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THE OXIDATION OF VOLATILES IN RESIDENTIAL
WOOD BURNING EQUIPMENT

Final Technical Report for the Period September 1980—February 1984

By
Philip C. Malte
Mark M. Thornton
Peter D. Kamber

April 1984
Date Submitted

Work Performed Under Contract No. FG02-80CE30760

University of Washington
Seattle, Washington

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THE OXIDATION OF VOLATILES IN RESIDENTIAL WOOD BURNING EQUIPMENT

I. PROJECT OBJECTIVES AND SCOPE

The objectives of this project are to measure, through the use of laboratory combustors, those conditions which promote complete combustion of wood volatiles in residential wood burning equipment. The conditions of interest are combustion temperature, residence time, stoichiometry, and air mixing. The project objectives are met through two laboratory approaches:

- 1) Model compound studies: In order to measure the overall rates of oxidative pyrolysis of biomass volatiles, and to determine the types of intermediate organic species which are likely to form as part of this process, model compounds have been reacted in a specialized jet-stirred reactor, which has been developed as part of this research.
- 2) High-intensity wood combustion: In order to study the clean combustion of wood, that is, to investigate the conceptual design features required for clean burning, and to ascertain the levels and types of pollutant and condensable species which are most difficult to oxidize, a high-intensity, research wood combustor has been developed and examined for the different phases of the wood burning cycle.

Although the objectives of the project have been met, it has not been possible, because of support limitations, to thoroughly explore several interesting aspects which have arisen because of this research. For example, a third laboratory system in which wood pyrolysis gas is injected directly into the a well characterized reactor, so that the kinetics and mechanisms of the gas-phase reaction of the actual biomass volatiles can be studied, could not be thoroughly developed. Refinements in the high-intensity wood combustor, which would bring its design features closer to practicality for the industry, could not be considered. Model compound studies, which are performed in the "production" jet-stirred reactor, and which have application to the thermochemical conversion of biomass as well as to combustion, are being completed without formal support, and consequently, only a limited experimental matrix is being undertaken.

II. SUMMARY

An expanded summary of the highlights of the research are presented, though the reader is referred to the subsequent sections of the report, which provide detail on each major aspect of the study.

A. Model Compound Studies

The literature on the pyrolysis of biomass, and in particular the literature on the pyrolysis of cellulose, lignin, and wood provides a catalog of the species and types of compounds which are released from biomass as it undergoes heating. Since our purpose has not been to study the pyrolysis of solid biomass, but rather to examine the gas-phase reaction of the volatiles released from the biomass, we have used this catalog of species as a departure point for our studies. By this we do not mean to imply that research on the pyrolysis of solid biomass is unimportant or unwarranted, for this is hardly the case, but rather, we have studied the gas-phase reactions because the completeness of combustion of biomass fuels, and the formation and destruction of pollutants from biomass fuels, are processes which are largely dependent on the gas-phase reaction of the volatiles. Thus, we have studied the pyrolysis and cracking of the biomass volatiles in an environment composed of steam, oxygen, and nitrogen.

We have applied a series of atmospheric pressure jet-stirred reactors to the study of the oxidative pyrolysis of biomass volatile model compounds at temperatures of 700 to 1200° C. In all cases, hydrogen and air are burned fuel-lean (giving about 10% O₂ in the reacting gases), and prevaporized model compound (at a concentration equivalent to a 1% yield of CO₂) is injected into the reactor. Gas samples are withdrawn from the reactor volume through a water-cooled, low-pressure sampling probe, and routed to a gas chromatograph for analysis. Condensable material is collected in traps and analyzed by gas chromatography and by gas-chromatography-mass spectrometry. Aqueous condensate and extracted tars are analyzed. Reactor temperature is measured by fine thermocouples of platinum-rhodium. The reader is referred to Chapter IV of this report for details on the sampling and analytical methods.

The first reactor, which is shown in Fig. 1 and described in Chapter V, was completely premixed, and consequently, the model compounds reacted extremely rapidly, because the hydrogen was burning simultaneously and producing super-equilibrium amounts of the active species, OH, O, H.

The second reactor, which is shown in Fig. 2 and described in Chapter V, had two chambers. Hydrogen and air were burned in one of the chambers to produce a hot stream of steam, oxygen, and nitrogen, and then this stream was injected into the second reactor which was also separately injected with prevaporized model compound carried in nitrogen.

Both of these reactors suffered from lack of homogeneity, though for different reasons. While concentrations of the major species (O₂, CO, CO₂) were nearly uniform, as was temperature, the very fast reaction of the organic material occurred preferentially in the feed jets of the first reactor, and in the second reactor, the use of the separate injection streams for the hydrogen-air products and the model compounds gave less than acceptable

Figure 1. Single-Chamber, Premixed Jet-Stirred Reactor

Figure 2. Dual-Chamber, Non-Premixed Jet-Stirred Reactor

mixing, and thus, regions of both nearly reacted and nearly unreacted model compound occurred.

The third reactor is the "production" reactor, and this is shown in Fig. 3 and described in Chapter VI. This reactor overcomes the above deficiencies by incorporating the pre-burner concept for gas generation, and by using the output stream, i.e. jet, of the gas generator to efficiently stir the organics reactor. Pre-vaporized model compound is injected into the jet immediately upstream of its entry into the organics reactor.

This reactor has been "tested" on pentane, and found to be homogeneous in organics concentrations for endothermic and thermally neutral pyrolysis. For the current configuration of the reactor, homogeneity is maintained for temperatures at or below 1000°C . Results for the oxidative pyrolysis and cracking of pentane, at $800 < T < 1000^{\circ}\text{C}$ and at a nominal residence time of 2 milliseconds, are shown in Fig. 4. The kinetics of loss of the pentane starting material and the intermediate olefins " C_2H_4 ", are shown in Fig. 5, and are found to be in very good agreement with results for the oxidation of n-paraffins in a turbulent flow reactor.

Thus, a major end product of this research is the development of a jet-stirred reactor which can be used to study the pyrolysis and cracking of organic model compounds. By increasing the residence time of the organics reactor, reaction at lower temperatures (500 to 800°C) can be studied, and by changing the composition of the pre-burner, reactions of interest to thermochemical conversion of biomass can be studied. For example, stoichiometric combustion of hydrogen and air would give an environment of mainly steam and nitrogen, and rich combustion would give an environment of hydrogen, steam and nitrogen. Furthermore, the system can be modified to seed the pre-burner product stream with CO and CO_2 to simulate biomass gasifier output streams, and if a nitrogen free environment is desired, the pre-burner can be fired on hydrogen and oxygen, with steam or CO_2 used for dilution for temperature control.

Since the reactor exhibits homogeneity for cases where the organic material does not react auto-catalytically, that is, the organic material does not produce substantial concentrations of the active species, OH , O , H , which cause rapid oxidation, the reactor is suited to the study of volatiles oxidation or, burn-off, in the secondary gases of residential solid fuel appliances, and with changes in the pre-burner gas composition as indicated above, the reactor is suited to studies of thermochemical conversion of biomass, e.g.

1. Pyrolysis yields from biomass model compounds as a function of temperature, environmental composition, and time,
2. Reaction of organic contaminants found in gasifier output streams, and
3. Reaction of carbon monoxide and hydrogen under gasifier output stream conditions, the objective being to understand these kinetics so that organic containments can be reacted to non-troublesome species without promoting significant CO and H_2 loss. For example, the kinetics of CO oxidation in an "unignited" environment are not understood, and in this regard, it is interesting to note that the CO loss kinetics in

Figure 3. "Production" Jet-Stirred Reactor, Showing Lower Chamber for Gas Generation by Hydrogen-Air Combustion, and Upper Jet-Stirred Chamber for Model Compound Reaction

Figure 4. Products of Oxidative Cracking and Pyrolysis of Pentane in "Production" Reactor

Figure 5. Multi-step chemical times for pentane oxidation.

Fig. 4 are at least two orders of magnitude slower than published global combustion rates for CO, which of course are for a more reactive environment.

The "production" reactor is currently being used (without formal support) to study the reaction of furan, furfural, and phenol at conditions identical to those shown in Fig. 4. Also, a separate project is underway to increase the surface area of the feed jet of the organics reactor, a procedure which will improve reactor homogeneity, so that the system can be used for studies at temperatures somewhat above those shown above. These results will be reported in the literature as they become available.

The preliminary results obtained in the first and second reactors, illustrated respectively in Figs. 1 and 2, are now summarized.

Model compounds burned in the first reactor were pentane, alpha-pinene, acetaldehyde, and methyl ethyl ketone, and results are shown and discussed in Chapter V. As explained above, because of the high reactivity of the reactor environment, only a minor fraction (< 10%) of the organic material remained unoxidized to CO, CO₂, and H₂O at temperatures as low as 700°C at 15 milliseconds nominal residence time. The important quantitative finding of these experiments, which has implication to the studies now underway, is that the measured CO-to-CO₂ ratio can be used to estimate the OH concentration in the reactor. The hypothesis is that for the conditions under study here, the only significant reaction involving both CO and CO₂ is the forward reaction:

Results for OH mole fraction by this method are plotted in Fig. 6, and compared to spectroscopic measurements at the higher temperatures, and to perfectly stirred reactor predictions. At high temperatures, the method must be corrected for the reverse of reaction (1), and at temperatures near or below the lowest temperatures shown in Fig. 4, other pathways for CO₂ formation can occur.

The second reactor has been used for a comparative study of pentane, alpha-pinene, furan, and furfural reaction, and results for light hydrocarbon yields are shown in Fig. 7. These results, for a 12 milliseconds nominal residence time, cover both the endothermic and exothermic regimes, with much of the data in the exothermic regime. In these experiments "ignition" occurred at about 1150K.

As noted from Fig. 7, furan and furfural gave significantly lower yields of the hydrocarbon gases than did pentane, with the exception that acetylene yields were high for furan. Alpha-pinene gave hydrocarbon gas yields intermediate between these extremes. The reaction of furan was similar to that of pentane, in that these compounds both had negligible condensibles yields. However, an important difference exists between furan and furfural reaction in that furfural reaction leads to high yields of organic material in the aqueous condensate. This analysis was conducted prior to any tar extraction processes. Later, tar analysis was conducted for the low temperature runs of furfural and alpha-pinene, and it was found that furfural

Figure 6. Measurements and Predictions of OH Mole Fraction vs. Temperature in Premixed Jet Stirred Reactor. (1) = Spectroscopic Measurements of Schmidt and Malte (1976). PSR = Perfectly Stirred Reactor Predictions at Measured Temperature. EQUILIBRIUM = Chemical Equilibrium Predictions at Measured Temperature

Figure 7. Yields of Hydrocarbon Gases from Model Compounds Reacted in Oxygen Rich Environment of Dual-Chamber Reactor

tar contained about 40% starting material, while the alpha-pinene tar was composed mainly of phenols. These results are described in Chapter V.

At the initiation of this project, it was decided to construct a woodstick pyrolyzer to provide a steady stream of wood gas to a jet-stirred combustion reactor. The pyrolysis unit is described in Chapter VII, and is based on the concept of slowly feeding a wood stick, of order a few millimeters thick, into an environment of hot nitrogen which serves to heat the stick convectively and to carry the wood gases to the combustion reactor. If the wood stick feed rate is sufficiently slow so that this rate controls the rate of pyrolysis, if the local heating rate of the stick is appropriate to the yield of organic volatiles, instead of mainly CO , CO_2 , H_2 , and H_2O , and if the rates of the secondary reactions in the gases flowing to the jet-stirred reactor are slow, a steady flow experiment can be conducted for the reaction of biomass volatiles in the jet-stirred reactor. Since the development of such a system is a major undertaking, it has not been feasible to completely develop and test the system under this project, though wood gas flow rates constant to within $\pm 50\%$ over 20 minutes run time have been obtained, and very limited experiments have been conducted for wood reacted in the second jet-stirred reactor (see Chapter V).

B. Wood Combustion Studies

The research wood combustor in which experiments have been performed is shown in Fig. 8. This system was developed after other arrangements of primary and secondary reaction chambers and various mixing schemes were evaluated and discarded. This research combustor has the elements required for clean combustion of wood, and it allows the combustion efficiency and pollutant emissions to be evaluated for the different parts of the burning cycle: 1) kindling startup, 2) steady-state volatiles burning, 3) refueling, and 4) char burning.

The elements of the combustor are the following:

- 1) Insulated primary and secondary chambers, in order to promote high temperature,
- 2) Vortex mixing directly above the fuel, in order to promote the ignition of all of the volatiles released from the wood,
- 3) Vortex mixing of secondary air into the primary gases, and
- 4) Catalytic afterburning, which in this application acts mainly to oxidize carbon monoxide.

The unique element in this design is the second item. Unless the volatiles streams issuing from the wood are mixed efficiently with the reacting gases, some of the streams do not ignite, and consequently, some volatiles leave the combustor as unreacted or partially oxidized "fuel." In this regard, it should be noted that the volatiles issuing from the wood contain water vapor and carbon dioxide as well as the combustible species, and exist as either gas or aerosol. Given the nonuniformities that occur in volatiles composition, the tendency in poorly mixed systems is for some volatiles streams to ignite easily, while other streams ignite with difficulty

Figure 8. Research Wood Combustor. (1) = Fuel Bed, (2) = Vortex Mixing Zone, (3) = Secondary Combustion Chamber, (4) = Honeycomb Catalyst, (5) = Heat Exchanger for Air Pre-Heating, (6) = Forced Draft Air Supply, (7) = Heat Transfer Chamber, and (8) = Stack

or not at all. The intense vortex mixing directly above the wood promotes ignition of all of the volatile streams by promoting homogeneity between the streams and by efficiently mixing the volatiles with the reactive burning gases. Furthermore, any liquid aerosol released from the fuel is quickly exposed to hot oxidizing gases, and the formation of soot aerosol is curtailed by the dispersion of the organics.

In order to accomplish the requisite vortex mixing, the research combustor is blown with a forced draft of air at an inlet static pressure head of 25 inches H₂O W.C.

Thermocouples are located in the different portions of the research combustor in order to record nominal temperatures, and gases and condensibles are sampled either before or after the catalyst. Typical results are shown in Fig. 9 for the different times of the burning cycle.

Carbon monoxide emissions are found to depend mainly on the theoretical air percentage, as shown in Fig. 10. For greater than 200% theoretical air and with the catalyst, CO emissions are less than 700 ppm and carbon-to-CO₂ conversion efficiencies are estimated to be greater than 98%. Under these conditions, the C₁-to-C₃ hydrocarbon emissions are less than 100 ppmC, with methane being the predominant hydrocarbon.

Condensate samples are analyzed by capillary column GC/MS methods, and are classified as phenols (phenol, cresols, dimethyl phenols, and methoxy benzenes), furfurals, and polyaromatic hydrocarbons. Although absolute particulate emissions have not been quantified, the emission of condensible material is very low compared to that of conventional woodburners, and therefore, organic carbon does not condense in the exhaust stack and the condensible catch is clear-to-pale yellow. The condensible emissions which do occur appear mainly as phenols during kindling startup. Much farther down the condensible emissions scale are the refueling and char burnout stages, the latter being mainly a source of PAH.

The predominance of phenols and furfurals in the condensibles catch confirms our selection of these species for our model compound studies.

This research has demonstrated the design features which can be used to obtain clean combustion of wood in residential-scale appliances. While it has been relatively easy to attain this goal in the research laboratory, the incorporation of these concepts into practical units will require further development. For example:

1. Mixing patterns and intensities which can be developed with low pressure blowers, i.e. those with a few inches H₂O W.C. static head, and which can be developed from the natural thermal patterns of the combustor need to be critically evaluated since mixing is so important to clean and efficient burning.
2. Slow burning: Since it is relatively easy to obtain nearly complete combustion at high combustion intensities, the challenge is to obtain continuous, nearly complete combustion at heating rates of order 10,000 Btu/hr.

Figure 9. Temperature-Time History of Wood Burn, and Emissions of CO and Hydrocarbon Gas. Inferred Theoretical Air and Carbon Conversion Rate Also Shown.

Figure 10. Carbon Monoxide Emissions from Research Wood Combustor

3. PAH: While smoke emitted from conventional wood stoves is a nuisance and irritant, this smoke is mainly raw fuel, i.e. the volatiles released from the wood. A worse situation could occur as the combustion temperature is increased, unless concomitant improvements in mixing occur, since in poorly mixed hot zones, the volatiles will react to soot and the carcinogenic soot precursors.
4. Operator "independent" system: Operator knowledge and patience is an important element in clean and efficient combustion of wood. With our research combustor, operator influence is critical only during kindling startup. The challenge is to design and automate the every-day wood burning appliance, so that it is much less operator dependent than is the case now.

C. Attainment of Objectives

As stated above the objective of this project has been to study the completeness of combustion of the volatiles as appropriate to residential wood combustion. The conditions of interest are temperature, residence time, stoichiometry, and mixing.

The model compounds studies provide the information on the temperature-residence time requirements for oxidation of the volatiles in air-rich environments. Since residential wood combustors operate overall quite air-rich, and since in this situation, combustion completeness involves oxidation of the organics in the air-rich, secondary gases of the combustion chamber, the kinetic information obtained by this research is appropriate to the practical problem. Furthermore, the temperature regime of 700 to 1000°C covered in the model compound studies is appropriate to the temperature regime found in mixed, insulated wood combustion chambers (see Fig. 9).

The model compound studies are appropriate to the species found unreacted in the effluent of mixed, insulated wood combustors. The phenols are important, and in our ongoing work, phenol oxidation is being examined. Furfural, which is also important, has been and is being examined, and alpha-pinene, which is associated with wood high in resin, has been examined. However, under the scope of this project it has not been possible to examine the oxidation of PAH, which is not strictly an important wood volatile, though it is important because it forms in flame zones, and is released during char oxidation. Model compound work appropriate to PAH oxidation in residential wood combustion environments should be addressed in follow-on research.

