

# Impacts of Alternative Fuels on Air Quality

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## Preface

The overall objective of this project is to determine the impact of alternative fuels on air quality, particularly ozone formation. This objective will be met through three steps: 1) qualitative identification of alternative fuel combustion products; 2) quantitative measurement of specific emission levels of these products; and 3) determination of the fate of the combustion products in the atmosphere, particularly in terms of depletion or conversion by hydroxyl radical attack. The alternative fuels of interest are methanol, ethanol, liquefied petroleum gas, and natural gas.

The role of the University of Dayton Research Institute (UDRI) in this project is two-fold. First, fused silica flow reactor instrumentation is being used to obtain both qualitative identification and quantitative emissions data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol, ethanol, liquefied petroleum gas, and natural gas. Secondly, a laser photolysis/laser-induced fluorescence apparatus will be used to determine the rates of reaction and reaction products of selected degradation products under atmospheric conditions.

This draft report contains the results of the first year of study. We have obtained qualitative data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol and ethanol. The most important findings are summarized below.

The thermal degradation of ethanol has produced a substantially larger number of intermediate organic by-products than the similar thermal degradation of methanol. Ethanol degradation by-products, which were firmly identified using GC-MS analysis, were acetaldehyde, formaldehyde, acetone, acetic acid and several light hydrocarbons including methane, ethane, ethylene, acetylene, and propylene. Methanol degradation by-products firmly identified using GC-MS analysis were formaldehyde, 1,2,3-trioxane, and acetone.

A second important finding from this initial work was the lack of stability of the organic intermediate by-products. The only by-products observed at temperatures where complete destruction of the parent fuel was observed were carbon monoxide, carbon dioxide and water vapor. This highly significant result suggests that these two alcohol fuels do not have a propensity to form higher molecular weight by-products, even under oxygen-free pyrolysis conditions. The propensity to form higher molecular weight by-products is an important characteristic of hydrocarbon fuels.

A qualitative comparison of the UDRI flow reactor data with previous engine tests yielded some positive results. For methanol, organic by-products observed in both types of tests were formaldehyde and acetone. The UDRI study did not detect measureable quantities of methane or other unburned hydrocarbons, as observed in the engine tests. For ethanol, we could locate only very limited data. Organic by-products observed in both tests included unburned hydrocarbons and aldehydes. The one available engine test did not report speciated data for direct comparison with the UDRI results.

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# Introduction

The National Renewable Energy Laboratory (NREL) is the field manager for the U.S. Department of Energy (DOE) Alternative Fuels Utilization Program (AFUP). The goal of the AFUP is to develop and advance technology that allows an effective, optimum use of nonpetroleum-based transportation fuels, while complying with modern constraints, such as vehicle emissions. For alternative fuels to be viable candidates to replace petroleum-based counterparts it must be demonstrated that their impact on air quality will be no worse than that of existing fuels and preferably show characteristics that will improve air quality. To make this determination, an extensive program is necessary to identify the atmospheric reactivity of the exhaust species from alternative fuels. For comparison purposes, similar analyses are being performed on advanced petroleum-based fuels.

Because of the nation's continuing concern about air pollution, Congress enacted the Clean Air Act Amendments of 1990. The provisions will force broad changes in fuels and vehicles. For example, reformulated gasolines and alternative fuels are receiving wide attraction as industry struggles to comply with the amendments. At the same time, there are many basic scientific questions about the benefits of switching to alternative fuels. The scientific community does not adequately understand the durability and emission performance of candidate alternative fuels. Additional research is needed, including the ultimate impact on air quality, to identify acceptable alternatives for conventional transportation fuels.

The overall objective of this project is to determine the impact of alternative fuels on air quality, particularly ozone formation. The objective will be met through three steps: 1) qualitatively identify alternative fuel combustion products, 2) quantitatively measure specific emission levels of these products, and 3) determine the fate of the combustion products in the atmosphere. The alternative fuels of interest are methanol, ethanol, liquefied petroleum gas, and natural gas.

