third electrode, thus eliminating the need for the transformer in the high voltage loop. The middle circuit has the disadvantage that neither electrode in the circuit is grounded. We implemented the design at the bottom of the figure.

through the transformer and into the spark gap. Though this discharge delivers very little energy to the gap, it provides a large voltage which breaks the gap down. Then the energy in the storage capacitor flows into the gap. The next sections will discuss measurements of the energy delivered to the gap.

A.4 Measurements of the Spark Energy

To monitor the performance of the final circuit, we measured the energy which it delivered to the spark gap. As with all electrical components, the instantaneous power to the gap is simply the product of the gap voltage and the current, and the energy is the time integral of the power. Thus by measuring the gap voltage and current as a function of time we were able to compute the energy delivered.

Before making these measurements, we developed an analytical model of the system, to predict the expected voltage and current signals. As discussed below, the model was able to predict many of the features of the curves, but the actual measurements were altered by unanticipated phenomena.

A.4.1 Analysis of the Ignition Circuit

Since the time scales for breakdown of the gap and for the discharge of the storage capacitor are disparate, the analysis of the dissipation of energy into the spark is straightforward. Breakdown occurs during about one-half microsecond, while the capacitor discharges during 100-200 microseconds. Relatively little energy is dissipated during breakdown, and it can safely be neglected.

The steady state voltage-current characteristics of an air gap between two electrodes have been studied thoroughly, and the typical behavior is depicted in Figure A.4.1.1. Although the initial ionization is accompanied by enormous variations in both current and voltage, the voltage drop across the ultimate arc remains relatively constant for a wide range of currents. Consequently, in the analysis of the ignition circuit, the spark gap is adequately represented as a constant voltage drop.

Similarly, for the sake of analysis, the ignition circuit can be partitioned into components which deliver the very high voltage pulse to break down the gap (high voltage power supply, transformer, and silicon controlled rectifier), and the simple loop which discharges the storage capacitor into the arc. Only the loop formed by the

Figure A.4.1.1 Typical steady state voltage-current characteristics of a spark gap.

transformer, capacitor, and spark gap participates during the dissipation of energy into the arc, and only these elements need be analysed.

In the analysis, the transformer is represented as an inductor and, since the voltage across the arc is constant, the spark gap is represented as a battery. The energy dissipation loop includes a capacitor, an inductor, and a battery in series, as shown in Figure A.4.1.2. Initially, the capacitor is charged to a voltage $V_c = V_o$, and the loop current is assumed zero until the gap has broken down. The voltages in the loop must sum to zero, so that

$$V_c + V_L + V_{sp} = 0 \quad (\text{A.4.1.1})$$

where the subscripts L, c, and sp designate the transformer, capacitor, and spark, respectively. This relation is recast into a differential equation for the instantaneous current flow by implementing the definitions of capacitor voltage,

$$V_c = Q/C \quad (\text{A.4.1.2})$$

and of voltage across the inductor,

$$V_L = L di/dt \quad (\text{A.4.1.3})$$

to obtain

$$L di/dt + Q/C + V_{sp} = 0 \quad (\text{A.4.1.4})$$

where L is the transformer inductance, Q is the charge on the capacitor, C is the capacitance of the capacitor, and i is the loop current. Differentiating with respect to time eliminates the constant voltage across the spark, and yields

$$d^2 i/dt^2 + i/LC = 0 \quad (\text{A.4.1.5})$$

Thus, the current is given by

$$i = A \sin(\omega t) \quad (\text{A.4.1.6})$$

where,

$$A = (V_o - V_s)(C/L)^{1/2}$$

$$\omega = (1/LC)^{1/2}$$

The voltage across the capacitor is given by

$$V_c = V_{sp} + (V_o - V_{sp})\cos(\omega t) \quad (\text{A.4.1.7})$$

The voltage across the inductor is given by

$$V_L = (V_{sp} - V_o)\cos(\omega t) \quad (\text{A.4.1.8})$$

Equations A.4.1.6 - A.4.1.8 provide the forms of the voltage and current traces one would expect to measure. We can now anticipate sinusoidal currents, and the capacitor and inductor voltages should resemble cosine waves.

A.4.2 Transient Circuit Current Measurements

To determine the energy dissipated in the gap, it is necessary to measure the instantaneous spark gap voltage and loop current. The transient measurements are complicated by the magnitude of the high voltage pulse which forms the arc, and by the short durations of the trigger and breakdown pulses. For instance, the voltage required for breakdown is typically 20 kV, and breakdown occurs in about one-half microsecond. After breakdown the gap voltage dramatically decreases to less than 100 V (as seen in Figure A.4.1.1), and remains constant for 100 to 200 microseconds. Both wide dynamic range and wide bandwidth are required in the diagnostic instruments for these large variations in the signal magnitude and frequencies.

Furthermore, the high voltages induce strong electric fields and large currents induce magnetic fields. Stray capacitances introduce inadvertent filtering, and the inherent inductances of the diagnostic components distort the transient current measurements. These effects can be confounding, especially with regard to voltage measurements. But a calibrated inductor is especially well-suited for current measurements in this circuit, because the currents are substantial.

Our transient current measurements are based on a Rogowski Coil. This device is a toroidal inductor which surrounds the current conductor. The magnetic field associated with the current in the wire induces a current in the coil which is sent through a calibrated shunt and measured. Rogowski coils are suitable for large currents, and do not involve any additional elements in the subject current loop, or any direct connection to the circuit. A properly shielded Rogowski coil is not susceptible to unwanted capacitive pickup from large electric fields.

However, the Rogowski coil cannot measure extremely high frequency signals. And its iron core will be saturated by large currents after extended continuous

The voltage across the capacitor is given by

$$V_c = V_{sp} + (V_o - V_{sp})\cos(\omega t) \quad (\text{A.4.1.7})$$

The voltage across the inductor is given by

$$V_L = (V_{sp} - V_o)\cos(\omega t) \quad (\text{A.4.1.8})$$

Equations A.4.1.6 - A.4.1.8 provide the forms of the voltage and current traces one would expect to measure. We can now anticipate sinusoidal currents, and the capacitor and inductor voltages should resemble cosine waves.