The question of stoichiometry for complete combustion has been addressed mainly in the studies with the research wood combustor. It is seen that even for mixed combustion, a stoichiometry of at least about 200% theoretical air is required to give asymptotic minimums in CO (see Fig. 10) and hydrocarbon gases (see Chapter VIII).

Mixing of the air with the volatiles and mixing of the air and volatiles with the flame gases are essential processes for complete combustion. For the research wood combustor, a vortex mixing pattern, driven by air injected tangentially into a circular cylinder, and swept across the top of the burning wood, has been an essential feature. The required static pressure head, from a centrifugal blower, is 25 inches H₂O W.C. With this approach, for a primary

combustion chamber size of 20 cm width and 10 cm height above the wood, this level of pressure head has been required to obtain the estimated combustion efficiencies of at least 98%. However, as implied above, future work remains to be done on design optimization involving mixing intensity, draft pressure, and combustion chamber geometry.

III. INTRODUCTION

A. Background: Residential Wood Combustion

The ready availability of residential space heaters that can be fired on solid fuels (i.e., wood and coal) is having an effect on how Americans heat their homes. In some regions of the nation, considerable heating is now being done with solid fuels. This change has been driven by a desire to reduce home heating costs and by threatened shortages of conventional heating fuels.

Recent studies indicate that wood is a significant renewable energy resource. Projections indicate that between 5 and 10 percent of the nation's energy requirements could be met by wood (Anon., 1979; Bethel, 1980). It is estimated that 1 quad (10^{15} Btu), or about 10 percent, of the nation's residential space heat could be produced by wood combustion. A residential wood-burning stove or fireplace insert typically heats between 75 and 100 square meters of living area, primarily by radiation. In wood-rich regions, such as the Pacific Northwest, 10 to 15 percent of the residential space heat could be produced on a sustained-yield basis by burning currently unused hardwoods (Bergvall et al., 1978).

However, the desire to burn wood for residential space heat, and the increased use of residential wood-burning appliances, as they now perform, pose some serious problems. These arise because present stove designs have evolved from a strongly empirical data base. The attendant combustion inefficiency and resultant air pollution are problems that now exist and could continue to grow (e.g., Cooper, 1980; DeAngelis et al., 1980). Technological steps that lead to significant improvements and optimization of residential wood-burning equipment need to be taken. The situation is acute since the sales of residential wood-burning appliances increased dramatically in the late 1970's and early 1980's. In 1980, it was estimated that 1 million units were sold in the United States (Cooper, 1980).

Wood stoves contribute significantly to the air pollution problem because of the carbon monoxide, organic vapors, and condensed carbonaceous materials emitted. Most important, the unburned organic matter contains substantial amounts of polycyclic organic matter (POM), including several known carcinogens and cancer-promoting agents (Peters, 1981). In short, wood smoke has many of the characteristics of cigarette smoke.

In a paper by Cooper (1980), several examples of community air pollution due to wood smoke were cited; e.g., in Vail, Colorado, Missoula, Montana, Medford, Oregon, and several towns in New England. In Portland, Oregon, on worst-case winter days, 30 to 40 percent of the suspended particulate matter is due to wood burning. Carbon monoxide emission factors as great as 100 to 400 grams per kilogram (g/kg) of burned fuel have been measured from wood stoves, and unburned organic emissions of between 10 and 20 g/kg are common. The organic pollutants are volatiles, condensed matter and condensibles, irritant aldehydes, carcinogenic POM, and cancer-promoting phenols.

The chemical and thermal inefficiencies associated with residential wood combustors lead directly to high pollutant emissions. These inefficiencies exist basically because current wood stoves do not burn the fuel completely to

CO₂ and H₂O. Instead, substantial amounts of carbon monoxide (CO) and organic vapors are released from the "firebox."

The chemical efficiency of a wood stove is tied strongly to the fuel burning rate, which is controlled primarily by the air admission rate. Air must thoroughly and rapidly mix with the volatiles at a sufficiently elevated temperature to react. However, the only mechanisms for air-volatiles mixing are (1) the natural draft of the stove, which is small (approx. 1 N/m² or 0.004 in. H₂O) and (2) the jetting action of volatile gases escaping from the wood. Mixing processes are consequently poor and pose a significant fluid mechanical problem. Pockets of organic volatiles and CO do not receive sufficient air in conjunction with sufficient heat to burn completely. This incomplete combustion results in a relatively low chemical efficiency. The problem is compounded further since the firebox of the wood stove is also used as the heat exchanger, thereby cooling the flame gases below the optimum temperature for complete combustion. On the other hand, there are some pockets of organic volatiles which receive heat in the absence of air and pyrolyze to soot particles.

Thermal inefficiency is also an important consideration in wood stove design. There is a large energy loss in typical stoves due to convection up the exhaust stack. This occurs because the exhaust gas temperature and throughput rate are too high. The exhaust gas temperature of present stoves is usually maintained above 300°F in order to limit the condensation of heavy organic vapors. The condensation products, known as "creosote," include organic acids, which present safety problems (Maxwell, 1980). In addition to the possible ignition of creosote deposits, the firebox combustion process may be significantly degraded due to the resultant reduction in the stove draft. The air throughput rate is much greater than it need be because of the poor air-volatile mixing characteristics of wood stoves. Typical stoves require substantial quantities of excess air to flow through the firebox, in the hope that all the fuel will eventually mix with oxygen and react. The high flow rate lowers not only thermal efficiency, but also chemical efficiency, since the flame gases become too cool to burn completely.

The situation in conventional residential wood combustors is conceptualized in Fig. 11. Within the "dashed envelope" the wood pyrolyzes, the char particles oxidize and gasify, and the volatiles react in luminous, poorly aerated flames. Since 80 to 90 percent of original fuel burns as volatile matter, the volatiles combustion process is very important to efficient combustion. Although copious amounts of air are admitted to the combustor, this air is not utilized efficiently in the combustion process, since the mixing of air with the initial volatiles and flame gases is a weak process, and since the secondary combustion process is a weak process because the gases cool due to heat loss from the combustor, and due to dilution by excessive amounts of air. Furthermore, unmixedness plagues this zone.

B. State-of-the-Technology and the Air Pollution Problem

Recently, the Oregon Department of Environmental Quality, DEQ (Kowalczyk et al., 1981) tested six commercially available wood-burning appliances thought to represent the "state-of-the-technology." These were an airtight box stove, a gasifier stove, a catalytic stove, an airtight stove fitted with a wire mesh filter (in order to trap particulate organic matter for subsequent

Figure 11. Concept of Combustion in Conventional Residential Wood Combustors

combustion), and two full home-heating, log-fired furnaces. Kowalczyk et al. concluded the following: "The major conclusion of this test program was that stove manufacturers still have considerable development work to do before a practical solution to the serious air pollution problem from wood heating can be claimed." Furthermore, Kowalczyk et al. stated: "In reviewing the availability of clean-burning RWC appliances, the DEQ quickly recognized that virtually no available appliances had been designed and tested as low emission units." We would like to add that, when one looks for innovation in clean wood-burning appliances, one finds that most of the progress is being reported by manufacturers and engineers in Canada (Trivett et al., 1981; Brandon et al., 1981; Short, 1981), Northern Europe (Crossley, 1980; Rustad and Olsen, 1981), and New Zealand (Pullen and Holden, 1981). The notable contributions of the U. S. to clean wood-burning are (1) the Hill furnace (Hill, 1979), which has been designed as a central furnace for homes and small commercial establishments, and (2) the Corning catalyst (Zimer et al., 1981), which has been designed to catalytically burn organic vapors following the primary combustion process.

The substantial unburned materials which are emitted from RWC appliances fall into the following classes:

1. Carbon monoxide: with emissions factors typically at 100 g/kg fuel burned, and sometimes as high as 400 g/kg (Cooper, 1980).
2. Total particulate matter: that is, condensed particulate matter of solid (soot, ash), liquid, or combined solid/liquid phases which are present in the effluent and which collect on a filter; and organic vapors which condense upon subsequent cooling, termed condensibles. Total particulate emissions may be 10 g/kg, but sometimes approach 100 g/kg (Kowalczyk et al., 1981).
3. "Creosote", a catch-all term for material which "plates-out" on the cooler stove and exhaust stack surfaces, and is not emitted as condensed and condensable material. Hubble et al. (1981) indicate that this material can have an emission factor near 2 g/kg at low burning rates, and a much lower factor at high burning rates.
4. Volatile hydrocarbons such as benzene (C_6H_6) and ethylene (C_2H_4), which have emission factors approaching 2 g/kg (Rudling et al., 1981) except for conditions of very poor combustion where their emission factors are higher.
5. Volatile aldehydes such as formaldehyde and acetaldehyde, with emission factors of 0.2 g/kg (Rudling et al., 1981), but which can be as high as 1 g/kg under poor burning conditions.

It is also useful to classify these emissions on the following alternative basis:

1. Elemental carbon (i.e., graphite) versus organic carbon of the particulate matter. Elemental carbon is an indicator of soot formation in the flame and has been found by Muhlbaier (1981) to represent typically less than 20 percent of the total condensed particulate carbon for a burn cycle. Softwoods, compared to

hardwoods, appear to yield somewhat higher elemental carbon levels, presumably because of their higher lignin content. Furthermore, the elemental carbon fractions in the particulate matter appear to be maximized at the point of maximum temperature in the burn cycle. This is expected, given the known characteristics of soot formation in flames (e.g., see Glassman, 1977).

2. Phenolic materials (Rudling et al., 1981), since these oxygenated materials can be cancer promoters.
3. POM or (polycyclic organic matter, including oxygenates), PAH or (polyaromatic hydrocarbons), since these materials are carcinogenic (Peters, 1981). PAH emissions appear to be close to 0.1 g/kg (Rudling et al., 1981); Cooper, 1980), although some investigators report emission factors as low as 0.01 g/kg (Hubble et al., 1981).

It is important to note that residential wood combustion, compared to the burning of other residential and commercial fuels (i.e., gas, oil, coal), accounts for most of the CO and hydrocarbon and about one-half of the particulate material emitted from residential and commercial heating systems in this country (Muhlbaier, 1981). Even more important, RWC appears to be the largest single source of POM in the U. S. (Peters, 1981). The breakdown by Peters (1981) is:

Residential Wood Combustion	35%
Agricultural Burns	11%
Prescribed Wildland Burns	10%
Forest Fires	13%
Automobiles (mainly gasoline)	20%
Industrial/Utility Coal Combustion	6%
Coke Production	6%

POM is important since it is a carcinogen or co-carcinogen (i.e., tumor promotor). Actually, POM exerts its carcinogenic behavior only after it is metabolized in the body of chemically-reactive species (Peters, 1981). All wood smokes tested by Peters (using Ames biological-mutagen test), were carcinogenic. Furthermore, most of the wood smokes tested by Peters were highly carcinogenic (CHO-cell tissue assay).

Thus, the "state-of-the-technology" in RWC technology, together with the increasing use of these devices is causing a very serious air pollution problem in this nation. In Figure 12, we have plotted total particulate emissions (i.e., condensed and condensible particulate) for typical wood-heating systems. The results from Kowalczyk et al. (1981) for the Oregon DEQ study are thought to be most representative, since these investigators tested six appliances and their data are for whole burns, i.e., kindling fire to cold coals. The Kowalczyk et al. results show very high emissions at low burning rates (i.e., 1 to 2 kg/hr), which is similar to overnight stove operation. With increased burning rates, emissions drop substantially. However, conventional wood stoves are limited to maximum burning rates of about 6 to 8 kg/hr. In order to obtain burning rates in the 10 to 20 kg/hr range, where total particulate emissions are lowest (about 2 g/kg), Kowalczyk et al. (1981) had to test a home-heating furnace which burns a large charge at

Figure 12. Total Particulate Emissions as a Function of Dry Burning Rate

high intensity. They also found that the use of post-flame cleanup devices, such as a catalyst or wire mesh, cut particulate emissions by about one-half.

The results of Hubble et al. (1981) are also plotted on Figure 12. The main difference between the tests of Hubble et al. and those of Kowalczyk et al. is that Hubble et al. only examined the hot, stable portion of the burn cycle. In particular, they did not collect emissions from cold startup. Kowalczyk et al. have estimated that one-half of the total particulate emissions occur during the first 17 percent of the burn. Finally, we have plotted, in Figure 1, results from Pullen and Holden (1981). These results are for a new stove designed specifically for low emissions. It is noted that this stove reaches a low emission state once the fire is brought up to a heating rate of only 1 kg/hr. Another point to be noted in Figure 1 is that for all of the tests conducted, there appears to be an asymptotic lower limit of about 2 g/kg for total particulate emissions. Thus, there may be a limit to the cleanliness to which logs and sticks can be burned in stoves and residential furnaces, unless drastic combustion modifications are made.

The results in Figure 12 show a strong correlation between emissions and burning rate; a correlation which Kowalczyk et al. (1981) found to hold for all of the appliances they tested. Furthermore, Hubble et al. (1981) have argued that this correlation also holds for the burning of both large and small sticks, although we believe that they may have over-interpreted their data, since large sticks have a low surface-to-volume ratio and small sticks have a high surface-to-volume ratio. Unfortunately, there was not a significant region of overlap where both stick sizes were tested at the same burning rate. Nonetheless, it appears that a general correlation exists for which total particulate emissions are inversely proportional to burning rate. An alternative correlation is given by Butcher and Ellenbecker (1981), and they have argued that emissions vary directly with the ratio of charge mass divided by burning rate. This is equivalent to a dependence on total burn duration time.

The thermal and "drawing" behavior of the conventional wood stove has been measured by Hubble et al. (1981) and their best linear approximations for excess air, firebox temperature, and stack temperature are plotted in Figure 13. (The corresponding emissions data have been shown in Figure 12.) With increased burning rate, the firebox temperature and the stack temperature increased in a linear fashion, whereas the excess air drawn into the stove decreased linearly. The location of the firebox temperature measurement was not given by Hubble et al., but we have assumed that this temperature is representative of the upper portion of the stove, away from the luminous flames.

In light of the above results of Hubble et al. on stove operating conditions and overall emissions, it is informative to examine some of their more detailed data. These detailed data were obtained for two conditions: (1) a slow, cool burn using large sticks and (2) a fast, hot burn using small sticks. Table I illustrates the important differences in these two types of burns.

Figure 13. Results of Hubble et al. (1981) for Temperatures and Excess Air. Conventional Residential Wood Combustor

TABLE I

SUMMARY OF RESULTS OF HUBBLE ET AL. (1981)

	<u>Cool, Slow Burn</u>	<u>Hot, Fast Burn</u>
Approx. Rate, kg/hr	1	8
Stick Diameter, cm	12	6
Approx. Excess Air, %	340	70
Approx. Firebox Temp., ° C	270	720
Approx. Stack Temp., ° C	70	430
Total Particulate Catch, g/kg	25	2
Portion of Catch Termed Condensible, g/kg	3	1.5
Creosote Catch, g/kg	3	0
Total Catch, g/kg	28	2
Extracts of All Catches		
(dominated by condensible catch)		
Alipatic Fraction, % (C ₈ to C ₂₇ alkanes & alkenes)	11	0
Polar Fraction, % (furfural, methyl furfural, phenols in hot case; also substituted phenols and methoxybenzenes in cool burn)	67	80
Aromatic Fraction (C ₁ -C ₃ substituted benzenes in cool burn; fused ring aromatics in hot burn)	22	11

These results indicate that the largest fraction of material emitted under cool, slow burning conditions is condensed particulate, i.e., condensed tars and perhaps some soot, whereas the largest fraction of material emitted under hot, fast burning conditions is condensible organic material. Furthermore, a marked difference occurred in the aromatic fraction. Under cool, slow burning conditions the aromatics were mainly single ring compounds, whereas under hot, fast burning conditions, fused ring aromatics accounted for about 40 percent of the fraction. That is, the higher temperatures, in conjunction with relatively poor mixing, promoted gas-phase reaction to fused ring aromatics

(and probably soot). Another indicator of this behavior is that Hubble et al. (1981) measured higher PAH contents for the hot, fast burn than for the slow, cool burn.

This finding is of special concern, since it indicates, as also pointed out by Peters (1981), that wood combustors designed to curtail CO and particulate emissions by using high temperatures may actually increase PAH emissions. As pointed out by Cooke and Allen (1981), PAH formation tends to occur in fuel-rich flame zones at temperatures of 600 to 800° C, followed by destruction at higher temperatures. It is interesting to note that the firebox temperature in the hot, fast burn falls within this range.

Although Hubble et al. (1981) have not reported a dependence of total particles on stick size, it appears nonetheless that stick size is of importance to burn behavior and emissions. Hubble et al. do report that their large and small sticks, when burned at nearly equal rates (i.e., 3 vs. 4 kg/hr) and at nearly equal stove temperatures, emitted nearly equal total particulate emissions, showing a marked difference in the condensed versus condensible fractions. The large stick gave mainly condensibles, whereas the small stick gave essentially condensed material. Conjecture on this point is somewhat dangerous at this time, given the limited data base and lack of information of the flame dynamics. Nonetheless, it is possible that sooting reactions may have been promoted during small stick burning.

It is also known that emissions can increase when wood of large surface-to-volume ratio is burned (Cooke and Allen, 1981). That is, due to the high surface area, the volatile release is enhanced to the point where the gas-phase oxidation process simply cannot handle the large amounts of devolatilization products. A similar situation appears to occur with respect to wood moisture content. Very wet wood yields a very dirty fire. However, a very dry wood may release large amounts of volatile matter upon heating, giving a situation akin to that for small sticks. Consequently, lowest emissions are frequently measured for sticks of intermediate moisture content.