The role of the University of Dayton Research Institute (UDRI) in this project is two-fold. First, fused silica flow reactor instrumentation is being used to obtain both qualitative identification and quantitative data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol, ethanol, liquefied petroleum gas, and natural gas. Secondly, a laser photolysis/laser-induced fluorescence apparatus will be used to determine the rates of reaction and reaction products of selected degradation products under atmospheric conditions.

This final report contains the results of the first year of study. We have obtained qualitative data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of methanol and ethanol. The following sections discuss in chronological order the experimental approach, results, a discussion of the results in relation to previous studies, and conclusions of the first year of study. At the time of preparation of this draft report (late February, 1994), we have initiated the quantitative studies of methanol and ethanol degradation. The results of these experiments will be presented and discussed in the annual report for the second year of the study. In the coming year, we plan to obtain both qualitative and quantitative data on the thermal degradation products from the fuel-lean (oxidative), stoichiometric, and fuel-rich (pyrolytic) decomposition of liquefied petroleum gas and natural gas. In addition, we will also initiate the laser photolysis/laser-induced fluorescence studies of selected degradation products from these fuels under atmospheric conditions.



## Experimental Approach

The experimental approach is divided into two sections. The first section describes the acquisition of qualitative thermal decomposition data using a 4.0-mm i.d. flow reactor with gas chromatographic/mass spectrometric (GC/MS) detection. These experiments were conducted to provide qualitative identification of the thermal decomposition products produced from the fuel-lean and fuel-rich degradation of methanol and ethanol. Subsequent experiments have been initiated to elucidate the quantitative thermal decomposition behavior of these two alternative fuels. Experiments involving more finely tuned GC and GC/MS analysis will be described in the second section of the experimental approach.

### Qualitative Experiments

Qualitative experiments were performed using a 4.0-mm quartz flow reactor coupled to a GC/MS analytical system. The design of this system has been discussed in detail previously [1]. We focus instead on a brief description of the operational and analytical features pertinent to these experiments.

Methanol and ethanol samples were purchased from Aldrich and used as received. GC/MS analysis of the methanol sample indicated that acetone was a contaminant at concentrations of ~1%. Significant amounts of methanol (~3 mole%) and isopropyl alcohol (~5 mole%) were observed in the ethanol sample. Experiments were conducted for four different fuel/oxygen equivalence ratios ( $\Phi$ ) ranging from fuel-lean to fuel-rich (fuel/oxygen equivalence ratio is defined as the actual fuel/oxygen molar ratio divided by the stoichiometric fuel/oxygen molar ratio). The fuel/oxygen equivalence ratio was controlled by *a priori* mixing of liquid fuel aliquots with oxygen (diluted in helium) in previously cleaned and dried glass sample vessels of known volume. Initial reactor concentrations were limited by the fuel vapor pressure. Table 1 summarizes the initial fuel/oxygen equivalence ratio and reactor concentrations examined in this work. The reactor mean, gas-phase residence time ( $t_r = 2.0$  s) and pressure ( $P = 1$  atm) were constant for all experiments. Exposure temperature was varied from 300°C to 900°C.

Table 1. Initial Fuel/Oxygen Equivalence Ratio and Reactor Concentrations

Fuel	$\Phi$	Initial Concentration, ppm
Methanol	0.7	1700
	1.0	1500
	1.5	2300
	$\infty$	1600
Ethanol	0.7	550
	1.0	770
	1.5	1200
	$\infty$	900

Following gas-phase sample injection, the gaseous reactants are swept by helium carrier from a heated inlet tube (250°C) into the quartz cylindrical flow reactor, where controlled high-temperature exposure occurs. The effluent products resulting from thermal exposure are then swept by gaseous carrier through another heated transfer path (275°C) and eventually into a liquid nitrogen trap held at -120°C. Once the collection process is complete, this trap is rapidly heated to 300°C, releasing the collected material to an in-line Hewlett Packard 5890 gas chromatograph. Compound separation is then obtained by programmed temperature gas chromatographic analysis. Detection and identification of effluent products was obtained with a Hewlett Packard 5970B mass selective detector. Data acquisition and analysis are performed with a Hewlett Packard 59970 ChemStation and the accompanying system software.