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service. Neither limitation entered into this application, because the ignitor fires in less than 200 microseconds and the measured signals were within the bandwidth reported by the manufacturer. Preliminary comparisons among measurements made with two different Rogowski coils and with prescribed voltages and a calibrated resistor designed for measuring currents validated this scheme. Transient current measurements are shown in section A.4.4.

A.4.3 Transient Circuit Voltage Measurements

Several voltage dividers were tested before we found an adequate design. A schematic for the first voltage divider design is shown in Figure A.4.3.1. For the breakdown voltage of 20 kV, a 1000 to 1 divider yields a peak output of 20 V, which is compatible with the available oscilloscopes. For a dividing resistance, R_2 , of 100 MOhm, the peak current is 0.2 mA, which is about five orders of magnitude less than the current through the arc. To meet the constraint on the 1000:1 attenuation of the subject voltage, the resistance to ground, R_1 , is specified as 100 kOhm.

However, the very large resistance of the divider brings the capacitance of the oscilloscope into play, causing inadvertent filtering. The equivalent circuit including the oscilloscope appears in Figure A.4.3.2. Note that the capacitance of the oscilloscope and the dividing resistances act as a low pass filter which passes only those signals at frequencies below a cutoff of about 15 kHz. Virtually all of the spark ignition signal was attenuated by this inadvertent filtering.

Our second voltage diagnostic was a combined resistive and capacitive divider described by Schwab,⁹⁰ and shown schematically in Figure A.4.3.3. This divider eliminated the low pass filter problem but added two additional complications. The first was simply one of fabrication methods. With so many connections among the various components, there was no way to reduce stray capacitances and inductances to a tolerable level. The second disadvantage is also rooted in the actual performance of the components (in contrast to their ideal behavior). Although the frequency response of this divider should be uniform, we found that signals with a frequency of 1 kHz were significantly attenuated. The attenuation is due to the actual behavior of the components in the divider, as represented in Figure A.4.3.4. Note that the actual behavior of both resistors and capacitors is determined by their effective inductances, and that resistors have capacitance (and conversely). Such complications were magnified in our first Schwab divider since 21 resistors and 20 capacitors were required to implement the design.

Figure A.4.3.1 The first (and simplest) voltage divider design tested for measuring the voltage across the gap.

Figure A.4.3.2 The equivalent circuit for considering the effect of the oscilloscope on the performance of the voltage divider shown in Figure A.4.3.1.

Figure A.4.3.3 The mixed resistor-capacitor network suggested by Schwab⁹⁰ for measuring large voltages.

Figure A.4.3.4 The actual circuit characteristics of resistors and capacitors. The nonideal features of these components have a strong bearing on their performance for high voltage and high current measurements.

A modified Schwab divider, in which the number of components was minimized, ultimately proved to be a reliable voltage diagnostic. Our instrument now includes only two resistors and two capacitors in a grounded box. This completely eliminates unwanted pickup and nearly eliminates the attenuation of 1 kHz signals. However, to obtain the proper capacitances and high voltage handling capabilities, air capacitors were fabricated in house; the initial problem of arcing across the capacitor plates when the component was subjected to 20 kV was overcome by folding the plates to give them rounded edges. It was also important to firmly anchor the plates within the enclosure to avoid a varying capacitance. Transient voltage measurements are shown in the next section.

A.4.4 Power Input to Spark

The ignition circuit was characterized by transient measurements using the Rogowski coil and the modified Schwab voltage divider. The current through the spark gap can be monitored at any point in the energy dissipation loop; in fact, we tested for stray current paths by monitoring the current at several points in the loop. The voltage across the gap was monitored directly. To determine the partitioning of the energy discharged from the storage capacitor among the transformer, capacitor, and spark gap, the voltage across the transformer was also measured. The voltage across the capacitor and the voltage across the wires and connections were also monitored to close the total energy balance for a complete discharge cycle.

Typical transient voltage and current measurements across the spark gap are shown in Figure A.4.4.1. These records were collected on a Nicolet digital storage oscilloscope. As expected, the voltage across the spark is nearly constant throughout the entire discharge cycle, at about 30 V. The transient current measurement indicates a significant departure from the sinusoidal waveform predicted by the analysis. The observed waveform is biased by the transformer, as explained below. Note also that the spark is extinguished after 150 microseconds, when the current falls to zero. At the end of the cycle, the voltage across the gap becomes equal to the final voltage across the storage capacitor. For the discharge shown in Figure A.4.4.1, about 25 mJ (225 V) remains in the storage capacitor after the cycle.

As seen in Figure A.4.4.2, the voltage across the transformer resembles an inverted cosine, as expected from the circuit analysis. This waveform is inverted because the voltage across the spark is smaller than the initial voltage across the capacitor ($V_s - V_o < 0$), giving a negative amplitude (cf. eq. A.4.1.8). Early in the

Figure A.4.4.1 Typical measured spark voltages and system currents.

Figure A.4.4.2 The measured inductor voltage and system current during sparking.

cycle the discharging capacitor powers the transformer but, later in the cycle, the transformer saturates and eventually re-energizes the storage capacitor.

The saturation of the transformer also accounts for the nonsinusoidal waveform. The effective inductance of the transformer varies during the cycle, becoming very small as the transformer saturates. Since the current through the loop is inversely proportional to the transformer inductance, the change in the spark current accelerates as the transformer saturates (this occurs at about 75 microseconds in Figure A.4.4.2). This behavior leads to peak currents which are significantly larger than those anticipated from the analysis.

The transient voltage across the capacitor, shown in Figure A.4.4.3, resembles a cosine wave with DC offset as predicted by the analysis. Of course the voltage decays as energy is dissipated into the spark, and the cosine is not symmetric.

These waveforms also describe the energy stored in each component. The associated time integrals of the voltage-current products through each component were computed from the digitized waveforms. This operation was very sensitive since the calculation for the energy storage in the capacitor and transformer involves the product of sine and cosine waves; slight phase shifts introduced by the measuring equipment would result in substantial computational error. We were, however, able to determine by calibration with a signal generator that instrument-caused phase shifts were negligible over the relevant frequency domain.