Of the basic wood stove designs which are available today, i.e., up-draft, cross-draft, side draft, and down-draft, it appears that the down-draft design offers the only marked improvement in emissions (Cooke and Allen, 1981). This is presumably due to the fact that in the down-draft design, burning volatiles are drawn down over the hot charcoals, leading to good "secondary" combustion of the gases as they flow out of the combustion zone. It is also clear from the results of Pullen and Holden (1981), plotted in Figure 12, that a stove with an insulated firebox is important for promoting complete combustion. It is also clear from the experience of Hill (1979) that well-mixed, high temperature, intense combustion promotes an effluent low in particulate matter. Those features which promote clean burning are discussed in detail in the next section.

C. Advances in Clean Wood Burning Technology

Those features which must be incorporated into the design and manufacture of residential wood-burning appliances in order to achieve more complete combustion of sticks and logs are generally known (e.g., see Osborne, 1981; and Shelton, 1981). It appears feasible to incorporate these features into

wood-burning systems which are designed for central residential or small commercial use. Furthermore, it appears feasible to attain reasonably clean burning operation during the hot, stable portion of the burn cycle. The major challenge is to design, engineer, and manufacture at competitive cost, wood-burning appliances which are of the popular room size, which are not a nuisance to operate, and which operate cleanly over the whole burn cycle.

Some of the designs which have been tried or are commercially available are illustrated schematically in Figure 14 and are described below. These include particle stokers and others which appear to enhance complete combustion.

1. Down-draft design: Although the experience with this design has not been universally good, Cooke and Allen (1981) do report markedly improved emissions compared to other designs (up-draft, cross-draft, side-draft), and most importantly, the stove uses the principle of volatiles oxidation promotion by direct interaction with the hot charcoals.
2. Insulated primary combustion chamber and well-stabilized secondary combustion: The design by Pullen and Holden (1981) uses an insulated primary combustion chamber as well as a well-mixed, well-stabilized secondary combustion process. The perforated passage between the primary and secondary chambers, plus the direct injection of preheated secondary air at this point, appears to break up and mix the gases, promoting good secondary combustion. The insulated primary chamber promotes high temperatures.
3. High intensity combustion (Hill, 1979): This design burns a charge of wood very intensely under reasonably well-mixed, high temperature conditions. In its present application, the system is designed as a central heating system and requires a heat storage system.
4. Catalyst (Zimer et al., 1981): The afterburning catalyst is potentially a very useful device, particularly in conjunction with other clean burning approaches. This is because the catalyst works best on the oxidation of organic vapors, including PAH and POM (76% reduction, Zimer et al., 1981). It is less useful for the elimination of condensed material, and is prone to clogging by such material.
5. Stokers: Central wood-heating furnaces for the home and the small commercial site have been advanced by the Canadians (Brandon and Murray, 1981; Short, 1981), and by the Northern Europeans (Crossley, 1980; Rudling et al., 1981). Brandon and Murray used biomass pellets with the pellets fed continuously onto the grate of a residential furnace (i.e., top-fed, fixed-bed). They reported emissions of only 0.2 g/kg condensible organics and 0.9 g/kg condensed organics. These findings are consistent with the Swedish experience (Rudling et al., 1981) for dry wood chips burned in a residential stoker. Furthermore, Rudling et al. (1981) measured PAH emissions of only 0.0005 g/kg; and much of the condensed particulate matter measured was due to bed agitation, i.e., the collected particulate was grey-white ash. These systems require a fuel supplier (or a chipper), a storage area, and when using chips, caution must be used to guard against the formation of toxic fungi in piles of wet chips.
6. Charcoal stokers: Charcoal stokers for central heating have been tested by the Norwegians (Rusted and Olsen, 1981). They obtained 86

1) DOWN-DRAFT STOVE

4) CATALYST (ZIMER ET AL, 1981)

2) LOW EMISSION STOVE
PULLEN & HOLDEN (1981)

5) STOKER FOR PELLETS
(BRANDON AND MURRY, 1981)

3) HIGH INTENSITY FURNACE
HILL (1979)

Figure 14. Wood Stoves and Furnaces for Clean Burning

percent system efficiency at 30 percent excess air with quite low emissions, with CO levels at 1100 ppm.

7. Fluidized bed combustion: Although not shown on Figure 4, fluidized bed combustion of wood is another innovative possibility for central heating. Trivett et al. (1981) have reported initial experiences with this approach. However, emission factors of about 20 g/kg were not particularly good compared to other systems. Presumably these emissions arose due to particulate discharge from the bed.

For central heating the Stoker systems, fed with biomass pellets, dry wood chips or charcoal appear to offer an excellent combination of convenience and low emissions. These systems are compatible with the forced draft distribution systems of homes and commercial establishments, and do not require expensive heat storage systems. These systems are attractive if the owner wishes to heat with wood and has access to the fuel. The major commercial problem at this time would appear to be fuel availability and distribution. The furnace technology is essentially at hand--clearly past the research stage.

Since our interest is in the development of clean systems which burn sticks and logs, especially in room-size units, we will now list and discuss those features which appear to be required to promote complete combustion. These features have been compiled from several sources (e.g., Osborne, 1981, and Shelton, 1981):

1. Temperature: The combustion process should occur in ceramic (fire-brick) lined chambers, which do not also serve as major heat transfer zones. Our work in Chapter VIII indicates that chamber temperatures should be 600 to 1000° C in order to promote the oxidation of polycyclic and complex organic material. This necessitates a modular design, at least with respect to separate combustion and heat transfer sections. This will lead to somewhat higher costs than today's appliances. Furthermore, the combustion air should be preheated, with this heat drawn from the downstream heat transfer section of the stove, in order to cause the combustor to operate at a higher enthalpy level.
2. Mixing: A well-mixed well-aerated combustion process is absolutely essential. Even if mean combustion temperatures of 800° C are approached or even exceeded, the resultant effluent will still be dirty (POM and soot) unless the combustion process is well-mixed and well-aerated. Several approaches are possible here:
 - a. If we settle for a poorly-mixed initial volatiles flame, then we have to design a secondary combustion process that is hot, well-mixed, well-stabilized, and has sufficient residence time in order to ensure oxidation of the complex organics and soot formed in the first stage. Pullen and Holden (1981) may have accomplished this, as explained earlier in this section, i.e., good secondary gas contact and mixing. However, intermittent ignition in the secondary chamber can be dangerous.
 - b. We prefer a design which leads to a well-mixed, well-aerated initial volatiles flame, with the air blown directly onto the burning sticks and logs; see Chapter VIII. This reduces the formation of complex organics and soot in the initial flame and reduces the size of the overall combustor. The volatiles released

directly from the pyrolyzing wood have smaller structures than those formed in dirty flames and have reduced oxidation times of 10 to 100 milli-seconds. This approach, similar to that taken by Hill (1979) requires the use of a mechanical draft. If the effluent is clean, an induced draft stack fan can be used. If a forced draft approach is used, then the fluid mechanics of the stove must be engineered so that the combustion chamber remains under a slight negative pressure relative to the environment. Otherwise, CO leakage would be an ever-present danger.

3. Controlled pyrolysis: One of the major difficulties in present wood-burning practices is that the pyrolysis of the wood is not controlled. For example, a large volatiles flame will radiatively heat a large area of the wood, but not all of the volatile matter released from the heated regions will find its way into the volatiles flame. This unburned organic material can be controlled by limiting the surface area of wood exposed to heating. This can be done by various feeding and shielding methods such as gravity feed (Hill, 1979), and can be promoted by focusing the air supply onto the desired burn region (Osborne, 1981). In point of fact, using mechanical design, the burn rate can be controlled by controlling the exposure of the wood surface to heating.
4. Char reaction: Two approaches are required here. First, in order to promote volatiles oxidation, the heat of char oxidation should be used as effectively as possible in the volatiles flame process, either by recirculation of the burning volatiles past the char burning regions, or by good contact between the char oxidation and volatiles oxidation processes. This probably precludes the use of completely separate gasifier and combustion modules. Second, the rate of char oxidation should be controlled to avoid cool char burning in the last stages of the burning cycle.
5. Catalyst: A catalyst should be used to ensure burn-off of pollutant gases.
6. Steadiness: The system should be engineered for a steady heat release rate, implying that the wood should be fed as evenly as possible. Furthermore, the air input should be controlled for desired stoichiometries in the 100 percent excess air range. Large excess air levels are indicative of poor combustion and lessen the thermal efficiency of the unit.

Our approach to clean combustion of wood in a residential-size unit is described in Chapter VIII.

D. Biomass Volatiles and Model Compounds

The products of pyrolysis of cellulose/lignin fuels are a complex function of heating rate, temperature, and wood size, structure, and composition. Shafizadeh (1968) has studied the pyrolysis of cellulose at slow heating rates and low temperatures: char was the primary product; the volatils consisted of CO, CO₂, and H₂O. At combustion conditions, volatiles consisting of both light gases and condensible vapors are the major (>80%) yield. The polymeric structure now undergoes fragmentation; and primary volatiles, thought to be mainly levoglucosan, form. The volatile yield becomes enhanced in species such as levoglucosan (Reed, 1979).

Lewellan et al. (1977) have summarized the overall situation: If the residence time of the primary volatiles in the solid structure is short, and if the temperature is moderate, then the important product of pyrolysis of the cellulose is condensible organic matter. However, if the primary volatiles are unable to escape readily from the solid structure, they tend to repolymerize to carbonaceous char. On the other hand, if the temperature of the solid structure increases, the primary volatiles react to gases and light condensibles, which become the important products of pyrolysis. If these gases and vapors are constrained to remain within the solid structure, then autocatalysis is promoted, leading to the evolution of more gases and an increase in the devolatilization rate.

The pyrolysis of lignin has received less study. Krieger et al. (1979) have subjected pellets of lignin to microwave heating, and product yields have been analyzed by capillary column gas chromatography. Of significance were yields of the condensible aromatics, such as phenol, the cresols, and guaiacol, all of which could be troublesome in the gas-phase flame.

The implications of these basic studies to residential wood burning are several. Most of the wood is burned as volatile material in the gas-phase. This is different from coal combustion, where typically less than 40-to-50% of the fuel is volatile. Second, a considerable amount of the volatile material is released as condensibles. Table II is a short list of some of the compounds found in biomass pyrolysis gas and wood smoke.

This list is not meant to be complete, since, for example, it does not include the primary volatile levoglucosan nor the PAH's found in wood smoke. However, the list does show representative light aldehydes and ketones found in pyrolyze gas, as well as furfural and phenols found in wood smoke. We have chosen a light aldehyde, acetaldehyde, and a ketone, methyl ethyl ketone, to examine briefly, and we have chosen to examine alpha-pinene because it is an important extractable in some wood species. Phenol is chosen because of the importance of phenols in wood smoke (see Chapter VIII), and furfural is chosen because it also is found in wood smoke (see Chapter VIII), but also appears in products of cellulose pyrolysis products, as does furan. These model compounds have been selected because they can be atomized and prevaporized for gas-phase reaction studies. Other model compounds would have to be injected into the reactor as an aerosol mist, or would have to be injected in lower concentrations. Finally, throughout our studies pentane is used as a reference compound, since the pyrolysis of n-paraffins have been studied previously (e.g., see Glassman, 1977), and provide an important verification of the behavior of our reactors.

TABLE II
SOME BIOMASS VOLATILES MODEL COMPOUNDS

Chemical Formula	Compound	Extractable ¹	Cellulose ² Pyrolysis	Lignin ³ Pyrolysis	Wood ^{4,5} Smoke	Normal Boiling Point (°C)	Model Compounds
CH ₂ O ₂	Formic Acid		X			101	
C ₂ H ₂ O ₂	Glyoxal		X			50	
C ₂ H ₄ O	Acetaldehyde		X			21	*
C ₃ H ₄ O	Acrolein		X			53	
C ₃ H ₆ O	Acetone		X			56	
C ₃ H ₈ O ₃	Glycerol		X			290	
C ₄ H ₄ O	Furan		X			32	*
C ₄ H ₆ O	Crotonaldehyde		X			104	
C ₄ H ₆ O ₂	2,3-Butanedione		X			88	
C ₄ H ₈ O	Methyl Ethyl Ketone		X			80	*
C ₄ H ₈ O	Butyraldehyde		X			76	
C ₅ H ₄ O ₂	Furfural		X		X	162	*
C ₆ H ₆ O	Phenol			X	X	182	*
C ₆ H ₆ O ₂	Catechol			X	X	245	
C ₇ H ₈ O	2-Cresol			X	X	190	
C ₇ H ₈ O ₂	Guaiacol			X		205	
C ₈ H ₈ O	Styrene			X		145	
C ₁₀ H ₁₆	Alpha-Pinene	X				156	*

1. Ward (1979)

2. Shafizadeh (1968 and 1981); and Shafizadeh and Lai (1972)

3. Krieger et al. (1979)

4. Cooper (1980); this study (Chapter VIII)

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IV. SAMPLING AND ANALYSIS

A review of sampling and analysis procedures for the gases, condensibles, and particulates found in the effluent of wood combustors is given in the Appendix. For the present research, since it has been required to sample and analyze the flame gases of the model compound reactors, and the effluent of a research wood combustor which has a high degree of combustion completeness, somewhat simplified sampling procedures have been found to work well, and on-line gas-chromatographic analyses have been emphasized. These procedures are described in this chapter.

A. Sampling and Gas Analysis in Model Compound Reactors

A clear fused quartz sample probe, described by Kramlich and Malte (1978), draws a sample stream from the jet-stirred reactor at a pressure of approximately 75 torr. The tip of this probe is a 0.5 mm nozzle in a 2 mm ID tube which produces essentially sonic flow. After passing through a short uncooled section, the gas enters the water-cooled heat exchanger of the probe and then is carried by a short Teflon tube to a set of traps which condense water at 273 K. Because of the low pressure, condensation in the probe and tubing is generally prevented. With furfural and wood gas combustion in the jet-stirred reactor, deposition of condensed material in the cooled probe does occur, a situation which requires probe rinsing. The probe flow rate of 8×10^{-4} mol sec⁻¹ amounts to about 1 percent of the jet-stirred reactor total molar flow rate.

The gas stream then is carried to a sample conditioning system where a portion is diverted to a sample storage loop for analysis by an on-line gas chromatograph (GC). Without interrupting the main sample flow, the gas in the storage loop can be isolated and compressed (without dilution) to any selected pressure less than two atmospheres for prompt separation and analysis by GC. This compression is accomplished by flowing helium into one end of the sample storage loop. While the helium and sample certainly do mix at this end of the 15 meter long tube, it is found that the gas at the far end remains undiluted. All parts of the pressurization system are swept with helium or are maintained at 353 K to forestall condensation of water or organic compounds. This system greatly increases the useful sensitivity of the GC, by concentrating the sample 10-fold and by introducing samples at a pressure which does not lead to large upsets in the detector baseline upon injection.

The GC is a Perkin-Elmer Sigma 1B. This instrument incorporates microprocessor control and on-line digital peak integration and data reduction. A two column (molecular sieve and porous polymer), two detector (hot wire detector-HWD, and flame ionization detector-FID) system is used for analysis. Porapak-T porous polymer material is used because of its high selectivity between lower boiling alkanes, alkenes, and alkynes. It also carries out the separation of CO₂ and air.

On-line gas samples of 0.1 ml volume, conditioned as above, are introduced at 1 atm and 423 K by means of a 10-port valve (Valco). (Columns and standard conditions used are as follows: molecular sieve 5A (Alltech): 1.82 m x 2.1 mm ID, 60/80 mesh, helium 15 ml/min, oven isothermal at 423 K; Porapak-T (Supelco): 1.82 m x 2.1 mm ID, 80/100 mesh, helium 15 ml/min, oven isothermal at 423

K or temperature programmed: 323 K hold one minute, then 10 K/min to 443 K.) The small sample size and low flow rates selected are the result of compromise and the need to preserve the efficiency of the Porapak-T column. Larger samples or higher flow rates worsen the separation of CO₂ and air, while lower temperatures unnecessarily delay the elution of pentane starting material. The temperature programmed run permits unambiguous recognition of the most important species in the samples, with a couple of notable exceptions in the C4 to C5 region which match either none or more than one of the reference compounds available.

Authentic reference gases are used both to establish retention times and also specific detector calibrations for each sample component. Gas mixtures are used as received from Airco Gas Products or Scott Environmental Technology. Most components are calibrated at at least two concentration levels. If necessary, non-linear effects are taken into account. Column conditioning and replicate analysis are particularly needed for the case of acetylene where significant on-column absorption is known to occur. FID quantitative accuracy is generally equal to the stated accuracy of the standard gases: $\pm 2\%$ of the reported value at or above the 100 ppm volume level. This accuracy deteriorates to $\pm 5\%$ in the range of 10-100 ppm volume. Data below 10 ppm volume are based on extrapolated response factors and are less reliable. High responses are linear up to the point where microprocessor overflows occur, roughly 10,000 ppm volume. HWD quantitative precision is as follows. Oxygen and nitrogen, both present in abundant amounts, have the same accuracy as the standards, i.e. $\pm 2\%$. The oxygen peak contains ambient argon as well. Carbon monoxide values are accurate to $\pm 2\%$ in the range of 1000 to 10,000 ppm. Under 1000 ppm the values are based on extrapolation and are unreliable below 200 ppm where it is believed column absorption occurs. Carbon dioxide values are accurate to $\pm 2\%$ in the range of 1000 to 10,000 ppm. Lower values are based on extrapolation. Carbon dioxide values must be explicitly corrected for ethylene and ethane which are also included in this peak.

Chromatograph output goes through a two step calculation before it is used. The first step corrects the CO₂ value for measured ethylene and ethane, and then normalizes both the molecular sieve and Porapak-T analyses to constant sample size. This step mainly allows for variable atmospheric pressure and variable amounts of water in the samples. The second step adjusts the sum of all carbon species to a constant 10,000 ppmC. This step takes account of the fact that some of the earlier runs were made with a slightly higher model compound flow rate, and also that there is some variation in pentane flow rate. In this way all of the runs may be compared to each other directly.