The effluent resulting from a single reactor exposure (unreacted parent material and reaction products) was directed to a 0.20-mm i.d., 20-m, DB-1 capillary column (J & W Scientific, Inc., film thickness = 0.4 mm). Individual reaction products were separated by programming the GC oven from -80°C to 260°C @ 15°C/min. Following GC separation, product detection was accomplished using the mass spectrometer. The mass spectrometer was operated in full-scan mode with an electron energy of 70 eV and an electron multiplier setting of 2600 units.

For this initial study, analytical standards were not used to confirm GC/MS identifications. The quality of the library matches and our overall experience in mass spectral interpretation and reaction kinetic theory have been used to classify the reaction by-products as "highly probable" or "tentative." This is discussed in the Results section of this report.

## **Quantitative Experiments**

The quantitative experiments will be conducted using a 11.3-mm quartz flow reactor (69 cm<sup>3</sup> volume) housed in a high-temperature three-zone Lindberg furnace (Model 5457). The furnace is designed for continuous operation at temperatures up to 1200°C, and the three zones are heated independently allowing precise control of the axial reactor temperature profile. This system will permit experiments to be conducted up to 1200°C, ~300°C higher than the qualitative experiments.

Following metered, gas-phase, sample injection, the thermal degradation by-products from the high-temperature flow reactor will be swept through a pyrex ice water trap held at ~0°C and then to the head of a GC column. The ice water trap has been designed and tested to isolate water vapor from the water-soluble partial oxidation products, e.g. aldehydes, acids and ketones. This will allow baseline GC separation and, ultimately, quantification of these important intermediates, which was not achieved in the qualitative experiments.

For each alternative fuel, two different sets of experiments will be conducted. In one set of experiments designed to isolate and quantify the lighter partial oxidation products, the analytical technique will consist of a poraPLOT Q fused silica capillary column coupled to a modulated Thermal Conductivity Detector. In a second set of experiments designed to isolate and quantify the heavier hydrocarbon pyrolysis products, the analytical technique will consist of a DB-5 fused silica capillary column coupled to a HP Mass Selective Detector. In these experiments, the downstream reactor transfer line will be heated to ~275°C to facilitate quantitative transport of these heavier by-products.

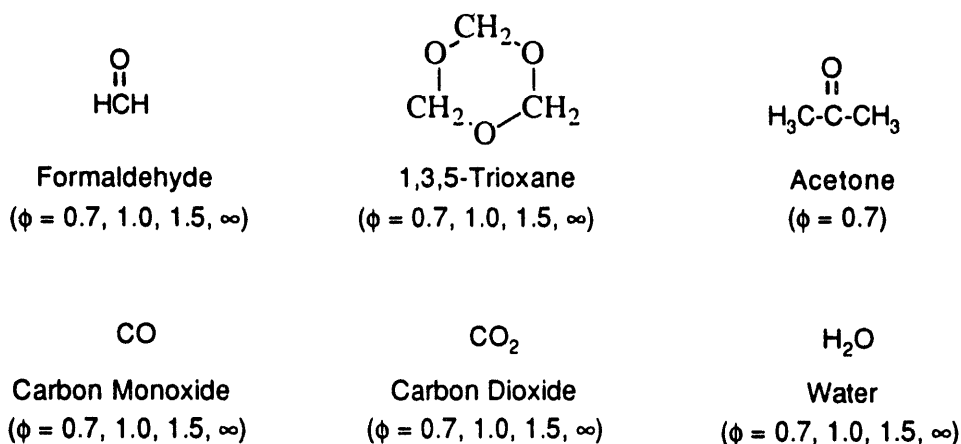
Analytical standards have been purchased and will be used to provide positive identification of thermal reaction by-products. By-product quantification will be obtained from analyte GC-TCD and GC-MS calibration curves.