An independent validation of the energy dissipation based on the current-voltage product is shown in Figure A.4.4.4. The energy in the capacitor is given by $CV_c(t)^2/2$, as well as by the initial energy minus the time integral of the current-voltage product. These alternate calculation strategies are compared in Figure A.4.4.4, and are consistent to within 20%. The agreement supports our earlier observation that the uncertainties due to phase shifts between the recorded voltages and currents are held to tolerable levels.

The partitioning of the energy dissipation among the components in the energy dissipation loop is shown in Figure A.4.4.5. In this particular cycle the storage capacitor was energized to 74 mJ (400 V). Even though the capacitor discharges completely during the initial 100 microseconds of the cycle, it is subsequently re-energized by the transformer to about 20 mJ. Thus only three-fourths of the initial energy is dissipated as the ignitor is fired. Most of this energy is dissipated in the transformer. Less than 10% is lost in the resistances of the connections.

Figure A.4.4.3 The measured capacitor voltage and system current during sparking.

Figure A.4.4.4 Comparison of the results of two independent methods for determining the transient energy storage in the capacitor during the spark event. The good agreement of these two curves confirms the accuracy of our voltage and currents measurements.

Figure A.4.4.5

The energy stored and dissipated in each element of the high voltage loop. The sum of these energies remains close to the initial energy stored in the capacitor, and acts as another confirmation of the accuracy of our measurements.

Consequently, about 20 mJ was dissipated in the spark. In summary, of the initial energy which is theoretically available for ignition, 25% remains in the capacitor, 25% powers the spark, 40% is dissipated in the transformer, and 10% is lost in the connections.

Energies dissipated in the spark for several initial voltages are tabulated below. The measurements demonstrate that the modified ignition circuit will deliver energies to the spark which exceed required minimum ignition energies for all mixtures of interest. The listed values provide an adequate range to check the effect of varying spark energy on laminar burning velocities, in order to assure that combustion rates do not depend upon spark energies.

Table A.4.4.1. Spark energies for various initial capacitor charge voltages.

Charge Voltage (V)	Spark Energy (mJ)
275	14
400	19
450	24
475	26

One aim of this analysis was to validate the much simpler measurement of energy dissipation based on the discharge from the storage capacitor. Provided that all of the energy leaving the capacitor was dissipated in the gap, the energy input could be calculated from the initial and final voltages across the capacitor, according to

$$E_{sp} = C/2(V_i^2 - V_f^2)$$

where C is the capacitance of the capacitor. However, the performance of this ignition circuit undermines the simple approach to measuring the ignition energy based on the energy discharged from the storage capacitor. More than half of the available energy is lost to the transformer and connections. To restore the validity of this approach, the transformer must be isolated from the energy dissipation loop, as in the three-electrode circuit.

Appendix B. Computer Program for Inferring Laminar Burning Velocities from Pressure Measurements

PROGRAM SU

C

C.....

C

C SU implements the analysis discussed in Chapter 3 to reduce
C pressure measurements from the constant volume bomb to
C burning velocities. The program uses Newton-Raphson
C iteration to solve the coupled set of equations, Eq. 3.2.3.5,
C 3.2.3.6, and 3.2.3.7, for the states of the reactants and
C products at a given bomb pressure (with given initial
C temperatures and pressures). These states then determine the
C burning velocity through Eq. 3.2.5.3. The product state is
C modeled with the approximate equilibrium model of Martin and
C Heywood,¹⁰ which is implemented in Subroutine NEWT.
C Subroutine UNBURN returns the internal energy and specific
C heat of the unburned gases at a specified temperature.
C Subroutine BIGNEW performs Gaussian elimination on the
C matrix formed by the Newton-Raphson Iteration method. The
C remaining subroutines (PRO (propane), MET (methane), CO2
C (carbon dioxide), etc.) return constants which are utilized
C to determine the specific heat and internal energy of the
C reactants. The main program sets up the Newton-Raphson
C iteration, and calls the subroutines.

C

C

C

C The only outputs from SU are the states of the gases, and the
C fraction of mass burned (x) as functions of time. The output
C for SU is processed by the program, BURNV, to spline fit the
C x-time curve, and calculate the burning velocity using
C Eq. 3.2.5.3.

C

C

C

Each step of the program is explained in detail below.

List of Variables

ACH(i) - variables for testing the convergence of the
Newton-Raphson iteration

A1(i) - constant in equations for determining the specific
heat of the reactants (see subroutine UNBURN for
its use)

B1(i) - constant in equations for determining the specific
heat of the reactants (see subroutine UNBURN for
its use)

C1(i) - constant in equations for determining the specific
heat of the reactants (see subroutine UNBURN for
its use)

CPH - specific heat of the unburned gases (J/mole K)

C2 - coefficient for the vibrational temperature in the
calculation for the internal energy of the burned
gases (see Eq. 3.2.4.10)

DC1P - derivative of SI1 with respect to pressure

DC2P - derivative of C2 with respect to pressure

DC1T - derivative of SI1 with respect to burned gas
temperature

DC2T - derivative of C2 with respect to burned gas
temperature

DCPHTU- derivative of CPH with respect to unburned gas
temperature

DEBP - derivative of EB with respect to pressure

DEBT - derivative of EB with respect to burned gas
temperature

C DELTA - ratio of XC and XH
 C DEUTU - derivative of EU with respect to unburned gas
 C temperature
 C DHFTP - derivative of HFT with respect to pressure
 C DHFTT - derivative of HFT with respect to burned gas
 C temperature
 C DMBT - derivative of MB with respect to burned gas
 C temperature
 C DMBP - derivative of MB with respect to pressure
 C DON1 - number of moles of product gas per mole of O₂ in
 C the reactants
 C DT - time interval between pressure samples (sec)
 C DUP - derivative of U with respect to pressure
 C DUT - derivative of U with respect to burned gas
 C temperature
 C DVBP - derivative of VB with respect to pressure
 C DVBT - derivative of VB with respect to burned gas
 C temperature
 C DYP - derivative of Y with respect to pressure
 C DYT - derivative of Y with respect to burned gas
 C temperature
 C EB - internal energy of the burned gases (kJ/kg)
 C EM - initial internal energy of the gases in the bomb
 C (kJ/kg), based on a reference temperature of 0 K,
 C and (H₂, O₂, C(s), etc.) molecules as the reference
 C species
 C EPS - $4 \cdot \text{DELTA} / (1 + 4 \cdot \text{DELTA})$
 C EU - internal energy of the unburned gases (kJ/kg)
 C F(i) - functions defined by Eq. 3.2.3.5-3.2.3.7 for the
 C Newton-Raphson iteration (see discussion below)
 C G - constant in calculation of derivatives for MB
 C HFT - heat of formation of the burned gases (see Eq.
 C 3.2.4.12-13)
 C HF(i) - heats of formation of the reactant species,
 C obtained from the subroutines
 C J(i,k) - derivative array for Newton-Raphson iteration (see
 C discussion below)
 C KA1 - equilibrium constant defined by Eq. 3.2.4.9