B. Treatment and Analysis of Condensate and Tars

Direct GC analysis by syringe injection of aqueous condensate before the tar extraction step is a quick way to estimate yields of components such as acetone and aldehydes, which are not detected in the subsequent tar analysis. Volatile polar organic compounds in solution are often a major part of the yield of condensed products, and although not identified specifically by this method, they are separated into general classes. Direct injections of the aqueous condensate are made by syringe onto the Tenax-GC column described above, and using only the FID. A quick separation is carried out isothermally at 473 K, and a more detailed separation is accomplished by temperature programming the chromatograph oven from 373 to 523 K at 10 K/min. For the

present work, the results given in Chapter V for these condensed compounds are based on a carbon response factor determined for propane.

In order to analyze for tars, the procedures described next are used. Residue, if any, is rinsed from the traps and probe with dichloromethane or methanol (Burdick and Jackson). This rinse is then combined with the condensate and extracted for one hour in a Wehrli extractor with 50 ml of dichloromethane refluxing rapidly. The extract is dried over anhydrous sodium sulfate, filtered with glass wool, and rinsed with extra dichloromethane into a Kuderna-Danish concentrator and is evaporated down to 1 to 2 ml as appropriate. All samples are kept frozen when not in use. Many of the samples darkened at first when they were exposed to light. Later, such exposure was avoided. This method has been tested and found to recover 95 percent of furfural from 1:500 (vol/vol) aqueous solution.

These extracted samples are chromatographically separated by fused silica open tubular (capillary) columns directly connected to the FID. Split or splitless injections are made depending on the concentration of the sample. Some of the components in the split injections show poor peak shapes, possibly resulting from adsorption or decomposition in the injector, even though a thoroughly deactivated liner packing (silanized glass wool and 1% SE-30 on Chromosorb W-HP) is used. Dilution and splitless injections are then used for these cases. (Chromatographic conditions are as follows: non-polar column (J & W): fused silica 30 m x 0.25mm, SE-30 coating, helium 210 kPa, 313 K for 1 min hold, then 4 K/min to 523 K; polar column (Hewlett Packard): fused silica, 20 m x 0.25 mm, Carbowax-20M coating, helium 140 kPa, 313 K for 1 min hold, then 5 K/min to 473 K; with injector in each case at 448 K, detector at 523 K).

Approximate Kovats retention indices are estimated for unknown components and are used only as a guide to possible identification. Assignments based on retention time are made only for compounds whose actual retention time on our system is known, since retention data are complicated by the splitless injection (Grob and Grob, 1978).

Quantitative determinations of the tars are made on the basis of FID responses. Each extracted sample is spiked with 0.1 gm/ l p-bromophenol as an internal standard. Wherever possible, response factors are determined relative to p-bromophenol with our own system. Otherwise where reliable literature response factors are not available, components are assumed to have the same response factor as p-bromophenol.

Mass spectra of the tars are obtained using a Hewlett-Packard 5985 gas chromatograph/mass spectrometer/data system (GC/MS). Samples are introduced by splitless injections on fused silica open tubular columns as above. Similar columns and conditions are employed. Electron impact mass spectra of 70 ev. are recorded during the whole of the useful chromatogram. The mass range scanned is 40 to 250 amu with 8 steps per amu. The column outlet discharges directly into the ion source which is maintained at 473 K. The transfer lines in which the column itself is carried are kept at 523 K.

Background subtraction and searches of the EPA/NIH mass spectral data base are made to confirm chromatographic assignments. Manual interpretation is also made by reference to tables (Abrahamsson et al., 1974; Stenhagen et al., 1969; Cornu and Massot, 1966) and by direct interpretation (McLafferty, 1966).

C. Temperature Measurement in Model Compound Reactors

Non-catalytic coated type R thermocouples register temperatures in the reactor. The coating is produced by a modification of the method of Kent (1970). These thermocouples are periodically checked against an optical pyrometer (Leeds & Northrup) to ensure that chemical degradation of the noble metal wires (Gordon Thermocouple Co.) has not occurred. A microscope stage positioning device has been adapted to permit precise location of the thermocouple bead at selected points inside the reactor. Thermocouple junction potentials are read with a high impedance precision DVM (Kiethley Instruments). The recorded temperatures have not been correct for radiation and conduction losses, since these effects are estimated to be small (< 20 K) for the present system.

D. Wood Combustion Studies

The modifications employed for the measurement of gases and condensibles, and temperature in the research wood combustor are discussed in Chapter VIII.

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V. MODEL COMPOUND STUDIES

Initial model compound studies have been conducted in the jet-stirred reactors shown above in Figs. 1 and 2. The reactor in Fig. 1 is completely premixed, while the reactor in Fig. 2 is non-premixed with respect to the organic model compound. The oxidation of model compound in the premixed reactor is rapid, since the reactivity of the reactor is high due to the simultaneous oxidation of the hydrogen, and consequently, only small amounts of organic species leave unreacted at air-rich conditions, even at temperatures as low as 700°C, and these unburned organic species are generally gases rather than condensibles and tars. The premixed reactor and its results are discussed below first. The model compounds burned in the premixed reactor are pentane, alpha-pinene, acetaldehyde, and methyl ethyl ketone.

Yields of condensibles and tars, as well as gases, are measured from the non-premixed reactor, and these results are presented below second. The model compounds burned in this reactor are pentane, alpha-pinene, furan, and furfural. The non-premixed reactor may be characterized as having model compound oxidization in the hot products of combustion of lean hydrogen and air.

Before these reactors and their respective results are discussed, the methods used for model compound atomization and vaporization are summarized. Since the model compounds studied in the premixed reactor had relatively low boiling points, except for alpha-pinene, it was feasible to use a simple syringe-infusion pump system. That is, an infusion pump operated at a set speed was used to push liquid model compound from a calibrated syringe into the premixed reactant feed stream. Upon injection into the reactant feed stream, the model compound flash-evaporated to vapor due to the marked reduction in its concentration. This system was marginal for alpha-pinene injection, and in this case, the reactant stream was heated in the vicinity of the injection point.

In general, though, for the types of model compounds of interest here, as listed above in Table I, a customized atomizer-vaporizer is required. Such a system has been developed as part of this research program, and the unit is described in Chapter VI. The unit has been used in conjunction with the non-premixed model compound studies of this chapter, and is an integral part of the production reactor system described in Chapter VI.

A. Premixed Reactor Description

The premixed reactor shown in Fig. 1 is described in detail by Malte et al. (1977) and Singh et al. (1979). This reactor is of 50 cc internal volume, is constructed of castable ZrO_2 , and accomplishes high-intensity combustion by backmixing seven small (1 mm), high velocity, premixed jets against the internal reactor walls.

The measurements have been performed for 11 to 18 milliseconds mean residence time, and in order to examine the stoichiometries and temperatures of interest to wood combustion, the reactor has been stabilized on fuel-lean hydrogen (fuel-air equivalence ratio = 0.30 to 0.50) burned with air. The

Figure 1. Single-Chamber, Premixed Jet-Stirred Reactor

Figure 2. Dual-Chamber, Non-Premixed Jet-Stirred Reactor

resultant temperature was variable from 700°C (973K) to 1200°C (1573K), and the corresponding unburned O₂ mole percentage was 13 to 8%.

When the reactor is fired exclusively on hydrocarbon fuels its operating temperature is 1400 to 1900K, and under air-rich conditions, oxidization of the organic species is very efficient. Under these conditions the reactor has essentially two zones:

1. By volume, a few percent (<10%) of the reactor contains the nonuniform reactant feed jets. These jets contain the premixed reactants, and because these jets entrain the recirculating bulk gas of the reactor, the active species (OH, O, H) contained in the entrained bulk gas cause rapid oxidative pyrolysis of the hydrocarbon fuel. Because the entrained active species are at super-equilibrium concentrations, and because they are forced mixed into the jets, the resultant oxidative pyrolysis of the fuel occurs very rapidly -- before the fresh reactants can thoroughly disperse into the bulk gas. Thus, oxidative pyrolysis reactions are concentrated in the early feed jets of the reactor, and lead to the feed jets being somewhat cooler and having less advanced combustion than the bulk gas of the reactor.
2. The bulk gas of the reactor is recirculating gas, which is essentially homogeneous in concentration and temperature, and which is strongly mixed every time it becomes entangled with a feed jet. For the type of stirred reactor used in this research, an average fluid particle makes approximately 10 round trips, or cycles, before it leaves the reactor. Unless the characteristic chemical time for oxidative pyrolysis is slow compared to the average cycle time, the oxidative pyrolysis occurs preferentially in the feed jets. In this case, the bulk gas may be thought of as a super-equilibrium post-pyrolysis zone, high in active species concentrations (though peak concentrations of OH, H, and O may occur on the edges or in the downstream regions of the jets), and in which the slower oxidative pyrolysis reaction occur as well as reactions of energy release and carbon monoxide oxidation.

Jet-stirred reactors of the present type are operated with mean residence times as low as 1 millisecond, implying a characteristic cycle time of 100 microseconds. But at typical combustion temperatures, the rate of the oxidative pyrolysis may still be faster, especially if the reactants are rapidly admixed with super-equilibrium concentrations of active species. In order to slow the rate of pyrolysis, and therefore, to obtain a favorable chemical-to-cycle time ratio, the temperature of the reactor can be lowered by operating the reactor very fuel-lean, or by premixing the reactants with inert diluents. However, when fired on hydrocarbon fuel, the jet-stirred reactor experiences lean blow-out in the 1300 - 1400K regime.

In order to work at lower temperatures yet, the reactor can be fired lean on hydrogen fuel, with the organic model compound added as a secondary or trace fuel. With hydrogen, we have found it feasible to maintain lean combustion in the reactor of Fig. 1 at temperatures as low as 700°C (about 1000K). It was thought that this regime, in which the hydrogen-air combustion gives active species concentrations of several hundred ppm in the bulk reactor gas, instead of a few thousand ppm associated with high temperature combustion, would allow the premixed organic model compound to mix thoroughly with the bulk gas prior

to significant pyrolysis. It appears that this situation was approached as the blow-out temperature of 700°C was approached, but that at higher temperatures (towards 1000°C, or 1300K), the reactor became progressively nonuniform.

The following fluid mechanical times are estimated for our premixed reactor at temperatures of 1000 to 1100 K (Malte et al., 1983):

- 1) Mean residence time: 1.8×10^{-2} s
- 2) Time for one cycle (or "round trip") of a fluid particle in the reactor: 2×10^{-3} s
- 3) Time for a jet eddy to mix (i.e., roll up) with surrounding fluid, based on concepts developed by Broadwell and Breidenthal (1981): 2×10^{-4} s.
- 4) Time for digested jet eddy fluid to mix to Kolmogorov scale (Breidenthal, 1981): 2×10^{-7} s.

The corresponding order of magnitude chemical times, from Fig. 20, discussed in Section V.G., for the total organic disappearance in the premixed reactor, are 10^{-4} to 10^{-3} s. Thus, the chemical times lie between the jet eddy mixing and cycle times.

The analyses for 1000 K shows that in order for significant pyrolysis to occur, a time equivalent to the cycle time is required. And since the jet eddy mixing time is short compared to this time, the hydrocarbon chemistry takes place in an environment which is essentially that of the bulk reactor, rather than that of the decaying inlet jet. Nonetheless, since the cycle time is not short compared to the characteristic chemical time, the reactor is only approaching the desired uniformity at the lowest temperatures. Although the throughput rate of the reactor could be increased in order to decrease residence time and cycle time, blowout would then occur at a higher temperature, and thus, the inherent difficulty is not necessarily alleviated.

Therefore, the results shown below for the premixed reactor should be regarded as follows:

1. The kinetics inferred for loss of organic material should be regarded as order of magnitude rates, except possibly at the lowest temperature examined. However, a comparison can be made of the relative rates of the model compounds.
2. The organic yields are useful for understanding the types of organic species which remain unburnt at these reactive conditions.
3. An important quantitative result is the inference of OH concentrations from the measured CO_2 -to-CO ratio.

B. Premixed Reactor Results

The yields from pentane reaction are plotted in Fig. 15. Ethylene was the dominant unburned hydrocarbon, which is expected. For the lowest temperature examined, 1010K, the rank order is $\text{C}_2\text{H}_4 > \text{C}_3\text{H}_6 > \text{CH}_4 > \text{C}_5\text{H}_{12} > \text{C}_4\text{H}_8 > \text{C}_2\text{H}_6 > \text{C}_2\text{H}_2$; and the total unburned hydrocarbon yield is 710 ppmC, or 7.1% of the starting material.

Figure 15. Premixed Reactor Results for Oxidative Cracking and Pyrolysis of Pentane.

Figure 16. Premixed Reactor Results for Oxidative Cracking and Pyrolysis of Alpha-Pinene

The results for alpha-pinene are plotted in Fig. 16. The C_2 hydrocarbons were again dominated by C_2H_4 , with only small amounts of C_2H_6 and C_2H_2 found. On Porapak T, chromatographic peaks for C_3H_6 and C_4H_8 were obtained; these results are plotted in Fig. 16. On Tenax, seven major chromatographic peaks occurred for $C \geq 3$. The sum of these peaks is also shown on Fig. 16. At the lowest temperature examined, 1020K, the hydrocarbon sum is 630 ppmC, a sum which is nearly identical to that obtained for the pentane combustion. The rank order is $CH_4 \approx C_2H_4 > C_3H_6 \approx C_4H_8 > C_2H_2 > C_2H_6$.

Unburned organic concentrations are not plotted for acetaldehyde and methyl ethyl ketone combustion. Only methane and C_2 hydrocarbons were found for these model compounds. Methane was first detected at 1200K, and increased to about 50 ppm in the case of C_2H_4O combustion, and to about 30 ppm in the case of C_4H_8O at the lowest temperature examined, about 1000K. In the case of C_2H_4O combustion, about 5 ppm of both C_2H_4 and C_2H_6 occurred at the lowest temperature; whereas for C_4H_8O combustion, C_2H_4 was the dominant C_2 and was about 40 ppm at the lowest temperature. Total organic yields from C_2H_4O and C_4H_8O combustion were about 100 ppmC at 1000K, or about a factor 7 less than the yields obtained for pentane and alpha-pinene combustion. Part of this difference may be due to failure to measure small concentrations of oxygenated organics due, for example, to low GC response factors and to loss to H_2O .

The CO and CO_2 yields are plotted in Fig. 17. At the highest temperature examined, 1550K, the yield of CO_2 was 97% and the yield of CO was 3%, which represents the GC detection limit. At 1000K, the yields were about 70% CO_2 and 25% CO. Because the yield of $CO_2 + CO$ is close to 100%, these data can not be used to determine by difference the total unburned organic yield.

C. Hydroxyl Radical

In order to gain insight on the reactivity of the H_2 -air combustion field in which the model compound reacts, measurement of active species concentrations is desirable. Optical methods can be applied to the absolute measurement of OH, though a simpler and quicker method of estimating OH concentration is desirable. In Fig. 6, a comparison is shown between OH concentrations predicted by the perfectly stirred reactor (PSR) model (Pratt and Wormeck, 1976) and concentrations estimated from the measured CO_2 -to-CO ratio.

The PSR results, as well as the equilibrium results obtained with the NASA CEC model (Gordon and McBride, 1971), have been obtained for the measured temperature, and are compared in Fig. 6 to OH results (circles) inferred from the measured CO_2 -to-CO ratio. (In this regard, the uncorrected thermocouple temperature has been used. Estimated corrected kinetic temperatures, when used instead, do not lead to significantly different results than shown in Fig. 6.)

The kinetic mechanism used in the PSR model is the following:

1. The mechanism and rate data given by Rogers and Chinitz (1983) are used for the bimolecular reactions involving H_2 , O_2 , H_2O_2 , OH, H, O, and HO_2 . There are 16 reactions.
2. The rate data for the recombination reactions $O + O + M \rightarrow O_2 + M$, $H + H + M \rightarrow H_2 + M$, and $H + OH + M \rightarrow H_2O + M$ are from the stirred

Figure 17. Premixed Reactor Results for CO and CO₂ Yields from Model Compounds

Figure 6. Measurements and Predictions of OH Mole Fraction vs. Temperature in Premixed Jet Stirred Reactor. (1) = Spectroscopic Measurements of Schmidt and Malte (1976). PSR = Perfectly Stirred Reactor Predictions at Measured Temperature. EQUILIBRIUM = Chemical Equilibrium Predictions at Measured Temperature

reactor study of Jenkins et al. (1967). The rate data for the reactions $H + O + M \rightarrow OH + M$, $H + O_2 + M \rightarrow H_2O + M$, and $OH + OH + M \rightarrow H_2O_2 + M$ are from Baulch et al. (1973), with third body efficiencies adjusted to 80% N_2 , 20% H_2O whenever possible.

3. Carbon monoxide oxidation is by the reaction $CO + OH \rightarrow CO_2 + H$, with rate data from Baluch and Drysdale (1974). For the present temperatures, the forward rate of this reaction is the dominant reaction involving CO and CO_2 . The reverse rate of this reaction becomes significant only at the highest temperatures examined. Other reactions, such as $CO + HO_2 \rightarrow CO_2 + OH$ and $CO + O + M \rightarrow CO_2 + M$ contribute, based on available data, only at the lowest temperatures examined; and for the present application these reactions do not appear to overtake the reaction $CO + OH \rightarrow CO_2 + H$.
4. The overall pyrolysis rate is that of Elelman and Harsha (1978), but with the pre-exponential factor increased by two orders of magnitude to give agreement with the present results for unburned hydrocarbon loss in the reactor.

As noted from Fig. 6, these computational results are compared to experimental results. The solid line in Fig. 6 represents the measurements of Schmidt and Malte (1976), obtained for the same reactor burning H_2 /air at 0.5 to 0.6 fuel-air equivalence ratio. These results, which have an estimated uncertainty of $\pm 30\%$, are approximately a factor 2 lower than the PSR results. It should also be noted that the PSR model for solely H_2 /air combustion gives very nearly the same results as for carbon included.