## Results

We first present the methanol degradation results. This is followed by the ethanol degradation results.

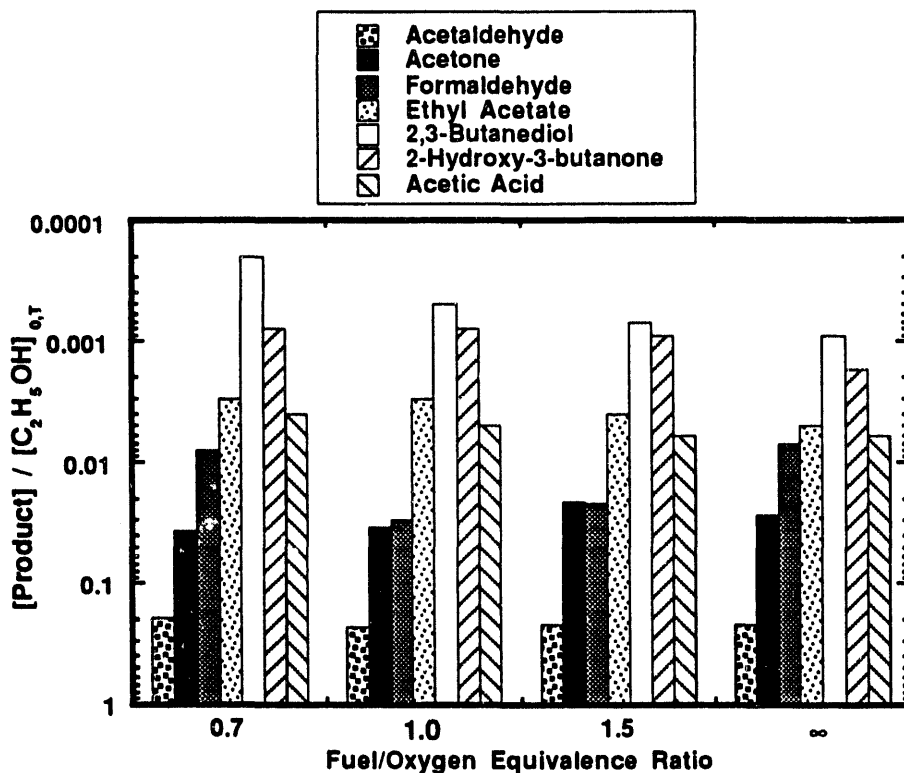
### Methanol Studies

In preliminary experiments, methanol degradation and intermediate by-product formation were observed between temperatures of 500°C and 850°C. Figure 1 presents the observed intermediate by-products and the higher temperature stable combustion by-products. Formaldehyde and 1,3,5-trioxane were observed for all four equivalence ratios investigated. Acetone was only observed under fuel-lean conditions. The mass spectra of formaldehyde, acetone, and 1,2,3-trioxane were in excellent agreement with library spectra and are considered highly probable by-products. Although acetone was observed as a contaminant in the stock methanol sample, comparison of high-temperature versus room temperature response ( $5 \times 10^6$  counts) indicates that it formed from the thermal degradation of methanol as well. The 1,3,5-trioxane mass spectra did not give as good a match with library spectra due to the low signals observed. However, we are quite confident that this identification is accurate based on studies reported in the literature where 1,3,5-trioxane has been used as the precursor to gas-phase studies of formaldehyde decomposition. We must also mention that there is a slight possibility that 1,3,5-trioxane is an analytical artifact and is the result of formaldehyde polymerization in the downstream reactor transfer lines. The authenticity of this by-product identification will be addressed in the quantitative studies of methanol degradation currently under way. The higher temperature combustion by-products observed were carbon monoxide, carbon dioxide, and water vapor. These inorganic by-products were observed under all four equivalence ratios investigated.