C	KA2	-	equilibrium constant defined by Eq. 3.2.4.9
C	M	-	mass of the gases in the bomb
C	MCP	-	mass of the products per mole of O ₂ in the
C			reactants
C	MF(i)	-	mole fractions of the reactants
C	MU	-	molecular weight of the unburned gas
C	P0	-	initial pressure (atm)
C	P1	-	instantaneous pressure (input from combustion bomb
C			measurement)
C	SI1	-	constant which multiplies TB in Eq. 3.2.4.10
C	SY	-	N ₂ /O ₂ ratio in the reactants
C	T	-	time (sec)
C	T0	-	initial temperature in the bomb (K)
C	TB	-	temperature of the burned gases (K)
C	TR	-	reference temperature (set to 298 K)
C	TU	-	temperature of the unburned gases (K)
C	TV	-	characteristic vibrational temperature for the
C			burned gases (K)
C	TVT	-	constant in the calculation for vibrational
C			temperature
C	U	-	extra number of moles of monatomic gas in the
C			burned gas due to dissociation of diatomic gas (per
C			mole of O ₂ in the reactants)
C	V	-	volume of the bomb (cm ³)
C	VB	-	specific volume of the burned gases (cm ³ /gm)
C	VU	-	specific volume of the unburned gases (cm ³ /gm)
C	X	-	fraction of the original mass which has been
C			burned at a given time
C	XC	-	total moles of carbon in the reactant gases
C	XH	-	total moles of hydrogen in the reactant gases
C	XO2	-	total moles of oxygen in the reactant gases
C	Y	-	extra number of moles of diatomic gas due to
C			dissociation of triatomic gas (per mole of O ₂ in
C			the reactants)
C			
C			
C			

```

EXTERNAL NEWT, HYD, MET, CO2, CO, BEN, BIGNEW, PRO
EXTERNAL O2,N2,UNBURN
DIMENSION J(5,5), F(5), ACH(5)
CHARACTER A*3,B*2,file*6,fnew*10
REAL*8 MT,MU,M,MCP,KA1,KA2,MB,J,TU,T0,P1,P0,V,X,EM,
+TV,Y,TB,SI1,C2,HFT,G,DON1,VB,TVT,EB,DMBT,DMBP,DVBT
+,DVBP,DC1T,DHFTT,DC1P,DC2P,DHFTP,DEBT,DEBP,VU,CPH,
+EU,DCPHTU,DEUTU,DT,EPS,SU,U,DYP,DYT,DUP,DUT,SY,F,
+ACH,DDX,DT2,XO,T,TBO,TSL,TSU,CZEC,TR,CPO2,CPN2,
+DCPO2,DCPN2,MFTOT,DTVTT,DC2T
REAL*8 MF(9),A1(9),B1(9),C1(9),HF(9),XC,XH,XO2,
+DELTA

```

C
 C The program asks the user for the initial pressure and
 C temperature in the bomb. It also requests the bomb radius
 C (76.2 mm), the number of samples in the pressure trace
 C (usually 200), the clock speed at which the samples were
 C taken (the data acquisition program requests the clockspeed
 C before acquiring signals), the number of channels for which
 C data were acquired during the experiment (to determine the
 C time between samples), the file which contains the pressure
 C trace, the volts to psi conversion factor defined by the
 C charge amplifier, and the initial input voltage from the
 C pressure transducer (this value is taken as a zero offset,
 C and subtracted from all subsequent samples). The clockspeed
 C is the number of computer clock beats between samples. Each
 C clock beat has a duration of 2.5 microseconds, so a
 C clockspeed of 100 gives a time between samples of 250
 C microseconds. If multiple channels are sampled, then the
 C samples are collected sequentially. In other words, if two
 C channels are sampled at 250 microseconds between channel,
 C then the time between samples on the first channel is 500
 C microseconds.

C
 C
 C
 C WRITE(*,*) ' What is the initial pressure in the
 bomb (atm)?'

```

      READ(*,*) P0
      WRITE(*,*) ' '
      WRITE(*,*) ' What is the initial temperature
(Kelvin)?'
      READ(*,*) T0
      WRITE(*,*) ' '
      WRITE(*,*) ' '
      WRITE(*,*) ' What is the radius of the bomb (mm)?'
      READ(*,*) RV
20    WRITE(*,*) ' '
      WRITE(*,*) ' What is the equivalence ratio, fi?'
      READ(*,*) FI
30    WRITE(*,*) ' '
      WRITE(*,*) ' How many samples are there?'
      READ(*,*) hman
      WRITE(*,*) ' '
      WRITE(*,*) ' What was the clock speed?'
      READ(*,*) clks
      WRITE(*,*) ' '
      WRITE(*,*) ' How many channels were used?'
      READ(*,*) chus
      WRITE(*,*) ' '
      WRITE(*,*) ' What file is the input in? (Leave off
.prn)'
      READ(*,618) file
618   FORMAT(A6)
      fnew = file//'.prn'
      write(*,*) ' '
      write(*,*) ' What is the psi/Volt conversion?'
      read(*,*) ampl
      write(*,*) ' '
      write(*,*) ' What is the pressure trace starting
number? (bits)'

```

C

C The lines below calculate the mole fractions of each species
C in the reactants (MF(i)), check the equivalence ratio (FI),
C and determine the N_2/O_2 ratio (SY).