The solid data points in Fig. 18 are from the present measurements in the premixed reactor. The OH mole fraction is determined from the equation:

$$X_{OH} = \frac{1}{t[M](k[CO]/[CO_2] - k'[H]/[OH])} \quad (2)$$

where t is the reactor mean residence time; k and k' are respectively, the forward and reverse rates of the reaction $CO + OH \rightarrow CO_2 + H$ (Baulch and Drysdale, 1974); the $[H]/[OH]$ ratio is taken from the PSR results (as stated above, this term affects the results only at the highest temperatures examined); and the $[CO]/[CO_2]$ ratio is taken from the data of Fig. 17.

Good agreement is noted between these experimental results and the PSR computation. Although direct spectroscopic measurement of OH should be undertaken to verify the accuracy of the CO_2 -to-CO ratio method for OH, the present agreement indicates that estimates of OH concentration can be obtained for the present type of reactor environment. The implications in this evaluation are the following:

- 1) The measured CO and CO_2 , and the inferred OH, are for the (uniform) bulk gas of the reactor.
- 2) The PSR computations offer reasonable prediction of OH in the bulk gas.

D. Non-Premixed Reactor Description

The non-premixed reactor used initially was a dual-chamber jet-stirred reactor shown in Fig. 2. Each chamber was one of the single jet-stirred reactors shown in Fig. 1. The left-hand chamber of the dual reactor was fired on hydrogen and air at conditions similar to those stated in Section VB for the single reactor. The nominal flow rate of the left-hand chamber was 1 gm/sec, the hydrogen-air equivalence ratio was controlled from about 0.3 to 0.55, giving temperatures in the right hand chamber of about 700 to 1200°C (1000 to 1500K), and unburned oxygen mole fractions of 13 to 7%. The burnt hydrogen/air gases flowed into the right-hand chamber as a jet of approximately 100 m/s velocity, and prevaporized model compound, carried in a stream of nitrogen of flow rate 0.2 gm/sec and of temperatures up to 200°C, was injected through the bottom jets of the right-hand chamber. Nominal residence time was 12 milliseconds.

In the upper 70 percent of the right reactor, for pentane additive, the relative standard deviations of temperature and oxygen were 5 and 8%, respectively, over 53 locations; and the relative standard deviations for carbon monoxide and carbon dioxide were 19 and 17%, respectively, over 18 locations. However, the reactor was less uniform with respect to unburned organic compounds; the relative standard deviation for unburned pentane was 114 percent. Consequently, the sample probe was positioned in an "average" location in order to compensate as much as possible for these effects.

Because of the nonuniformities in the organics composition of the reactor gases, results must be regarded cautiously. While trends for the different model compounds, pentane, alpha-pinene, furan, and furfural, can be compared since all of the model compounds were reacted in essentially identical environments, the kinetics of organics oxidation are at best order of magnitude inferences. It should be appreciated that this reactor has been used as the first step in the development of the dual-reactor approach for model compound oxidation studies. The "production" dual-reactor is discussed in Chapter VI.

E. Non-Premixed Reactor Results for Gases

Results for the non-premixed, dual, reactor are plotted in Figs. 7, 18, and 19. In Fig. 18, the $\text{CO}+\text{CO}_2$ yield and the $\text{CO}/(\text{CO}+\text{CO}_2)$ ratio are plotted. For this reactor, greater than 99% conversion to $\text{CO}+\text{CO}_2$ occurred for $T \geq 1300\text{K}$, whereas near 1000K, the conversion to $\text{CO}+\text{CO}_2$ was only about 15%, which is a much lower conversion than obtained for the pre-mixed reactor. With decreasing temperature, the $\text{CO}/(\text{CO}+\text{CO}_2)$ ratio increased and tended to unity at a temperature of about 1030K. Below this temperature, the small amount of oxidized carbon which was measured was increasingly CO_2 .

Total gas-phase organic yield is plotted in Fig. 19. The term "closure" indicates a carbon balance. Closure is indicated for pentane combustion, and nearly for alpha-pinene and furan combustion. For furfural combustion closure based on gas-phase measurements was not obtained. As discussed in Section V.H., furfural combustion gives more carbon in the aqueous condensate than the other species, and this is at least partly responsible for the lack of closure.

Figure 7. Yields of Hydrocarbon Gases from Model Compounds Reacted in Oxygen Rich Environment of Dual-Chamber Reactor

Figure 18. CO and CO₂ Yields from Model Compounds in Dual-Chamber Reactor

Figure 19. Gas Phase Organic Yields from Model Compounds in Dual-Chamber Reactor. Closure = Carbon Balance.

The yields of CH_4 , C_2H_2 , C_2H_4 , and C_3H_6 are plotted in Fig. 7. For pentane combustion, $\text{C}_2\text{H}_4 > \text{C}_3\text{H}_6 > \text{CH}_4$, as also indicated for the premixed reactor. For alpha-pinene combustion, the relative yields of C_2H_4 , C_3H_6 , and CH_4 are also similar to those noted for the premixed reactor. For furan and furfural combustion, the yields of C_2H_4 , C_3H_6 and CH_4 are markedly lower than for pentane and alpha-pinene combustion, but C_2H_2 becomes an important intermediate hydrocarbon.

F. Discussion of Yields

Results for the intermediate hydrocarbons shown in Figs. 7, 15, and 16 may be interpreted on the basis of the starting organic material. The pentane results in Fig. 7 are consistent with the flow reactor results of Dryer and Glassman (1978), which are: $\text{C}_2\text{H}_4 > \text{C}_3\text{H}_6 \gg \text{CH}_4$. The maximum in the alkene concentrations at about 1030K indicates that the reactor residence is appropriate for optimal net production of the alkene intermediates. The methane maximum occurs at a slightly greater temperature (or at a slightly longer time). The pentane results in Fig. 15 also show a dominance by intermediate C_2H_4 . However, in the case of Fig. 15, the methane is relatively more important than for the case of Fig. 7. This indicates that the residence time of the premixed reactor was greater than that required for maximum alkene production. The methane, which requires more time and higher temperature to oxidize, became relatively more important as the reactor reactivity increases.

The chromatograms of the gas-phase organics for alpha-pinene combustion were very complex compared to the chromatograms for pentane combustion. Approximately 20 GC peaks were noted in the C_3 to C_{10} range for alpha-pinene. The total yield of this material (assuming alkane GC response factors) is plotted in Fig. 15, and is seen to be the dominant material for alpha-pinene combustion. The results in Figs. 16 and 7 indicate that C_2H_4 is also an important intermediate in alpha-pinene combustion and that propylene and butene occur in proportion to the ethylene.

The results for furan and furfural combustion are not discussed in detail. However, because of the structure of these compounds, acetylene is an intermediate hydrocarbon.

G. Discussion of Kinetics

The kinetics of oxidative pyrolysis of a hydrocarbon may be regarded in several ways, as summarized below in Chapter VI. One approach is to consider the loss of starting material, and another approach, which is used frequently in the modeling of combustion kinetics, is to express the overall oxidative pyrolysis as:

With this approach, with respect to experimental interpretation, the hydrocarbon in equation (3) may be thought of as the total unburned organic material in the reactor, i.e. starting material and intermediate organic species. For a homogeneous reactor, it follows that the data may then be arranged to give the chemical time, t_c , for oxidative pyrolysis:

$$t_c/t = 1/([CH_{y/x}]_0/[CH_{y/x}]-1) \quad (4)$$

where $[CH_{y/x}]_0$ is the input concentration (10,000 ppmC) and $[CH_{y/x}]$ is the measured total organic concentration in the reactor (ppmC). If the kinetics of the starting material loss are considered, then this last term is simply the concentration of starting material remaining unburnt in the reactor. In terms of overall reaction rate, R, we write:

$$t_c = x[CH_{y/x}]/R \quad (5)$$

where x is the effective carbon atom number for the mixture of organics in the reactor, or if only starting material loss is considered, x corresponds to the starting material chemical formula.

In Fig. 20, experimental rate data for the premixed reactor are plotted in two forms. The middle curve with the open symbols is based on the total organic material found in the reactor for pentane (circles) and alpha-pinene (squares) combustion. The lower curve with the open symbols is for the pentane combustion, and it is based on the unburnt pentane found in the reactor.

The upper curve with the closed symbols is for the non-premixed reactor, and is based on the "closure" curve in Fig. 19 and thus, represents loss of total organic material.

As implied above, the rate data measured for the premixed reactor are somewhat reliable, especially at the lowest temperatures examined, since the reactor was approaching homogeneity. The rate data measured for the non-premixed reactor are order of magnitude estimates because of the reactor nonuniformities. However, it is clear that the organic material reacted considerably more slowly in the H_2 -air burnt gases of the non-premixed reactor than in the H_2 -air combustion environment of the premixed reactor.

Comparison of these rate data to the prediction of oxidative pyrolysis rates for present conditions by application of published results of others is a tenuous process. Published overall rate data (Duterque et al., 1981; Edelman and Harsha, 1978) are based on measurements in jet-stirred reactors operated at higher temperatures. Additional published overall rate data are based on measurements in completely different systems, such as a turbulent flow reactor (Hautman et al., 1981), and on comparisons to laminar flame speed data (Westbrook and Dryer, 1981).

Nonetheless, application of these published rate data indicate the following: the rates of Duterque et al. (1981), for propane, Edelman and Harsha (1978) for chain hydrocarbons, and Hautman et al. (1981), for propane and other n-paraffins reacted at temperatures of interest here, when extrapolated and applied to the present conditions, fall within a factor ± 5 of the non-premixed data in Fig. 20. On the other hand, the rate of Westbrook and Dryer (1981) is closest to the premixed data, being a factor 5 to 10 faster than our measurements. Instead of belaboring the agreement and disagreement between the present rate data and the published rate data for overall oxidative

Figure 20. Chemical Times for Loss of Organic Material in Premixed and Dual-Chamber Reactors. Application of Rate Expressions to Premixed Reactor Conditions: (1) Edelman and Harsha (1978); (2) Duterque et al. (1981); (3) Hautman et al. (1981) (Starting Material); (4) Hautman et al. (1981) (Intermediate Hydrocarbons); and (5) Westbrook and Dryer.

pyrolysis, the topic is continued more satisfactorily in Chapter VI. What can be concluded here is that alpha-pinene has an overall oxidative pyrolysis rate similar to that for pentane, and though more work is required for furan and furfural, it appears that for first order engineering purposes, the overall rate of oxidative pyrolysis of furan and furfural can be also represented by that for pentane. And as discussed in Chapter VI, it appears that the rate of oxidative pyrolysis of pentane is best represented for the type of environment of interest here by the two-step mechanism of Hautman et al. (1981).

H. Condensed Phase Results

Analysis of the aqueous condensate and tars obtained for the model compounds reacted in the non-premixed reactor are discussed in this section. Also, very limited data of the reaction of wood gas, injected from the wood stick pyrolyzer discussed in Chapter VII, are presented.

Figure 21 shows the yield of organic material in the aqueous condensate. This includes volatile polar organic compounds in solution. Pentane and furan additives gave little condensed material, whereas alpha-pinene and furfural gave larger amounts, especially furfural at the coolest temperatures. Wood pyrolysis gas, although not studied over the whole temperature range, produced condensed material yields similar to alpha-pinene and to furfural (at 1050 K).

The five most abundant classes of condensed compounds from alpha-pinene, as separated by temperature programmed runs, gave the same declining trend with increasing temperature for $T > 1050$ K. This implies that relative product speciation measured at one temperature may be a good indicator of relative abundance at other temperatures. It also implies that a single oxidative pyrolysis mechanism may have been operating in the reactor for $T > 1050$ K.

Table III summarizes the findings of the tar analysis for alpha-pinene, furfural, and wood gas. All three cases represent the temperature for highest total condensed (aqueous condensate and tars) product yield. Tar yields from pentane and furan are not shown since they are essentially nil. Tar weight yields are essentially similar for the alpha-pinene and the wood gas. However, the yield of tar from furfural is less.

TABLE III
SUMMARY OF TAR YIELDS AND COMPOSITION

weight percent by class					
additive	tar yield	phenols	alcohols	others	unassigned
alpha-pinene	0.303 g/kg	61.9	11.3	4.7	14.9
furfural	0.090 "	5.9	2.6	39.9	51.6
wood gas	0.175 "	18.0	1.8	0.9	79.3

Figure 21. Fraction of Input Carbon Measured in Aqueous Condensate. Reaction in Dual Reactor.

Tables IV, V, and VI show the breakdown of the tar components of alpha-pinene, furfural, and wood gas, respectively. Along with the name and weight percent of each component is indicated the nature of the evidence used for identification. Compounds identified (tentatively) by only one method are minor components and are listed as traces. In this respect, unchecked library matching of mass spectral peaks in complicated chromatograms is unsatisfactory (Rosenthal, 1982).

The analysis with the greatest definition is that for alpha-pinene, Table IV. The predominance of phenols is the main feature of the alpha-pinene results. It is likely that some of the unassigned components could be matched up with dimethyl, trimethyl, and tetramethyl substituted phenols for which reference material was not on hand. Reference mass spectra of these isomeric compounds resemble each other greatly, and thus, little unequivocal progress can be made by mass spectrometry alone. Species such as furfural and tetrahydrofurfuryl alcohol are common to the other additive cases. The only known component having 10 or more carbon atoms is 1, 4-naphthalenediol.

Unburned starting material is the main feature of the furfural results, Table V. In addition, four major components show mass spectra closely related to that of furfuryl alcohol. Other components have structural similarities to furfural. The two phenols are assigned on the basis of chromatographic data; mass spectra uncomplicated by close eluting components have not been obtained. Production of trace phenol (C_6H_6O) from combustion of furfural ($C_5H_4O_2$) implies aggregation of carbon species in the flame, or possibly in the probe.

The wood pyrolysis gas tar components which have been identified, Table VI, are consistent with those found for alpha-pinene. Substantially higher boiling components are also found which are relatively abundant, and many of the other unassigned peaks are likely to be phenols. The unassigned peaks are not included in the ranking.

In summary, though the overall oxidation of the different model compounds is similar with respect to temperature, the nature of the unburned organic material is strikingly different for the different model compounds. The pentane reference compound gives very well defined experimental results, with measured CO , CO_2 , and C_1 to C_5 hydrocarbons giving a carbon mass closure. The results for alpha-pinene are also well defined. Although the chromatograms for the gas phase material are complex, and include unidentified components, approximate carbon mass closure is obtained. Furthermore, most of the condensed tar components are identified, and are seen to be phenols. Of the model compounds examined, alpha-pinene gives the most tar, although this is less than 0.1% (by mass) of the starting material. Results for furan are dominated by unburned C_5 material in the gas phase.

Furfural gives the largest amounts of condensed polar organic material, approaching 10% of the input carbon, and its tar yield is dominated by starting material. However, carbon mass closure is not obtained, and the cause of this needs to be identified.

The tars produced by the combustion of wood pyrolysis gas contain phenols also produced by the combustion of alpha-pinene, as well as a number of high boiling components yet to be assigned. Since the extractable materials are typically a small fraction of the wood, and since furfural produced only little phenol, the measured phenols are probably from the lignin fraction of the wood.

TABLE IV
ALPHA-PINENE TAR COMPOSITION

Name	Rank	Wt %	SE-30	C-20 M	MS
phenol	1	37.6	+	+	+
o-cresol	2	13.7	+	+	+
benzyl alcohol	3	10.1	+	+	+
unassigned	4	7.8	-	-	-
2,5-dimethylphenol	5	6.6	+	+	-
2,4-dimethylphenol	6	5.7	+	+	-
1,4-naphthalenediol	7	2.6	+	+	-
3,5-dimethylphenol	8	2.4	+	+	-
furfural	9	2.1	+	+	-
3,4-dimethylphenol	10	2.0	+	+	-
unassigned	11	1.4	-	-	-
unassigned	12	1.3	-	-	-
tetrahydrofurfuryl alcohol	13	1.2	+	+	-
3,5-dimethylphenol	14	1.1	+	+	-
unassigned	15	1.0	-	-	-
other unassigned	-	3.5	-	-	-

Trace components: acenaphthene, guaiacol, 2,6-dimethoxyphenol

Combustion temperature: 1062 K

TABLE V
FURFURAL TAR COMPOSITION

Name	Rank	Wt %	SE-30	C-20 M	MS
Furfural	1	39.9	+	+	+
*	2	8.0	-	-	+
unassigned	3	7.9	-	-	-
*	4	6.6	-	-	+
unassigned	5	5.8	-	-	-
unassigned	6	4.3	-	-	-
unassigned	7	4.0	-	-	-
*	8	3.7	-	-	+
p-cresol	9	3.7	+	+	-
unassigned	10	3.4	-	-	-
unassigned	11	2.8	-	-	-
unassigned	12	2.7	-	-	-
tetrahydrofurfuryl alcohol	13	2.6	+	+	+
*	14	2.5	-	-	+
2,5-dimethylphenol	15	2.2	+	+	-
other unassigned	-	0.9	-	-	-

Trace components: furfuryl alcohol, acetic acid, guaiacol, catechol

* all four peaks related to m/e 98.1 and possible isomers of furfuryl alcohol.