**Figure 1. Methanol oxidation and pyrolysis products.**

The effect of equivalence ratio on the maximum relative response of intermediate by-products have been determined by normalizing by-product response to the initial, non-degradative methanol response (at that temperature). The results are shown in Figure 2. Acetone was the highest-yield intermediate by-product with a normalized response of 0.28. The normalized response of formaldehyde was independent of equivalence ratio, with an average value of  $0.12 \pm 0.02$ . 1,3,5-trioxane normalized response was very small ( $\leq 0.01$ ) and decreased slightly with increasing equivalence ratio. All intermediate by-products exhibited maximum concentrations at relatively low temperatures (600°C to 700°C).



**Figure 2. Normalized, semi-quantitative response of intermediate methanol thermal degradation by-products as a function of equivalence ratio.**

Semi-quantitative thermal degradation profiles as a function of equivalence ratio are presented in Figures 3, 4, 5, and 6. For fuel-lean, stoichiometric, and fuel-rich conditions, the thermal degradation of methanol was insensitive to equivalence ratio, initiating at 500°C, and with nearly complete degradation observed at 750°C. Under oxygen-free pyrolysis conditions, methanol was observed to be somewhat more stable, as complete degradation required temperatures of 850°C. For all equivalence ratios, the organic intermediates were observed to be thermally fragile, degrading at temperatures at or below that required for the complete degradation of methanol. An important result of the qualitative methanol decomposition studies was the lack of formation of stable organic, intermediate reaction by-products. Of particular note was the lack of stable, unburned hydrocarbons. Carbon monoxide, carbon dioxide, and water vapor were the only reaction by-products observed to be more stable than the parent fuel.

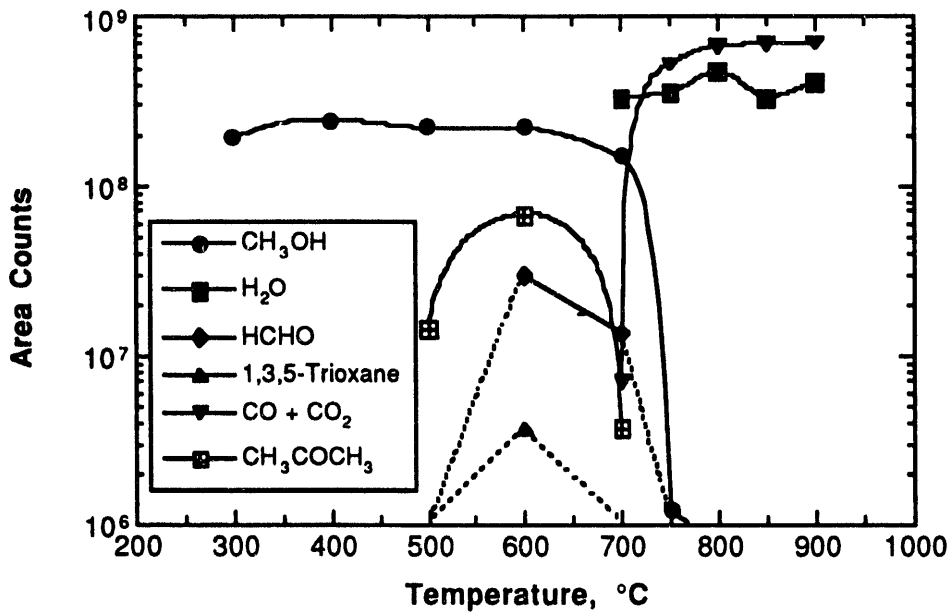


Figure 3. Semi-quantitative thermal decomposition profile for methanol.  $\Phi = 0.7$ ,  $t_r = 2.0$  s.  $[\text{CH}_3\text{OH}]_0 = 1710$  ppm. Dotted lines represent trends in data to estimated detection limits.