C


```

C      MF(1) - CO
C      MF(2) - CO2
C      MF(3) - H2O
C      MF(4) - H2
C      MF(5) - CH4
C      MF(6) - C3H8
C      MF(7) - C6H6
C      MF(8) - N2
C      MF(9) - O2

```

```

C
C      read(*,*) nbeg
C      MF(1) = .0423
C      MF(2) = .0272
C      MF(3) = .091
C      MF(8) = .6195
C      MF(5) = .0196
C      MF(6) = .0046
C      MF(7) = .00874
C      MF(4) = .0315
C      MF(9) = .1647
C      DO 777 II = 1,7
777    MF(II) = MF(II)*FI
C      MF(8) = MF(8)+MF(3)
C      MF(3) = 0.
C      MFTOT = 0.0
C      DO 778 II = 1,9
778    MFTOT = MFTOT + MF(II)
C      DO 779 II = 1,9
779    MF(II) = MF(II)/MFTOT
C      XC = (MF(1)+MF(5)+3*MF(6)+6*MF(7)+MF(2))
C      XH = (4*MF(5)+8*MF(6)+6*MF(7)+2*MF(4))
C      DELTA = XC/XH
C      EPS = 4*DELTA/(1.+4*DELTA)
C      XO2 = MF(9)+MF(2)+.5*MF(1)
C      FI = XC/(EPS*XO2)
C      SY = MF(8)/XO2

```

C
C
C
C
C
C
C
C
C
C

Then subroutines are called to return constants for the thermochemical data (heats of formation and specific heats) of the reactants. The formula for the specific heat is $c_p = A1 + B1 \cdot T + C1 \cdot T^2$. The open commands open the output file and the input pressure data file.

```
CALL PRO(A1(6),B1(6),C1(6),HF(6))
CALL BEN(A1(7),B1(7),C1(7),HF(7))
CALL MET(A1(5),B1(5),C1(5),HF(5))
CALL CO(A1(1),B1(1),C1(1),HF(1))
CALL O2(A1(9),B1(9),C1(9),HF(9))
CALL N2(A1(8),B1(8),C1(8),HF(8))
CALL CO2(A1(2),B1(2),C1(2),HF(2))
CALL HYD(A1(4),B1(4),C1(4),HF(4))
66 OPEN(1,FILE='OUT.PRN',STATUS='NEW')
   OPEN(2,file=fnew,status='old')
   PAUSE ' Hit <ctrl/prtscrn> if you wish to engage
the printer.'
```

C
C
C
C
C
C
C
C
C

The next section calculates the time between samples (DT), the finish time (TFIN), and then outputs all of the information determined so far to the screen and the output file.

```
dt = chus*clks*2.5e-6
tfin = dt*(hman-1)
WRITE(*,*) ' '
WRITE(*,*) '      DT,    FI,    P,    TU,    TFIN,    SY'
WRITE(*,*) ' '
WRITE(*,100) DT, FI, P0, T0, TFIN, SY
WRITE(1,100) DT, FI, P0, T0, TFIN, SY
100 FORMAT(E12.5,F7.4, 4F8.2)
WRITE(*,*) ' '
```

```

WRITE(*,*) ' A1, B1, C1, HF, EPS'
WRITE(*,*) ' '
DO 799 IJ = 1,9
799 WRITE(*,110) A1(IJ), B1(IJ), C1(IJ), HF(IJ), EPS
WRITE(1,110) A1(IJ), B1(IJ), C1(IJ), HF(IJ), EPS
110 FORMAT(5E14.6)
C
C The next section calculates the pressure from the computer
C acquisition. When the computer acquires the pressure signal,
C it assigns the acquired voltage a number between 0 and 4096.
C 0 corresponds to -10 volts, 2048 corresponds to 0 volts, and
C 4096 corresponds to 10 volts. The formula for P1 below
C converts these assignments back to pressure, in atm. In the
C formula, AMPL is the voltage to pressure conversion assigned
C by the charge amplifier, in volts/psi. This section also
C calculates the molecular weight of the unburned gases (MU),
C the volume of the bomb (V), and the mass in the bomb (M).
C
C
C
C
C read(2,*) bit
C p1= (bit-nbeg)/2048*10*ampl/14.7+P0
C t = 0.0
C TU = T0
C MU = 28*MF(1)+44*MF(2)+28*MF(8)+16*MF(5)+44*MF(6)
C MU = MU + 78*MF(7)+2*MF(4)+32*MF(9)
C V = (4.*3.141592654*((RV/10)**3))/3.
C
C Note: V is in cm**3. M is in gms.
C
C M = P0*V*MU/(82.05*T0)
C CALL UNBURN(MU,CPH,EM,TU,DCPHTU,DEUTU,A1,B1,
+C1,HF,T0,MF)
C WRITE(*,*) CPH,MF(1),MF(2),MF(3),MF(4)
C WRITE(*,*) MF(5),MF(6),MF(7),MF(8),MF(9)
C X = .001
C ICO = 0
C TV = (3256-2400*EPS+300*SY)/(1-.5*EPS+.09*SY)

```

MCP = (8*EPS +4)*FI+32+28*SY

Y = 2.

TB = 1997.

WRITE(*,*) 'M,EM,MU,V'

WRITE(1,*) M,EM,MU,V

WRITE(*,*) M,EM,MU,V

TR = 298.

C

C

C

C

C

C

C

C

C

C

C

C

C

200 KA1 = 5.819E-6*EXP(.9674*EPS+35810./TB)
KA2 = 2.961E-5*EXP(2.593*EPS+28980./TB)
CALL NEWT(TB,P1,KA1,KA2,EPS,FI,SY,Y,U,DYP,
+DYT,DUP,DUT)

IF(FI.GT.1) GOTO 130

MB = MCP/(1 + (1-EPS)*FI+SY+Y+U)

SI1 = 5+(7-6*EPS)*FI+5*SY+3*Y+U

C2 = 2*(1+(5-3*EPS)*FI+SY-3*Y-U)

HFT = 1000*Y*(121.5+29.59*EPS)+117500.*U

HFT = HFT + (20372*EPS-114942)*FI

G = (-MCP)/((1+(1-EPS)*FI+SY+Y+U)**2)

GOTO 140

130 DON1 = (2-EPS)*FI+SY+Y+U

MB = MCP/DON1

SI1 = 2+2*(5-3*EPS)*FI+5*SY+3*Y+U

C2 = 2*(4+(2-3*EPS)*FI+SY-3*Y-U)

HFT = 1000*Y*(121.5+29.59*EPS)+117500*U

HFT = HFT+(20372.*EPS+19448.)*FI-134390.