Combustion temperature: 1011 K

TABLE VI
WOOD PYROLYSIS GAS TAR COMPOSITION

Name	Rank	Wt %	SE-30	C-20 M	MS
1,4-naphthalenediol	1	10.4	+	+	-
3,5-dimethylphenol	2	2.4	+	+	-
3,4-dimethylphenol	3	1.7	+	+	-
benzyl alcohol	4	1.7	-	+	-
o-cresol	5	1.5	+	+	-
m-cresol	6	1.1	+	+	-
furfural	7	.7	-	+	-
2,5-dimethylphenol	8	.6	+	+	-
2,4-dimethylphenol	9	.3	+	+	-
5-hydroxymethylfurfural	10	.2	+	+	-
tetrahydrofurfuryl alcohol	11	.1	+	+	-
unassigned		79.3	-	-	-

Traces: phenol, p-cresol, guaiacol, naphthalene, catechol, resorcinol,
2,6-dimethoxy phenol

Combustion temperature: 1052 K

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VI. PRODUCTION REACTOR

The concept of the homogeneous jet-stirred combustion reactor is attractive because of its simplicity and because reactions occur in a field of time-mean uniformity. However, attaining these properties in a real reactor can be elusive, as indicated above. The approach described here, because of the objective of studying hydrocarbon cracking and oxidative pyrolysis, is to obtain homogeneity by decreasing the temperature and active species concentrations in the reactor. This is accomplished by stirring the reactor with a nearly sonic jet of hot gas from a pressurized hydrogen-air burner, with the prevaporized hydrocarbon material seeded into this hot gas jet immediately before the jet enters the stirred reactor.

In order to further improve the homogeneity of the jet-stirred reactor, it will be necessary to decrease the fluid particle cycle time relative to the mean residence time of the reactor, so that the average time for a fluid particle to make one cycle in the reactor is not large compared to the chemical time of interest. The toroidal reactor (e.g., Nenniger, 1983) is a possible approach in this regard.

Since the rates of hydrocarbon cracking and oxidative pyrolysis increase sharply with increasing temperature, there exists some temperature at which the characteristic chemical time of a particular reaction becomes comparable to the cycle time. Because of this, an experimental upper temperature limit is established by measurement. This temperature is that at which input material concentrations first deviate from homogeneity, as determined by comparing the concentration along the jet centerline to the concentration in the bulk of the reactor.

With the "production" reactor it is possible to study the cracking and pyrolysis reactions of organic model compounds quantitatively, so long as the overall reaction remains endothermic or thermally neutral. It is possible to measure overall oxidative pyrolysis rates appropriate to organics burnout in combustion systems, and to ascertain conditions which provide the highest yields of desirable products of thermochemical conversion, such as the light olefins. Although present results are for oxidizing conditions, the reactor can also be operated for chemically reducing conditions. Because of the obvious difficulty of quickly seeding the hot gas jet with model compounds, especially with difficult-to-vaporize biomass volatiles model compounds, a simple single jet configuration is used.

In this chapter the "production" reactor system is described, and detailed proof-of-concept experiments on pentane are reported. Currently the reactor is being applied to studies of the oxidative pyrolysis of furan, furfural, and phenol, and as indicated above, these results will be reported separately as they become available.

A. Reactor System

The reactor consists of three major parts. The first is the lower burner which houses a manifold of hydrogen-air diffusion flames in a refractory-lined pressure chamber. High flow rates at fuel-lean conditions lead to temperatures

Figure 3. "Production" Jet-Stirred Reactor, Showing Lower Chamber for Gas Generation by Hydrogen-Air Combustion, and Upper Jet-Stirred Chamber for Model Compound Reaction

Figure 23. Atomizing Vaporizer

Fig.23. Model 5 Single-Jet Stirred Reactor

Full Size

Dimensions in inches

as high as 1325 K at pressures up to 200 KPa. The outlet of this chamber is an Inconel jet nozzle assembly which constricts the exit to sustain approximately sonic exhaust velocities. Within the jet nozzle assembly a pre-vaporized stream of organic additive carried in nitrogen is mixed into the high velocity jet. The outlet tube of the jet nozzle assembly extends into the lower burner chamber in order to minimize the entrainment of refractory chips into the jet. Figure 3 is a schematic diagram of the single jet reactor system.

The additive is pre-vaporized in nitrogen in a separate atomizing vaporizer unit, the second part of the reactor system. This is shown in Fig. 22. The liquid model compound is loaded into the pump chamber and pressurized with nitrogen to about 10 psig. This pressure, in conjunction with a fine metering valve, is used to set the model compound flow rate. The metered liquid flows into the second chamber, i.e. the atomizing vaporizer, where it becomes entrained in a small, high velocity stream of nitrogen. This high velocity stream of liquid and nitrogen "shoots" into the bulk of the second chamber, where it mixes with the bulk of the nitrogen carrier gas. The shearing action created by the high-velocity jet as it mixes with the slow bulk stream is the mechanism for fine atomization. Vaporization is assured by preheating the bulk nitrogen flow to about 200°C (by using a tube furnace), and by maintaining the mixed nitrogen-model compound stream at elevated temperature as it flows to the reactor. Additional hot nitrogen is mixed into the nitrogen-model compound stream downstream of the atomizing vaporizer in order to bring the total flow rate to the desired level, nominally, 0.2 g/s.

The third major part of the reactor system is the jet stirred reactor, which is fed at its base by the jet nozzle assembly. Little reaction of the hot air, steam, and additive occurs before the mixture reaches the highly turbulent part of the jet-stirred reactor because the high velocity jet crosses the reactor volume in a very short time (typically 50 microseconds). Small drain holes limit the escape of gas such that the reactor operates slightly above ambient pressure. The model 5 jet-stirred reactor used in the pentane experiments is shown in Figure 23. The model 6 reactor contains a reflector of solid Inconel, and a model 7 reactor is being designed with a manifold of small feed jets.

The model 5 reactor jet inlet is 4.4 mm in diameter. The reactor base diameter is 15.9 mm, the reactor height is 44.45 mm, and its maximum diameter is 25.4 mm. The reactor has 4 equally spaced 3.6 mm diameter drain holes centered 6 mm up from the base, and 3 more drain holes of the same size 25 mm above the base. The reactor has a height/inlet diameter ratio of 10:1. The exit area/inlet area ratio is about 4.7:1, also substantially smaller than usual. The reactor volume is 15.8 cc. The reactor is heavily insulated.

Dry compressed air is supplied after being filtered and passed over a scrubber to remove corrosive gases and oil contaminants. Hydrogen and nitrogen (Airco Gas Products) are used as supplied. Reagent grade n-pentane (98% pure isomer, J.T. Baker) is used without further purification.

All fluid flows into the reactor system are measured by variable-area rotameters (Fischer - Porter Co.). Air and hydrogen flows are determined from Fischer - Porter calibration data. Nitrogen flows are calibrated with a wet-test meter (Precision Scientific). The pentane flow rate is calibrated

volumetrically. All Bourdon-tube pressure gages are standardized with a dead weight tester.

B. Reactor Homogeneity

The stirred reactor approaches the homogeneous stirred model for unignited conditions. These are conditions where the heat supplied by the lower burner sustains pyrolysis of the input material without overall exothermic reaction being sufficient to increase the temperature of the reactor greatly. Typically there is observed a temperature range below which the reactor temperature is very stable. However, if the temperature exceeds this range, even momentarily, the reactor temperature rises quickly to a substantially higher value which is also stable. At this point the temperature of the stirred reactor exceeds that of the lower burner. This phenomenon is illustrated in Figure 24. Ignition is assumed to coincide with the increase in temperature in the reactor. Under the higher temperature conditions, significant species concentration gradients occur, most notably for pentane starting material and the intermediate cracking product ethylene. As might be expected from consideration of known global oxidation rates, not all species concentrations are affected equally. Carbon monoxide and carbon dioxide are much better mixed than hydrocarbon species. Figure 25 illustrates these effects. For conditions bordering on ignition, some gradient in temperature exists. Fortunately, the range of values observed is small ($\pm 10K$). Based on these facts, both the probe and thermocouple can be positioned in representative locations where large errors caused either by wall or center jet effects can be ruled out. The probe is located at 27 mm (9 mm off centerline) and the thermocouple at 30 mm (6 mm off centerline). These distances refer to the outside of the reactor housing. The reactor wall and centerline are at 22 and 36 mm respectively.

C. Results

The reactor conditions make it possible to study the pyrolytic reactions of pentane in an environment where kinetic control limits the reactions resulting in oxidation.

The cases examined at approximately 2 ms residence time range from low temperatures of about 1000K, at which only minimal cracking and essentially no oxidation occur, to high temperatures of 1300K at which only one third of the input carbon remains unoxidized. Of the portion unoxidized, the majority is ethylene, with pentane and propylene being next in concentration. Thus, conditions of optimum yield of ethylene can be identified.

The temperature of the reactor is adjusted by varying the rate of hydrogen flow. Because the thermal inertia of the reactor is large, it is helpful to establish a working curve of reactor temperature versus hydrogen setting (Figure 24). In practice this curve is nearly linear, and permits obtaining a desired temperature without time consuming fine adjustments.

Because of the varying hydrogen flow rate, different values of the total molar flow rate, reactor residence time, and fuel/air ratio apply for each of the different temperatures studied. These data are compiled in Table VII. The molar flow rate includes the input pentane flow rate, but not the various intermediate species formed. These species are neglected because for the cases

Fig.24. Lower Burner and Stirred Reactor
Temperature vs. Hydrogen Setting .

Figure 25. Profiles of Temperature, CO, CO₂, and Hydrocarbons in Production Reactor. Upper Case is Nearly Homogeneous. Lower Case, at Ignited Conditions, is Inhomogeneous in Hydrocarbon Concentrations.

studied, their effect on the total molar flow rate and reactor residence time is small. The total molar flow rate assumes complete combustion of hydrogen.

Table VIII lists the gas composition found at various temperatures, and Figure 4 shows the trends in some of these data graphically. The values of CO_2 present at low temperature, higher than the values of CO present for these cases, probably represent ambient CO_2 in the input air, rather than actual CO_2 formed in reactions of pentane. Figure 4 shows that intermediate cracking products, such as ethylene, pass through a maximum near 1220 K. At this temperature, ethylene comprises 27% of the total carbon present, exceeding unreacted pentane starting material.

Among the cracked products, olefins greatly predominate. At a lower temperature case, 1093K, ethylene exceeds ethane by 62:1 and propylene exceeds propane by 14:1. Essentially all of the straight chain C4 material is 1-butene. However, C5 material is n-pentane with traces of a C5 olefin indicated. Two additional components elute in the C4 to C5 region but, unfortunately, the methods in use do not sufficiently distinguish the various forms of butadiene from 1- or 2-butyne to permit identification. An unassigned peak eluting slightly earlier than propyne is thought to be allene. Within the expected uncertainty in pentane flow rate, the input carbon flow rate and observed product carbon flow rate are in agreement.

TABLE VII
PRODUCTION REACTOR OPERATING CONDITIONS

1. Temperature (K)	1068	1093	1136	1169	1219	1253
2. Molar flow rate (gmol/s)	0.0826	0.0829	0.0830	0.0831	0.0835	0.0837
3. Mean residence time (ms)	2.18	2.13	2.04	1.99	1.89	1.83
4. H_2 -air fuel-air equivalence ratio	0.353	0.370	0.378	0.401	0.432	0.450
5. Total fuel-air equivalence ratio (actual)	0.438	0.454	0.467	0.477	0.503	0.517
6. O_2 mole fraction (wet)	0.116	0.113	0.110	0.107	0.101	0.097
7. H_2O mole fraction	0.126	0.132	0.138	0.142	0.153	0.158

Figure 4. Products of Oxidative Cracking and Pyrolysis of Pentane in "Production" Reactor

TABLE VIII
 PRODUCTION REACTOR NORMALIZED GAS COMPOSITION (PPMC)
 PENTANE MODEL COMPOUND

1. Temperature (K)	1068	1093	1136	1169	1219	1253
2. Methane	13	27	77	144	240	209
3. Ethylene, ethane	229	540	1494	2357	2720	2113
4. Acetylene	-	1	9	36	141	201
5. Propylene, propane	186	387	836	1123	960	823
6. C ₃	1	3	6	13	23	23
7. Propyne	-	2	3	11	25	26
8. 1-Butene, n-butane	87	175	355	406	297	189
9. C ₄	4	12	68	126	132	102
10. C ₄ to C ₅	7	7	31	40	61	60
11. n-Pentane, others	9186	8573	6671	4773	2171	965
12. Sum of UHC	9713	9725	9581	9030	6768	4709
13. CO	-	-	132	736	2720	4136
14. CO ₂	287	275	237	234	512	1155
15. Sum total	10,000	10,000	10,000	10,000	10,000	10,000
16. CO ₂ without baseline CO ₂	-	-	-	-	305	965
17. Sum total without baseline CO ₂	9713	9725	9763	9766	9793	9810

The rank order of cracking products is generally consistent with results reported by Princeton University researchers for n-paraffin reaction in a turbulent flow reactor, e.g., see the articles by Dryer and Glassman (1978) and Hautman et al. (1981) and the text by Glassman (1977). The rank order is:

with C_2H_4 and C_3H_6 predominant at low temperature and C_2H_4 predominant at the highest temperatures shown in Figure 4.

D. Kinetic Interpretation

Overall rates of reaction of hydrocarbons are available in several forms in the literature. As discussed by Westbrook and Dryer (1981), there is the single-step reaction,

the two-step reaction,

and the oxidative pyrolysis step of the quasi-global mechanism,

which is followed by the elementary mechanisms for CO and H_2 oxidation.

A more detailed approach for the hydrocarbons is the multi-step mechanism of Hautman et al. (1981),

followed by overall steps for CO and H_2 oxidation. The term C_nH_m represents the intermediate hydrocarbons, which for the pyrolysis of aliphatic hydrocarbons, are mainly ethylene followed by propylene. A multi-step approach is also used by Duterque et al. (1981) in their mechanisms for benzene and isooctane combustion, e.g., for benzene,

An approach which includes the intermediate free radicals is that of Creighton (1977), applied to methane combustion,

where the intermediate radical, R, is

The data have been interpreted for the rate of loss of total organic material by the application of equation (4), as done above for the initial model compound studies. Results are plotted in Fig. 26, along with dashed curves to represent the results from the initial studies (Fig. 20). The range in the chemical times obtained for the different reactors is not unexpected, because even though all reactors had the same overall stoichiometries, the initial reactors had mixing influences, and the active species concentrations in the reactors were different. Furthermore, application of the published rates for reaction of all organic material to CO and H₂ by reaction (3), or (9), gives poor agreement to the "production" data. Values from the Edelman and Harsha (1978) rate are high (i.e. long chemical time), and values from the Westbrook and Dryer (1981) rate are low (i.e. short chemical time).

A very satisfactory interpretation of the "production" data is obtained by application of the multi-step mechanism of Hautman et al. (1981), i.e. equations (10) and (11) above. This interpretation is seen in Fig. 5, where the inferred chemical times for loss of pentane starting material and intermediate hydrocarbon material are plotted. This is a much improved method of interpreting the present results. The data reduction equation for C₅H₁₂ loss is,

$$t_{c1}/t = 1/([C_5H_{12}]_0/[C_5H_{12}]-1) \quad (16)$$

where t_{c1} is the chemical time, $5[C_5H_{12}]$ is line 17 of Table VIII, and $5[C_5H_{12}]_0$ is line 11 of Table VIII. The data are in agreement with the application of the rate expression of Hautman et al. (1981).

The data reduction equation for intermediate "C₂H₄" loss is:

$$t_{c2}/t = 2[C_2H_4]/([CO] + [CO_2]) \quad (17)$$

where t_{c2} is the chemical time, $2[C_2H_4]$ is all hydrocarbon material except C₅H₁₂, i.e. line 12 minus line 11 in Table VIII, [CO] is line 13 in Table VIII, and [CO₂] is line 16 in Table VIII. Application of the reaction rate, RR₁₁, of Hautman et al. (1981), following the convention for [C₂H₄], shows agreement to the present results, except for some drop-off at the lower temperatures. This less than excellent agreement at the lower temperatures may be due to inaccuracies in the data for the very small values of [CO] and [CO₂] observed at low temperatures. Another way to explain this is to note that at the lower temperatures, intermediate hydrocarbons are mainly being formed rather than destroyed, whereas the rate expression is for destruction. At the higher temperatures, where destruction is enhanced, excellent agreement is obtained between the present and the published rate data.

The oxidation of CO to CO₂ in the present reactor is very slow, which is expected because active species formed in the lower hydrogen - air burner recombine before reaching the jet-stirred reactor, and since the hydrocarbon material at endothermic and thermally neutral conditions is not generating significant active species. The data reduction equation for the chemical time

Figure 26. Time for Oxidative Pyrolysis. Results from Figure 20 Also Plotted.

Figure 5. Multi-step chemical times for pentane oxidation.

for CO oxidation is,

$$t_{c3}/t = [CO]/[CO_2] \quad (18)$$

and if this oxidation is assumed to be accomplished exclusively by the forward rate of the elementary reaction $CO + OH \rightarrow CO_2 + H$, using the rate constant of Baulch and Drysdale (1974), the inferred hydroxyl radical levels are 29 ppm at 1219K and 62 ppm at 1253 K, values which are one order of magnitude greater than chemical equilibrium values for the same conditions.

E. Conclusion

Based on the results reported herein, which indicate reactor homogeneity in hydrocarbon concentrations at endothermic and thermally neutral conditions, and which show excellent agreement to published multi-step rate data for oxidative pyrolysis of aliphatic hydrocarbons -- the published data being mainly for propane reaction in a turbulent flow reactor -- the "production" jet-stirred reactor system is being used for studies of the pyrolytic reaction of biomass volatiles model compounds.

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VII WOOD STICK PYROLYZER

Wood pyrolysis gas is produced in a separate thermal pyrolysis unit illustrated in Fig. 27. This unit heats nitrogen in an electrical furnace, and the hot nitrogen then flows over a wood stick in an immediately adjoining, insulated, stainless steel, pyrolyzer section. Each wood stick is fed into the pyrolyzer by a motorized screw drive system. The stick feed rate essentially controls the pyrolysis rate, which is ca. 0.01 gm/sec and corresponds to roughly 2500 ppmC in the combustion reactor of Fig. 2. The pyrolysis gas produced in this manner, and carried in the N_2 of ca. 0.2 gm/sec, passes through a short, insulated line to the reactor.² The nominal gas temperatures are: 500°C pyrolyzer inlet temperature, 300°C pyrolyzer exit temperature, and 200°C reactor injection temperature. The wood sticks, 47 cm x 4 cm x 0.5 cm (38 cm useful length) with 20% moisture content (dry basis), are prepared from billets all cut from the heartwood of a single log of Douglas fir, pseudotsuga menziesii.