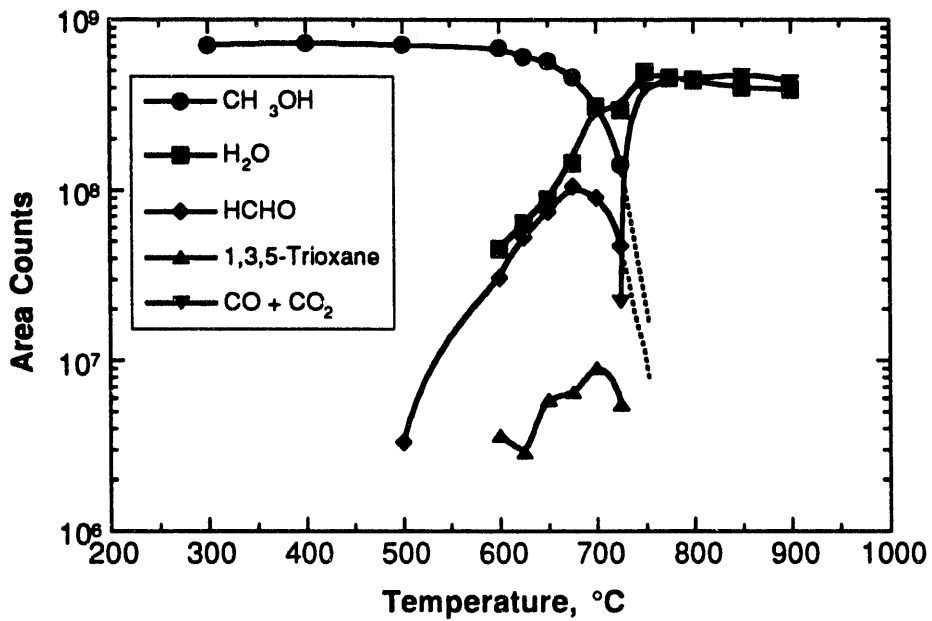


Figure 4. Semi-quantitative thermal decomposition profile for methanol.  $\Phi = 1.0$ ,  $t_r = 2.0$  s.  $[\text{CH}_3\text{OH}]_0 = 1500$  ppm. Dotted lines represent trends in data to estimated detection limits.

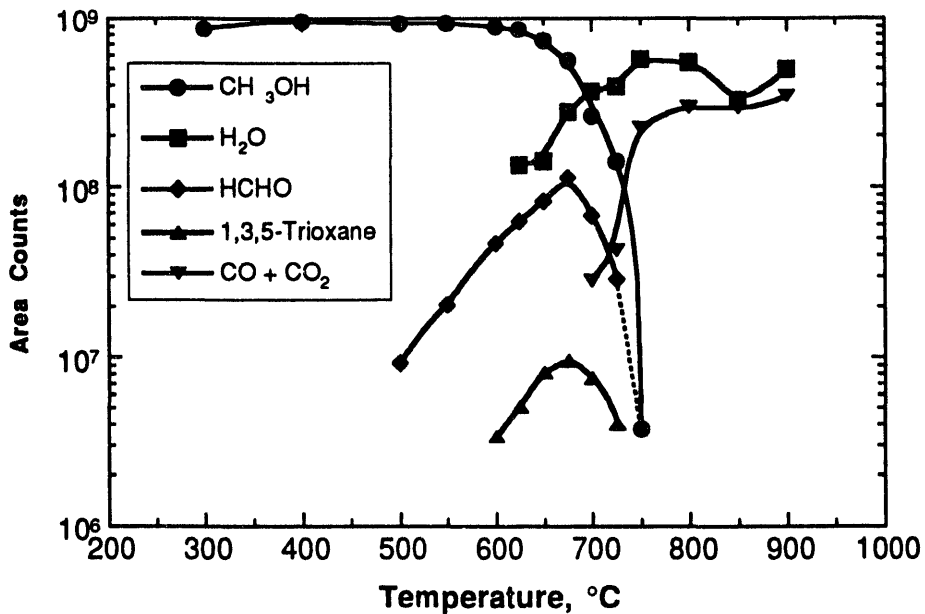


Figure 5. Semi-quantitative thermal decomposition profile for methanol.  $\Phi = 1.5$ ,  $\tau_r = 2.0$  s.  $[\text{CH}_3\text{OH}]_0 = 2315$  ppm. Dotted lines represent trends in data to estimated detection limits.