+ -6500.*(FI-1)/EPS

```

      G = (-MCP) / (DON1**2)
140  VB = 82.05*TB / (P1*MB)
C
C  VB IS IN cm^3/gm. H is in kJ/kg.
C
      TVT = TV / (EXP(TV/TB) - 1.)
      EB = 8.314 * (SI1*TB + C2*TVT + HFT) / (2*MCP)
      DMBT = G * (DYT + DUT)
      DMBP = G * (DYP + DUP)
      DVBP = -VB * (1. / P1 + DMBP / MB)
      DVBT = 82.05 / (MB * P1) * (1. - TB * DMBT / MB)
      DC1T = 3 * DYT + DUT
      DTVTT = ((TVT / TB) ** 2) * EXP(TV / TB)
      DC2T = -2 * (3 * DYT + DUT)
      DHFTT = 1000 * (121.5 + 29.59 * EPS) * DYT + 117500 * DUT
      DC1P = 3 * DYP + DUP
      DC2P = -2. * (3 * DYP + DUP)
      DHFTP = 1000 * (121.5 + 29.59 * EPS) * DYP + 117500. * DUP
      DEBT = 8.314 * (SI1 + TB * DC1T + C2 * DTVTT + TVT * DC2T
++DHFTT) / (2 * MCP)
      DEBP = 8.314 * (TB * DC1P + TVT * DC2P + DHFTP) / (2 * MCP)
      VU = 82.05 * TU / (P1 * MU)
      CALL UNBURN(MU, CPH, EU, TU, DCPHTU, DEUTU, A1, B1,
+C1, HF, T0, MF)
      J(1,1) = vb - vu
      J(3,1) = 0.
      J(2,1) = eb - eu
      J(1,2) = X * DVBT / VU
      J(3,2) = 0.
      J(2,2) = X * DEBT
      J(1,3) = -(X * VB - V / M) / (VU * TU)
      J(3,3) = -LOG(TU / T0) * DCPHTU / 8.314 - CPH / (8.314 * TU)
      J(2,3) = (1 - X) * DEUTU
      F(1) = (X * VB - V / M) / VU + 1 - X
      F(3) = LOG(P1 / P0) - CPH / 8.314 * LOG(TU / T0)
      F(2) = X * EB + (1 - X) * EU - EM
      CALL BIGNEW(F, J, ACH, TU, TB, x)
      ILOOP = ILOOP + 1

```

```

      IF(ICO.LT.5) ABCD = 1E-2
      IF(ICO.GE.5) ABCD = 5E-5
      IF((ABS(ACH(1)/X).GT.ABCD).OR.(ABS(ACH(2)/TB)
+ .GT.1E-5)) GOTO 200
      IF(ABS(ACH(3)/TU).GT.1E-5) GOTO 200
      WRITE(*,*) ' Number of iterations was: ', ILOOP
      ILOOP = 0
      t = ico*dt
      ico = ico+1
      RFLAME = (3*M*X*VB/12.56637)**.333333333333
      WRITE(*,*) ' '
      WRITE(*,*) '      T,      P1,      TU,      TB,      X,      Rf'
      WRITE(*,*) ' '
      WRITE(*,120) T, P1, TU, TB, X, RFLAME
120    FORMAT(9E12.5)
      WRITE(1,120) T, P1, TU, TB, X, VU, VB, RFLAME
      if(ico.EQ.hman) goto 142
      read(2,*) bit
      p1 = (bit-nbeg)/2048*10*ampl/14.7 +p0
      GOTO 200
142    CLOSE(1,STATUS='KEEP')
      close(2,status='keep')
1000  STOP
      END

```

C

C *This subroutine implements the approximate equilibrium scheme*
C *discussed in Section 3.2.4 to return the state of the burned*
C *gases. The input variables are the burned gas temperature*
C *and the pressure. The output variables are Y, U, and their*
C *derivatives with respect to burned gas temperature and*
C *pressure.*

C

C

C

C

```

      SUBROUTINE NEWT(TB, P1, KA1, KA2, EPS, FI, SY,
+ Y, U, DYP,DYT, DUP, DUT)

```

C

```

      REAL*8 A,B,C,D,E,F1,F2,KA1,KA2,TB,P1,SY,Y,U,

```

```

+DYP,DYT,DUP,DUT,X,BIG,T1,T2,DUT1,DUT2,DUT3,
+DKA1T,DKA2T,DEN,EPS
J = 0
IF(FI.GT.1.0) Y = Y + FI - 1.
11  A = EPS*FI - 2.*Y
    B = FI*(1.-EPS) +1 +Y +SY
    C = KA2*A +KA1*Y
    D = KA1*Y*(1-FI+Y)
    E = 4*P1*KA1*KA2*Y-EPS*FI+2*Y
    F1 = A*B*C - D*E
    F2 = -2*B*C + A*C + (KA1-2*KA2)*A*B
    F2 = F2 - KA1*(1-FI+2*Y)*E - D*(4*P1*KA1*KA2 +2.)
    X = Y - F1/F2
    IF(ABS((X-Y)/Y).LT.1E-6) GOTO 31
    J = J+1
    IF (J.GE.30) GOTO 21
    Y = X
    GOTO 11
21  WRITE(*,111)
111  FORMAT( '      More than 30 iterations for Y with no
+convergence.')
    STOP
31  U = D/C
    DKA1T = -.2083784*EXP(.9674*EPS+35810./TB)/(TB**2)
    DKA2T = -.858098*EXP(2.593*EPS+28980/TB)/(TB**2)
    BIG = 1./B - 2./A - (4.*P1*KA1*KA2+2)/E
    BIG = BIG - 1./Y - 1./(1.-FI+Y) + (KA1-2.*KA2)/C
    T1 = (1./KA1 - Y/C + 4*P1*KA2*Y/E)*DKA1T
    T2 = (4.*P1*KA1*Y/E - A/C)*DKA2T
    DYT = (T1+T2)/BIG
    DUT1 = (1./KA1-Y/C)*DKA1T
    DUT2 = (1./Y + 1./(1.-FI+Y) - (KA1-2.*KA2)/C)*DYT
    DUT3 = A/C*DKA2T
    DUT = U*(DUT1 + DUT2 - DUT3)
    DEN = 1./B - 2./A - (4*P1*KA1*KA2+2)/E
    + -1./Y -1./(1.-FI+Y)
    DEN = DEN + (KA1 - 2.*KA2)/C
    DYP = 4.*KA1*KA2*Y/(E*DEN)