The configuration illustrated in Fig. 27 allows the wood stick to be heated by both radiation (from the tube furnace) and by convection. In order to provide mainly convective heating, a "blockage" plate is placed between the electrical furnace and the pyrolysis section. On the other hand, in order to provide mainly radiative heating, the long pyrolysis section shown in Fig. 27 is replaced with a short section of 5 cm length, which serves simply as an interface between the electrical furnace and wood feeder mechanism.

Only the most essential tests have been performed on the unit in the convective heating mode. Carbon supply rate to the combustion reactor of Fig. 2 was found to be constant within $\pm 50\%$ over a period of 20 minutes. Residual char yields were found to be about 20%, with a $\pm 50\%$ variation from stick to stick. Unfortunately, under the scope of the present grant, it was not possible to calibrate the pyrolyzer for output composition -- a major undertaking -- nor to run many experiments with the unit. For the present studies, it was felt that the model compound measurements would provide more definitive kinetic results, and it was felt that present experiments with wood (Chapter VIII) should address issues of mixing and engineering requirements for clean burning.

WOOD STICK PYROLYZER

DRIVE MOTOR

FEED SCREWS

PUSHROD

PISTON

STICK CHAMBER

GAS TO REACTOR

INSULATOR

STICK

PYROLYSIS

CHAMBER

ELECTRIC FURNACE

GAS INLET

ACCESS PORT

SCALE

1:10

Fig. 27. Wood Stick Pyrolyzer

VIII WOOD COMBUSTION STUDIES

The research wood combustor is shown in Fig. 8, and has the following design features for the promotion of nearly complete combustion:

- 1) Insulated primary and secondary chambers for high temperature:
 - A) Pyrolysis, gasification (i.e. char burning), volatiles ignition, and first-stage volatiles combustion occur in the primary chamber.
 - B) Second-stage volatiles combustion occurs in the secondary chamber.
- 2) Vortex mixing directly above the wood in the primary chamber acts to promote the ignition of all of the volatiles streams released from the wood. This is a key element in the present design, and is a potential patentable item.
- 3) Vortex mixing of secondary air into the primary gases occurs at the start of the secondary chamber
- 4) Catalytic afterburning in a commercial honeycomb catalyst: In this application, the catalytic afterburning acts mainly to oxidize carbon monoxide, since organic concentrations entering the catalyst are low because of the efficient reaction in the primary and secondary chambers.

The research wood combustor of Fig. 8 has evolved from earlier arrangements we have tried and discarded. Likewise, the air injection pressure and flow patterns used in the final combustor have evolved from trial and error. In our first research wood combustor, the primary chamber was not injected with a forced draft of air, but rather, the forced draft of air was used only to drive a vortex mixing pattern in the secondary chamber. With this arrangement the primary chamber was almost exclusively a pyrolysis chamber, while the secondary chamber was essentially the sole combustion chamber. This approach was discarded for two reasons: 1) it was found difficult to completely oxidize the smokey pyrolysis gas in the secondary chamber, and 2) an arrangement for heat transfer to the primary chamber was required.

Several arrangements of inlet air injection and swirl have been tried in order to obtain clean combustion over the entire operating cycle of a burn. For the present design in Fig. 8, it has been found necessary to use a centrifugal blower which has a relatively high static pressure head of 25 inches H_2O W.C. During the steady-state portion of burn, the forced draft of air is split approximately 5 gm/sec to 2 gm/sec between the primary and secondary chambers. This arrangement gives a strong vortex pattern above the wood in the primary chamber. Attempts to decrease the primary air, and thus, increase the secondary air, lead to smoke-free combustion so long as a fresh stick of wood is not added to the fuel bed. In order to assure smoke-free operation even during refueling, the 5 gm/sec to 2 gm/sec arrangement has been found to be necessary.

The nominal average burning rate in the research combustor is 30,000 Btu/hr, corresponding to about 0.5 gm/sec of wood burned, or about 0.25 gm/sec

Figure 8. Research Wood Combustor. (1) = Fuel Bed, (2) = Vortex Mixing Zone, (3) = Secondary Combustion Chamber, (4) = Honeycomb Catalyst, (5) = Heat Exchanger for Air Pre-Heating, (6) = Forced Draft Air Supply, (7) = Heat Transfer Chamber, and (8) = Stack

of carbon converted to gas. For a nominal wood composition (Reed, 1979) of:

the stoichiometric air-to-dry fuel mass ratio is 6.3 and thus, at the nominal total air flow rate of 7 gm/sec, the theoretical air is approximately 220%.

In order to obtain smoke-free operation during startup, it is necessary to operate only the upper forced air draft as the kindling fire is being ignited, and then over a period of 15 minutes, to progressively add forced air draft to the primary chamber as increasingly larger pieces of wood are added to the chamber. At kindling ignition, ambient air is drawn into the primary chamber through a port in the loading door.

A. Combustor Details

The overall dimensions of the research wood combustors are L:W:H = 70:40:90 cm. The volume of the primary chamber above a nominal load of wood is 8 liters, and the volume of the secondary chamber is 5 liters. At nominal steady-state operating conditions the residence times are 0.65 seconds and 0.25 seconds, respectively, for the primary and secondary chambers.

The combustor is constructed of the following materials and components:

- 1) The outer walls are welded mild steel of thickness 0.32 cm.
- 2) High temperature firebrick (1540°C) from Chicago-Wellesville Corp. is used to line the primary and secondary chambers. An airset, high-temperature (1700°C), silica base, Chicago-Wellesville Corp. mortar is used to seal the bricks and provide structural rigidity.
- 3) The honeycomb catalyst is a Corning Catalytic Wood Stove Combustor (model number 65-84). The Corning Co. recommends locating the catalyst in a region where temperatures are at least 260 to 315°C, but no higher than 900°C. Also, the catalyst should be located away from direct flame impingement. For the present application, a bypass to the catalyst is not provided since there is negligible possibility of catalyst plugging.
- 4) A stainless steel heat exchanger is used to preheat the secondary air to temperatures of 350 to 400°C.
- 5) The air blower, located external to the woodburner operates with a 25 inch H₂O static pressure. The blower is from a Hoover Co. upright vacuum cleaner. This type of blower is required in order to provide a high air flow rate (4 to 10 gm/sec) at a high pressure head. The flow schematic for the forced draft of air to the combustor is shown in Fig. 28.
- 6) The exhaust stack of 20 centimeters diameter stove pipe is 6 m high.

The combustor has the following permanent instrumentation, which is illustrated schematically in Fig. 29:

Figure 28. Forced Draft Air Flow System for Research Wood Combustor

Figure 29. Instrumentation for Research Wood Combustor

- 1) Surface temperatures, fire-brick temperatures, and non-reactive gas temperatures are measured with type K thermocouples.
- 2) Reaction chamber temperatures are measured by Pt/Pt-13% Rh thermocouples. The thermocouple beads are coated with a non-catalytic material.
- 3) Static pressure probes are located in the different chambers of the woodburner.
- 4) Blower air flow rate is measured by a rotameter or by calibrated pitot-static probes.

All thermocouple outputs are collected by a data logger and sent to a PDP 11/44 computer for analysis.

B. Sampling and Analysis

Generally, the procedures outlined above in Chapter IV were used. Therefore, only the special features and essential aspects of sampling and analysis of the wood combustor are given here.

Samples were withdrawn via a stainless steel tube from a region behind the catalyst in the woodburner's heat transfer section, or from the woodburner's secondary chamber. The stainless steel line was maintained hot ($>80^{\circ}\text{C}$) with a heating tape until the sample reaches traps. Organic material was not found in this line for forced air operation of the woodburner. A double ice-bath condensate trap was used to remove water and condensable organics, and the connecting glassware was rinsed with solvent after each run, and the rinse was added to the sample.

Following the condensation traps, the dry gas was passed through a filter and routed via Teflon line to the Perkin-Elmer Sigma IB gas chromatograph. Pressure in the sample line was 100 torr.

A two column (Porapak-T and molecular sieve), two detector (HWD and FID) setup was used for gas analysis. The system was programmed either for major species (O_2 , N_2 , CO , and CO_2) and quick hydrocarbon analysis, or for detailed hydrocarbon analysis.

Collected condensate samples were treated by liquid-liquid and, as necessary, acid-base-neutral extraction. After these treatments, the samples were separated and analysed by gas chromatography or combined gas chromatography/mass spectrometry (GC/MS). The Perkin-Elmer Sigma IB GC with flame ionization detector separated individual samples by the splitless injection technique of narrow-bore, non-polar, fused silica open tubular column. Similar methods on Hewlett-Packard 5985 A GC/MS/Data System produced mass spectra and reconstruction chromatograms of sample components. Both methods produced qualitative identification and semi-quantitative results for comparison. Data were not corrected for specific response factors.

All mass spectra were obtained at unit mass resolution by electron impact ionization at 70eV. The ion source was maintained at 200°C . Identification,

where possible, was made on the basis of four factors:

- 1) GC retention time of authentic material or closely related compounds.
- 2) Reference to mass spectral libraries, authentic mass spectra, or automated searches of the EPA/NIH mass spectral search list (see Chapter IV).
- 3) Analysis of mass spectral fragmentation patterns.
- 4) Observation of parent ions of compounds such as PAH known to be subject to minimal fragmentation under these conditions.

The spectra of all positively identified components were scrutinized to ensure that they were not caused fortuitously by the presence of contaminants.

C. Experimental Matrix

The independent parameters examined were the following:

- 1) Wood type: A mixture of coastal Douglas fir and Idaho larch, or western Washington alder. All fuels were air dried to approximately 10% moisture content, dry basis.
- 2) Catalyst: Sampling was conducted before the catalyst in the secondary chamber, just after the catalyst in the heat transfer section, or without the catalyst (at the "after" position).
- 3) Draft: Forced air draft, from total flow rates of 4 to 10 gm/sec. During kindling startup, as noted above, the forced draft to the primary chamber was significantly reduced.
- 4) Time: The four major portions of the burn cycle were examined, including kindling startup, steady-state volatiles burn, refueling, and char burnout.

Data interpretation was conducted by assuming that the following overall reaction equation was valid:

Since the dry mole fractions of CO_2 , CO, total gas-phase hydrocarbons CH_w , O_2 , and N_2 were measured, and since atoms of C, H, O, and N were conserved, it was possible to determine the instantaneous air amount, i.e. parameter "a," with the following assumptions:

- 1) The amount of C, H, and O in condensible organics and tars was negligibly small, which is a reasonable assumption for most of the present work for the purpose of estimating the local fuel-air stoichiometry.
- 2) The z/y ratio of O to H in the fuel remained at the value given above for nominal wood, except during char burning for which the assumption

of $z = 0$ is made. In this regard, please note that the z/y is little affected by the fuel moisture, since even in dry wood the ratio is close to 2.

The determination of parameter "a" is equivalent to the determination of the local theoretical air percentage, T.A.%, and since the absolute air flow rate was measured, it was possible from this value and from the measured mole fractions of CO_2 , CO , and CH_w to infer the local carbon consumption rate, C.C.R. (gm/sec).

Characteristic theoretical air percentages are listed below for the different phases of the burn cycle:

- 1) Kindling startup: 225 to 525% T.A.
- 2) Volatiles burning: 250% T.A.
- 3) Refuel: 125 to 275% T.A.
- 4) Char burning: 310 to 610% T.A.

D. Experimental Results

The experimental results for the concentrations of gas, and the inferred values for the overall theoretical air percentage and carbon conversion rate are shown in Table IX for the different phases of seven burns. Also given is the nominal temperature in the combustor. This is the average of the thermocouple readings of gas temperature in the primary chamber, secondary chamber (before catalyst), and heat transfer chamber (immediately after catalyst). For the experiment 013 without the catalyst, a plate with holes to simulate the catalyst pressure drop was used in the place of the catalyst. For the kindling startup phase, the flow rate of ambient air sucked through the port in the door was not measured. Therefore, because absolute air flow rate was not known, the exhaust gas measurements (as mole fractions) could not be converted to carbon conversion rates. Finally, it should be noted that two of runs exhibited abnormal CO_2 to O_2 ratios, which may be indicative of sampling or analysis errors.

The temperature-time histories of the runs are plotted in Fig. 9 and in Figs. 30 to 33. Also shown on these figures are the measurements of CO and total C_1 -to- C_3 hydrocarbons, and the inferred values of theoretical air percentage and carbon consumption rate.

The continuous temperature records are shown for the primary chamber (pyro./comb. chmb.), secondary chamber (before catalyst), and immediately after the catalyst. Typically, these readings were within 100°C of one another, with the primary chamber reading usually being highest. The most reliable reading of gas temperature was probably that within the secondary chamber, since the effect of radiation gain or loss from the thermocouple bead was least for this chamber. That is, luminous flaming combustion did not occur in this chamber, rather it occurred in the primary chamber, and also, the thermocouple view of a cold environment was also restricted.

The gas samples were drawn continuously, though the filling of the GC sample collection loop (see Chapter IV) only occurred at the discrete times noted in Fig. 9 and in Figs. 30 to 33. This filling required approximately one

TABLE IX
EXPERIMENTAL RESULTS FOR WOOD-BURNS

Run	Description (T, °C)	%O ₂	ppm CO	%CO ₂	ppmC UHC	T.A. %	gm/sec C.C.R.
010-	Douglas Fir/Larch, Sampling After Catalyst (Fig. 9)						
1	Kindling startup (500)	14.5	317	8.0	274	336	*
2	Char burn (450)	16.5	450	5.5	908	483	.090
3	Refuel (900)	8.8	597	11.3	18	169	.420
4	Char burn (500)	17.5	103	3.9	10	613	.070
011-	Alder, Sampling After Catalyst (Fig. 30)						
1	Kindling startup (600)	12.4	285	8.9	22	245	*
2	Volatiles burn (900)	11.0	198	11.7	---	226	.240
3**	Refuel (900)	5.2	13,000	12.2	---	127	.480
4	Char burn (600)	15.9	176	4.9	---	407	.110
012-	Alder, Sampling Before Catalyst (Fig. 31)						
1	Kindling startup (700)	16.7	1,621	6.3	671	528	*
2	Refuel (600)	4.6	10,800	16.7	406	125	.530
3	Char burn (450)	14.8	6,018	6.3	---	371	.160
4	Refuel (750)	8.2	979	12.4	321	162	.410
5	Char burn (600)	14.5	6,030	6.4	14	313	.170
013-	Alder, No Catalyst (Not plotted)						
1	Kindling startup	15.9	1,385	5.6	38	410	*
2	Volatiles burn	12.3	1,800	10.0	98	255	.240
3	Char burn (warm)	15.7	995	4.7	10	383	.170
4	Refuel (hot)	14.0	710	10.0	52	283	.250
5	Refuel (hot)	9.9	2,275	10.0	5	186	.380
6	Char burn (high air)	19.9	2,100	1.0	8	1,700	.040
014-	Douglas Fir/Larch, Sampling After Catalyst (Not plotted)						
1	Kindling startup	11.6	590	10.3	70	228	*
2	Volatiles burn	12.6	386	9.4	51	262	.130
3**	Refuel (hot)	9.6	1,580	8.7	707	178	.280
4	Char burn (lean)	17.0	499	3.8	10	518	.170
5	Refuel (hot)	12.8	347	8.3	11	264	.270
6	Char burn	15.7	357	4.8	11	370	.300
015-	Douglas Fir/Larch, Sampling After Catalyst (Fig. 32)						
1	Kindling startup (450)	14.1	282	8.0	8	328	*
2	Volatiles burn (450)	12.9	360	8.0	69	258	.300
3	Char burn (550)	17.5	528	3.2	17	582	.140
016-	Douglas Fir/Larch, Sampling After Catalyst (Fig. 33)						
1	Kindling startup (550)	---	658	---	45	390	*
2	Volatiles burn (750)	---	214	---	31	241	.310

* Door port open during kindling startup

** Outside nominal CO₂ vs. O₂ behavior

Figure 9. Temperature-Time History of Wood Burn, and Emissions of CO and Hydrocarbon Gas. Inferred Theoretical Air and Carbon Conversion Rate Also Shown

Conditions
wood: alder
With catalyst

Figure 30. Experimental Results for Wood Burn 011

Conditions
Before Catalyst
wood: alder

Figure 31. Experimental Results for Wood Burn 012

Conditions
With catalyst
wood: nominal

Figure 32. Experimental Results for Wood Burn 015

Conditions
With catalyst
wood: nominal

Figure 33. Experimental Results for Wood Burn 016

minute, and thus, the results for the gases are the average concentrations which existed in the combustor during the collection interval.

Figures 10 and 34 show, respectively, the results for CO and total C₁-to-C₃ hydrocarbon emissions. For sampling after the catalyst, and for a theoretical air percentage greater than 200%, CO emissions are equal to or less than 600 ppm, and in the case of char burning, the CO is typically in the 100 to 200 ppm range. With the catalyst removed, or for sampling ahead of the catalyst, CO emissions are five-fold higher (except at the lower theoretical air percentages). Thus, for this application, with unburned organic emissions minimized by the high intensity combustion, a significant action of the catalyst is CO oxidation. The C₁-to-C₃ hydrocarbon emissions, shown in Figure 34, show considerable scatter when plotted versus theoretical air percentage, and with respect to the catalyst. Clearly, other factors affect these emissions, such as local mixing and temperature. The predominant species is methane, which is known to burn more slowly than higher order alkanes and alkenes. Furthermore, hydrocarbon gases greater than C₃ are not observed in our samples. For the most part, the hydrocarbon gas emissions are below 100 ppmC, and thus, are not a substantial problem.