```

```

DUP = U*DYP*(1./Y + 1./(1.-FI+Y) - (KA1-2.*KA2)/C)
IF (FI.GT.1.0) Y = Y - FI + 1.
RETURN
END

```

C
C
C
C
C
C
C

This subroutine solves the $f=Jx$ matrix equation formulated in the main program, and returns the x vector. Gauss elimination is used.

```

SUBROUTINE BIGNEW(B,AA,X,tu,tb,exx)
DIMENSION AA(5,5), B(5), X(5), A(5,6)
REAL*8 A,B,X,EX,Y,AA,tu,tb,exx
nnn = 2
x(3) = b(3)/aa(3,3)
b(2) = b(2) - x(3)*aa(2,3)
b(1) = b(1) - x(3)*aa(1,3)
DO 41 I = 1,NNN
DO 41 J = 1,NNN
41  A(I,J) = AA(I,J)
DO 42 I = 1,NNN
42  A(I,NNN+1) = B(I)
DO 1 J = 1,NNN
DO 2 I = J,NNN
2   IF(A(I,J).NE.0) GOTO 3
WRITE(*,*) 'NO UNIQUE SOLUTION.'
STOP
3   DO 4 K = 1,NNN+1
EX = A(J,K)
A(J,K) = A(I,K)
4   A(I,K) = EX
Y = 1./A(J,J)
DO 5 K=1,NNN+1
5   A(J,K) = Y*A(J,K)
DO 6 I = 1,NNN
IF(I.EQ.J) GOTO 6

```



```

      Y = -A(I,J)
      DO 7 K = 1,NNN+1
7     A(I,K) = A(I,K)+Y*A(J,K)
6     CONTINUE
1     CONTINUE
      DO 8 I = 1,NNN
8     X(I) = A(I,NNN+1)
      tu = tu - x(3)
      tb = tb - x(2)
      exx = exx - x(1)
      RETURN
      END

```

C
C
C
C
C
C
C
C
C
C
C
C

This subroutine determines the specific heat and internal energy of the reactants. The input variables and parameters are the unburned gas temperature and the constants for the specific heat equation, $c_p = A_1 + B_1 \cdot T + C_1 \cdot T^2$. The temperature derivatives of the specific heat and the internal energy are also returned. Note that these properties are not a function of pressure, so no pressure derivatives are necessary.

```

      SUBROUTINE UNBURN(MU,CPH,EU,TU,DCPHTU,DEUTU,A1,
+ B1,C1,HF,T0,MF)
      REAL*8 MU,CPH,EU,TU,DCPHTU,DEUTU
      REAL*8 A1(9),B1(9),C1(9),HF(9),CPHI(9),CPI(9)
      REAL*8 DCPH(9),DCP(9),T0,MF(9)
      CPH = 0.0
      EU = 0.0
      DEUTU = 0.0
      DCPHTU = 0.0
      DO 781 II = 1,9
      CPHI(II) = A1(II) + B1(II)*(TU+T0)/2
++ C1(II)*((TU+T0)/2)**2

```

```

      CPI(II) = A1(II) + B1(II)*(TU+298)/2
      ++ C1(II)*((TU+298)/2)**2
      DCP(II) = B1(II)/2 + C1(II)*(TU+T0)/2
      DCPH(II) = B1(II)/2 + C1(II)*(TU+298)/2
      CPH = CPH + MF(II)*CPHI(II)
      EU = EU + 1/MU*MF(II)*(HF(II)+CPI(II)*(TU-298))
      DCPHTU = DCPHTU + MF(II)*DCPH(II)
781  DEUTU = DEUTU + 1/MU*MF(II)*(CPI(II)
      ++ (TU-298)*DCP(II))
      EU = EU - 8.314*TU/MU
      DEUTU = DEUTU - 8.314/MU
      RETURN
      END

```

```

C      This subroutine lists the thermodynamic constants for
C      hydrogen.

```

```

C
C

```

```

      SUBROUTINE HYD(A1,B1,C1,HF)
      REAL*8 A1,B1,C1,HF
      A1 = 29.0801
      B1 = -.8372E-3
      C1 = 2.0135E-6
      HF = 8472.46
      RETURN
      END

```

```

C      This subroutine lists the thermodynamic constants for
C      methane.

```

```

C
C

```

```

      SUBROUTINE MET(A1,B1,C1,HF)
      REAL*8 A1,B1,C1,HF
      A1 = 14.1529
      B1 = 75.5322E-3
      C1 = -17.9998E-6

```

HF = -56908.67

RETURN

END

C *This subroutine lists the thermodynamic constants for oxygen.*

C

C

C

SUBROUTINE O2(A1,B1,C1,HF)

REAL*8 A1,B1,C1,HF

A1 = 25.7355

B1 = 12.985E-3

C1 = -3.8637E-6

HF = 8685.95

RETURN

END

C *This subroutine lists the thermodynamic constants for*

C *benzene.*

C

C

SUBROUTINE BEN(A1,B1,C1,HF)