Finally, in Fig. 35, the inverse relation between carbon conversion rate and theoretical air percentage is demonstrated.

E. Condensate Samples

Relative condensate analyses have been made for the "most interesting" runs. These were runs for which the condensate showed some discoloration. The collection time for each sample was 10 ± 2 minutes, and this overlapped the 1 minute time required to take a gas sample. For the burn of Fig. 9 the times for condensate collection were:

- 1) Kindling startup (run 010-1): Collected from 20 to 30 minutes
- 2) Refuel (run 010-3): Collected from 120 to 130 minutes
- 3) Char burn (run 010-4): Collected from 170 to 180 minutes

Condensate sample analyses obtained by the GC/MS method are shown in Table X. These analyses indicate the percentage of each class of compound in a sample, and they also provide a qualitative comparison of the condensible organic emissions for the different portions of the burn cycle.

Condensible organics occurred primarily during kindling startup, with phenols being the predominant species. Our classification of phenols includes phenol, cresols, dimethyl phenols and several species of methoxy benzenes, which are in some cases neither resolved from nor distinct in their mass spectral fragmentation from phenol compounds. Furfurals also appear during startup, and in this case, the classification may also include 2,5 dimethyl furan and isomers of furfural. When fresh fuel was added to the burner, phenols, furfurals, and aromatics were emitted, though in much smaller amounts than during startup. During high temperature volatiles burning, little if any condensed organic material was detected.

Figure 10. Carbon Monoxide Emissions from Research Wood Combustor

Figure 34. Sum of C_1 -to- C_3 Hydrocarbon Gases Emitted from Research Wood Combustor

Figure 35. Carbon Conversion Rate vs. Theoretical Air for Research Wood Combustor

TABLE X
INTEGRATED ION ABUNDANCES AND NORMALIZED PERCENTAGES
FOR WOOD COMBUSTION CONDENSATE

Run	Furfurals	Phenols	PAH	Total	Comments
010-1	2,988 28%	7,471 69%	325 3%	10,784 100%	Kindling startup
010-3	Trace	144 88%	20 12%	164 100%	Refuel
010-4	BDL (below detection limit)	BDL	Trace	Trace	Char burning
011-3	Trace	310 65%	164 35%	474 100%	Refuel
012-1	BDL	8,266 99.6%	30 0.4%	8,296 100%	Kindling startup
012-5	1,788 75%	BDL	604 25%	2,392 100%	Char burnout
Natural Draft	708 1.5%	47,882 98%	235 0.5%	48,825 100%	Volatiles burn (Catalyst, Smokey)

The greatest inconsistency in the condensate sample analyses occurred for the char burning portion of the cycle. For example, for run 010-4 all of the material was below the detection limit of the mass spectrometer, except for trace amounts of aromatics. However, for run 12-5, substantial PAH was observed, as well as furfurals. Since char is known to contain aromatic material, the observation that PAH is emitted during some stages of char burnout is not unexpected. Polycyclic aromatic hydrocarbons include seven (7) mass number (m/z) values which are the parent ions of likely pollutants and isomers: Napthalene (m/z 128), acenaphthene (m/z 154), fluorene (m/z 166), anthracene and phenanthrene (m/z 178), pyrene (m/z 202), chrysene (m/z 228), and benzopyrene (m/z 252).

Also listed in Table X are condensate analyses for a volatiles burn with natural draft, instead of forced draft. A very large increase in condensible organics is seen, especially the phenols.

F. Conclusions

The experimental woodburner, with forced draft and vortex mixing above the fuel and in the secondary chamber exhibits very low emissions and a combustion efficiency estimated to be better than 98% (if the catalyst is present, and greater than 200% theoretical air is used). The woodburner total operational

time was 100 hours, and for this time, no condensed organics were observed in the heat transfer section or in the exhaust stack.

The results presented demonstrate that essentially complete, very clean combustion is feasible for relatively small woodburners if the design includes forced draft mixing, insulated reaction chambers, and a catalyst. "Smokeless" operation is obtained for the complete burn cycle, unless the kindling startup process is handled poorly. Once the burner is at operating temperature, the addition of new fuel does not contribute to "smoking" since the volatiles released from this fuel burn at high temperatures ($>700^{\circ}\text{C}$).

Publication

The following conference papers or articles have resulted to date from this research. Furthermore, the vortex mixing approach used in the primary chamber of the woodburner is under review for patentability.

Thornton, M. M., and Malte, P. C. (1981) "Combustion Rate of Model Wood Volatiles," in Proceedings of 1981 International Conference on Residential Solid Fuels, pp. 851-872, Oregon Graduate Center, Beaverton, OR.

Thornton, M. M., Malte, P. C., Kamber, P. D., and Hertzberg, J. R. (1981) "Combustion of Wood Volatiles," Paper 31-81 presented at 1981 Fall Meeting of the Western States Section of the Combustion Institute, Tempe, AZ, October (1981).

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APPENDIX

Review of Sampling and Analysis Procedures for the Effluent of Residential Wood Combustion

A. Sampling

A wide variety of analytical techniques are used to study the emissions of woodburners, and most of these techniques are based on sampling a portion of the gases and smoke from the stack (e.g., Hubble et al., 1981; DeAngelis et al., 1980; Cook and Allen, 1981; Muhlbaier, 1981; Rudling et al., 1981; Peters et al., 1981; and Butcher and Ellenbecker, 1981). Under these conditions, the "modified EPA method 5" shown in Figure A1, or a similar sampling system is appropriate. This system is designed to separate different classes of emissions from the sampled gases and smoke either for storage or for prompt analysis. The system consists of three main parts, described below in sequence.

The first part consists of a sample probe, pressure probe, particle glass filter, and the associated plumbing and heaters. The effluent is generally sampled at a temperature high enough to forstall the deposition of creosote in the sample probe. Heated filters and sometimes impactors collect the particulate fraction of the sample, i.e., the particulate fraction at the collection temperature. The probe flow rate is adjusted to maintain isokinetic sampling conditions. Dilution methods are used to help avoid reactions or condensation on the walls of the probe (Anon., 1980; and Kausch, 1978).

The second part of the sampling system consists of a series of traps and filters intended to remove condensible material from the sample. Traps may contain water, solvents, adsorbents such as XAD-2 resin, Tenax-GC, silica gel, activated charcoal, or more specialized reagents such as sodium bisulfate. Back-up filters cope with the problem of aerosol formation in the traps. Initial stages are usually maintained at the temperature of melting ice, while later stages are sometimes kept at dry ice temperature. The XAD-2 resin adsorber has been used by several investigators; for example, Cooke and Allen (1981) used it to trap PAH (polycyclic aromatic hydrocarbons). Likewise Tenax-GC can be used to trap organic materials. The silica gel (i.e., the last trap in Figure A1) catches remaining organics, and if activated, it also removes remaining water, which is necessary for the subsequent dry flow rate measurement. Rudling et al. (1981) used the sodium bisulfate reagent in order to trap aldehydes.

The third and final part includes a pump to move the sample, flow instruments to measure the amount of the sample, and a valving arrangement to route the sample stream to various on-line analysers. Gases analyzed in this way include O_2 (e.g., paramagnetic analyzer), CO (e.g., nondispersive infrared spectroscopy or "NDIR" analyzer), CO_2 (e.g., NDIR analyzer), total hydrocarbons (heated flame ionization detectors or "FID"), and NO_x (e.g., chemiluminescent analyzer). The gases also may be routed to a gas chromatograph.

This complex system is plagued by a number of problems, however. It is difficult to maintain isokinetic sampling during wide variations in combustion rate. Reverse-type Pitot tubes are used to manually monitor the flue flow

Figure A1. Sample Train for Wood Combustion Effluent

rate. Therefore, the sample flow rate can be manually adjusted in order to maintain isokinetic sampling. However, what is needed is automatic monitoring and sample flow rate adjustment. Another problem is filter plugging and deposition of creosote. And if glass fiber filters are kept hot (near the manufacturers recommended maximum temperature) questions arise concerning reactivity of the particle catch (Anon., 1980). It is likely that particles collected on such hot filters undergo considerable weight loss, upsetting both particle phase and gas phase measurements. In some experiments it appears that the particulate collection temperature fluctuates correspondingly with the temperature set in the flue, which can vary from 50 to 400 °C (Hubble et al., 1981). This obviously can have an important effect on the portion of the sample termed "condensed particulate" and that portion termed "condensable." In other experiments, the particulate collection device has been held at a reported temperature; e.g., 150-200°C (Rudling et al., 1981) and 120°C (Cooke and Allen, 1981). If only the total catch is reported and analyzed, then the temperature of the particulate collection region is not as important as when the investigator seeks to distinguish between "particulates" and "condensibles" as a function of burner operations.

The large size of the sample system, and its low flow rate, dictated by pressure drops across filters, make sampling very slow and thus unresponsive to events of short duration in the wood burner, particularly episodes of high emissions associated with start-up and fuel loading. The large number of components in the system makes collection of the materials for later analysis laborious. It also appears that unreasonably large amounts of sample are often collected, in opposition to the excellent sensitivity of GC/FID and GC/MS used for analysis. This indicates that some improvement should be possible here, though in order to analyze rapid stove transients, continuous methods such as nondispersive infrared spectroscopy (NDIR) for CO and total hydrocarbon (THC) analysis by heated flame ionization detectors (FID) will continue to be needed. And as clean burning systems are developed, with less particulate matter in the flue, it should be possible to monitor real time variations of condensibles and organic vapors in the flue using laser absorption and fluorescent methods being developed for other combustion systems. Also, attention needs to be directed to greater reliance on on-line gas chromatography for rapid measurement of the volatile organics.

Finally, it should also be noted that the sampling discussed here is for the flue gas. During the development of clean burning systems, it may also be necessary to sample the combustion region. However, this will present substantial questions on the recombination of flame and hydrocarbon radicals in the sample probe as the sample is quenched (Kramlich and Malte, 1978). There is no clear answer here, except for very low pressure sampling (1 torr) as used in on-line mass spectrometric analysis.

B. Analysis of Gases

A variety of different on-line gas analyzers is used. Molecular oxygen is analyzed by paramagnetic reluctance, CO and CO₂ by non-dispersive infrared absorption, total hydrocarbons by flame ionization or combustion to CO₂, and NO_x by chemiluminescence. Flame ionization on-line total hydrocarbon analyzers are often not calibrated for a representative mixture of gases (Haack et al., 1981). The difficulty here lies in the fact that FID response factors vary widely for the oxygenated constituents in wood smoke.

Some systems subject sample gases to on-line gas chromatographic analysis, particularly for separation of the hydrocarbon species present. Molecular hydrogen, O_2 , N_2 , CH_4 , CO and CO_2 can be determined by hot wire detection, though sensitivity is usually poor for H_2 , and CO_2 usually requires a dual column technique. Trace hydrocarbons are readily determined by flame ionization detection, but closely related species, especially in the range C_3 - C_6 , are often not separated by the porous polymer-packed columns in general use. Sophisticated micro-bore columns for this purpose are not commercially available. Nitrogen and sulfur containing species are detected by thermionic emission and flame photometric detectors, respectively. Some systems permit injection of gas samples at an increased pressure for increased response to species such as CO, which is sometimes near its detection limit.

C. Treatment of Condensed Samples

Condensed and filtered samples are treated in a variety of ways to prepare them for analysis. In general, the goal of these procedures is to separate the compounds of interest from the many possible interfering substances present in wood burner emissions. The large amount of water and the plethora of organic species found in these samples make some established separation methods unworkable, and modifications are required. Methods used with success include continuous liquid/liquid or solid/liquid extraction, ultrasonic extraction of filter samples (Eiceman et al., 1979), and selective separation into acidic, phenolic, and neutral fractions with HPLC separation of these fractions (Liao and Browner, 1978; and Browner, 1980). Also, methods are available to improve recoveries of volatile organic species such as benzene (Haack et al., 1981).

Some similarities exist with the treatment of other experiments. For example, the treatment of nearly clean condensed water from efficiently operating wood burners resembles the situation found in the analysis of waste water (Kuo et al., 1977). However, general methods or those developed for trace components in ambient air experiments may be less applicable to wood burning because of vastly different component levels, e.g., see Hoinig et al. (1981), Imhoff et al. (1981), Farwell et al. (1979), and Snook et al. (1979).

A standard workup procedure, which is recommended by the EPA (Osborne, 1981) for wood smoke, is illustrated in Figure A2. This workup procedure is consistent with the sample train shown in Figure A1. A main feature of the workup procedure in Figure A2 is organic extraction via methylene chloride (CH_2Cl_2). Other solvents and workup procedures are employed in order to separate the organics into various groups. For example, in Sweden, Rudling et al. (1981) have used a procedure which promotes the separation of polycyclic aromatic hydrocarbons (PAH) and phenols. To begin with, the condensate is collected in a buffered pH 7 aqueous solution in order to isolate organic acids as their salts. This condensate, as well as the probe and filter wash, are first extracted with CH_2Cl_2 in order to test for PAH, this material is evaporated and redissolved in cyclohexane, and then partitioned using DMF (dimethyl formamide) prior to GC-FID analysis for PAH.

In order to test for phenols, the dried extract is redissolved in isooctane/diethylether, with the ether extract mixed with 0.5M NaOH in order to take up the phenols into the aqueous phase where they are acetylated to form chromatographable esters. This workup procedure indicates what can be done if detailed information is sought. Another separation procedure is that used by

Figure A2. Sample Work-Up Procedure (Osborne, 1981).

Hubble et al. (1981), and other investigators, where following CH_2Cl_2 extraction, the sample is separated into aromatic, aliphatic, and polar components using silica gel column chromatography. And for the measurement of polar compounds by GC-FID, derivatization by trimethylchlorosilane is sometimes used (Shafizadeh and Lai, 1972).

D. Analysis of Condensed Samples

Stored and prepared samples are analyzed by a wide range of techniques. These include atomic absorption spectrometry and inductively coupled argon plasma emission spectrometry for elemental analysis, ion chromatography and ion selective electrode analysis for inorganic ions, and infrared absorption spectrometry for characterization of organic functional groups. The Ames test is used for mutagenic activity, colorimetric determination is used for aldehyde derivatives, and size exclusion or gel permeation chromatography is used to determine molecular weight range. Other methods include thermogravimetric analysis or other thermal techniques for characterizing particulate matter (Muhlbaier, 1981; Cadle and Groblicki, 1980), high performance liquid chromatography with UV or fluorescence detection, (mainly used for study of ambient samples), packed column or open tubular (capillary) column gas chromatography with flame ionization or mass spectral detection, and direct insertion probe mass spectrometry both at unit mass resolution and at high resolution. We concentrate our attention on GC/FID and GC/MS methods.

Gas chromatographic separation of wood burning emissions is carried out in a number of ways. Flash vaporization injection techniques are most commonly applied to the worked-up sample. Alternative methods such as direct injection using the solvent effect (Grob and Grob, 1978), direct on-column injection, and double column techniques should be investigated, however, for wood smoke analysis. Furthermore, accurate Kovats retention indices for comparison to the literature (Zweig and Sherma, 1972) are not obtained for components in wide boiling range mixtures separated by temperature programmed chromatography. In the literature, packed column separations are often carried out even though major components are unlikely to be resolved. Wall coated open tubular (capillary) columns offer much better separation for appropriately prepared samples.

E. Mass Spectrometry

Mass spectral identification of wood burning emissions is a valuable method which has not been fully explored in wood smoke analysis. It is usually carried out after a prior chromatographic separation. High resolution mass spectra permit direct assignment of ion elemental composition in most cases (Lee et al., 1977; Hase and Hites, 1976), and appearance potentials are useful in molecular beam studies of wood burning species (Milne and Soltys, 1981). However, typical published sources give little indication of optimal inlet and source conditions, or any discussion of mass discrimination effects on subsequent peak assignments. Sample chromatographic peaks are usually assigned based on the similarity of an abbreviated form of the sample spectrum to reference spectrum from a computerized library of mass spectra (Hertz et al., 1971). Although generally reliable in many cases, such techniques cause difficulties when applied to wood burning emission samples. Appropriate reference spectra and authentic material are often not available and mass

spectrometers of different geometry are often used to acquire sample and reference spectra (Heller and Milne, 1978, and Cornu and Massot, 1966).

Chromatographic peak deconvolution routines are used for cases where peaks are not cleanly resolved. These routines are not effective in every case, however (Rosenthal, 1982). Mass spectral library search routines perform poorly in cases where a number of different components all present nearly the same ions, particularly in the case of isomeric compounds. Some search routines are not tested for performance on spectra from realistic sample matrices. Some mass spectral libraries lack entries for likely wood burning emissions. For these and other reasons, some investigators rely upon manual assignment of mass spectra both by use of tabulated spectra and direct interpretation (Browner, 1980; McLafferty, 1966). Thus, although mass spectra offer a high potential for detailed wood smoke analysis, much work remains to be done.

F. Recommendations on Sampling and Analysis

While a great deal of effort has gone into analysis of wood burning emissions, much improvement remains to be made. Improvement would be particularly helpful along the following lines:

- . Reduction in the size of the sample train and the time of sampling, thereby affording observation of transient burning.
- . Determination of whether it is possible to rigorously separate particle phase and gas phase samples.
- . Adoption of techniques leading to higher recoveries of volatile organic compounds. This is especially important since most investigators have overlooked these compounds, and since these compounds can have emission factors of the same order of magnitude as particulate/condensable emission factors (Rudling et al., 1981).
- . Adaptation of existing techniques to enhance chromatographic performance; i.e., separations of "train catch," and applications of on-line analysis of volatile organics.
- . Use of existing methods to gain more reliable mass spectral assignments.
- . Development of methods to characterize non-gas chromatographable emissions. This is especially important since approximately one half of PAH are not chromatographable.

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