REAL*8 A1,B1,C1,HF

A1 = -1.7121

B1 = 324.9215E-3

C1 = -110.6318E-6

HF = 114700.586

RETURN

END

C *This subroutine lists the thermodynamic constants for*

C *nitrogen.*

C

C

SUBROUTINE N2(A1,B1,C1,HF)

```
REAL*8 A1,B1,C1,HF
A1 = 27.3095
B1 = 5.2325E-3
C1 = -0.0042E-6
HF = 8673.4
RETURN
END
```

```
C   This subroutine lists the thermodynamic constants for
C   propane.
C
C
```

```
SUBROUTINE PRO(A1,B1,C1,HF)
REAL*8 A1,B1,C1,HF
A1 = 10.0883
B1 = 75.5322E-3
C1 = -17.9998E-6
HF = -66850.42
RETURN
END
```

```
C   This subroutine lists the thermodynamic constants for carbon
C   monoxide.
C
C
```

```
SUBROUTINE CO(A1,B1,C1,HF)
REAL*8 A1,B1,C1,HF
A1 = 26.8741
B1 = 6.9697E-3
C1 = -0.8205E-6
HF = -105185.8
RETURN
END
```

C This subroutine lists the thermodynamic constants for carbon
C dioxide.
C
C

SUBROUTINE CO2 (A1,B1,C1,HF)

REAL*8 A1,B1,C1,HF

A1 = 26.0188

B1 = 43.5177E-3

C1 = -14.8394E-6

HF = -383969.222

RETURN

END

PROGRAM BURNV

C
C
C This program receives output from SU, and calls a subroutine
C in the Sandia Math Library (SMOO) to compute a smoothed X-time
C curve, where X is the fraction of mass burned. The subroutine
C also returns dx/dt . Then BURNV determines the burning
C velocity, and prints all of this information to an output
C file.
C
C
C List of Important Variables
C
C
C BURNVEL - the computed laminar burning velocity
C R(i) - the smoothed values of the burned mass fraction
C R1(i) - the first derivative returned by the smoothing
C routine
C R2(i) - the second derivative returned by the smoothing
C routine
C X(i) - the time values to be sent to the smoothing routine
C Y(i) - the mass fraction burned values to be sent to the
C smoothing routine
C DY(i) - the weighting functions described in Section 3.2.5
C
C All other variables are as listed above. The other arrays
C listed below are the working arrays for the smoothing routine.
C
C
C CHARACTER file*6,fnew*10
C REAL X(200),Y(200),DY(200),S,A(200),B(200),C(200)
C REAL D(200),R(202),R1(202),R2(202),T(202),T1(202)
C REAL U(202),V(202),MASS,BURVEL,DT,FI,PI,PE,P1,TU
C REAL TE,A1,B1,C1,HF,EPS,EM,MU,VOL,VU,VB,TB, TIME,EXX
C WRITE(*,*) ' '
C WRITE(*,*) 'Name of the file to read from (leave off
C .prn).'C READ(*,6) file

```

6      FORMAT(A6)
      fnew = file//'.prn'
      write(*,*) ' '
      open(1,file=fnew,status='old')
      WRITE(*,*) 'Name of the file to write to (again
leave off .prn).'
      READ(*,618) file
618    FORMAT(A6)
      fnew = file//'.prn'
      write(*,*) ' '
      open(2,file=fnew,status='new')
      WRITE(*,*) 'DY1?'
      READ(*,*) DY1
      WRITE(*,*) ' '
      READ(1,*) DT,FI,P1,TU,TE
      READ(1,*) A1,B1,C1,HF,EPS
      READ(1,*) MASS,EM,MU,VOL
      PI = P1
c      X(1) = 0
c      Y(1) = 0
      DY(1) = 0
c      DO 50 I = 1,10
c50    READ(1,*) TIME,gr1,P1,TU,TB,gr2,EXX,VU,VB
      DO 100 I = 1,200
99     READ(1,*, END=150) X(I),gr1,P1,TU,TB,gr2,Y(I),VU,VB
      N = I
100    IF(X(I).LT.X(I-1)) GOTO 98
      GOTO 150
98     WRITE(*,*) 'TIMES OUT OF ORDER'
      GOTO 99
150    PE = P1
      S = N
      WRITE(*,*) 'NUMBER OF LINES IS',N
      WRITE(*,*) 'NUMBER OF S IS',S
      DO 200 I=1,N
200    DY(I) = DY1
c200   DY(I) = .05/(PE-PI)
      DO 205 J=1,N

```

```

205  WRITE(*,*) X(J),Y(J),DY(J)
C
C
C    The subroutine is called here, and returns the smoothed
C    curve, and the time derivatives.
C
C
      CALL SMOO(N,X,Y,DY,S,A,B,C,D,R,R1,R2,T,T1,U,V,IERR)
      REWIND 1
      READ(1,*) DT,FI,P1,TU,TE
      READ(1,*) A1,B1,C1,HF,EPS
      READ(1,*) MASS,EM,MU,VOL
      WRITE(2,2) DT,FI,P1,TU,TE
      WRITE(2,2) A1,B1,C1,HF,EPS
      WRITE(2,2) MASS,EM,MU,VOL
      WRITE(2,*) S,IERR
      WRITE(2,*) ' '
C    WRITE(2,2) X(1),PI,TU,Y(1),R(1),R1(1),R2(1),BURVEL
2    FORMAT(8E12.6)
C    DO 60 I = 1,10
C    READ(1,*) TIME,gr1,P1,TU,TB,gr2,EXX,VU,VB
C60  WRITE(2,2) TIME,P1,TU,TB,EXX,VU,VB
      DO 300 I=1,N
      READ(1,*,END=350) TIME,gr1,P1,TU,TB,gr2,EXX,VU,VB
C
C
C    The burning velocity is calculated below using Eq. 3.2.5.3.
C    The variable, TEMP, is a temporary variable, which has been
C    used to reduce the complexity of the equation for BURVEL.
C
C
      TEMP = (113.0973/MASS*(VB*R(I))**2)**.33333333
      BURVEL=(R1(I)*VU/TEMP)
      WRITE(*,*) TEMP, BURVEL
300  WRITE(2,1)X(I),P1,TU,TB,EXX,R(I),VU,VB,R1(I),R2(I),B
      URVEL
1    FORMAT(14E12.6)
325  CLOSE (1)

```



```
CLOSE (2)  
STOP  
350 WRITE(*,*) 'Length mismatch.'  
GOTO 325  
STOP  
END
```

END

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