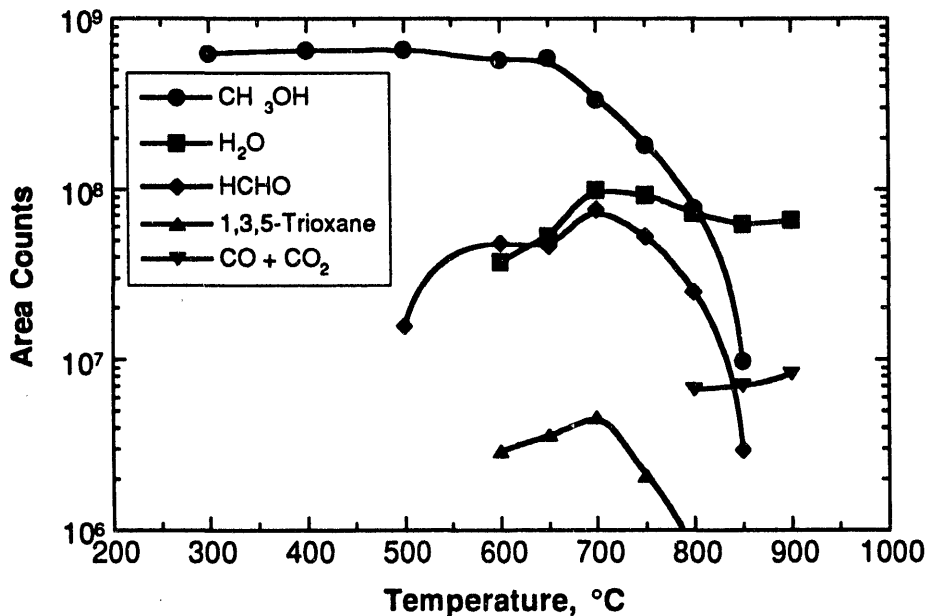


Figure 6. Semi-quantitative thermal decomposition profile for methanol.  $\Phi = \infty$ ,  $\tau_r = 2.0$  s.  $[\text{CH}_3\text{OH}]_0 = 1580$  ppm.

## Ethanol Studies

In preliminary experiments, ethanol degradation and intermediate by-product formation were observed between temperatures of 500°C and 825°C. Figure 7 presents the observed intermediate by-products and the higher temperature stable combustion by-products. Seven partially oxidized organic by-products were detected. All of these intermediate by-products were observed for all four equivalence ratios investigated. These by-products were (in decreasing relative response) acetaldehyde, acetone, formaldehyde, acetic acid, ethyl acetate, 2,3-butanediol and 3-hydroxy-2-butanone. An additional trace product could not be identified. The mass spectra of acetaldehyde, formaldehyde, acetone, and acetic acid were in excellent agreement with library spectra and are considered highly probable by-products. Ethyl acetate, 2,3-butanediol, and 3-hydroxy-2-butanone are considered tentative by-products due to a lower quality match of the experimental mass spectra with library spectra. The lower quality with library spectra is due to several factors, including the low levels of detection of these compounds. Several unburned hydrocarbons, methane, ethene, acetylene, and propene, were also observed under different experimental conditions. The mass spectra of these conventional by-products were in excellent agreement with library spectra. The higher temperature combustion by-products observed were carbon monoxide, carbon dioxide, and water vapor. These inorganic by-products were observed under all four equivalence ratios investigated.

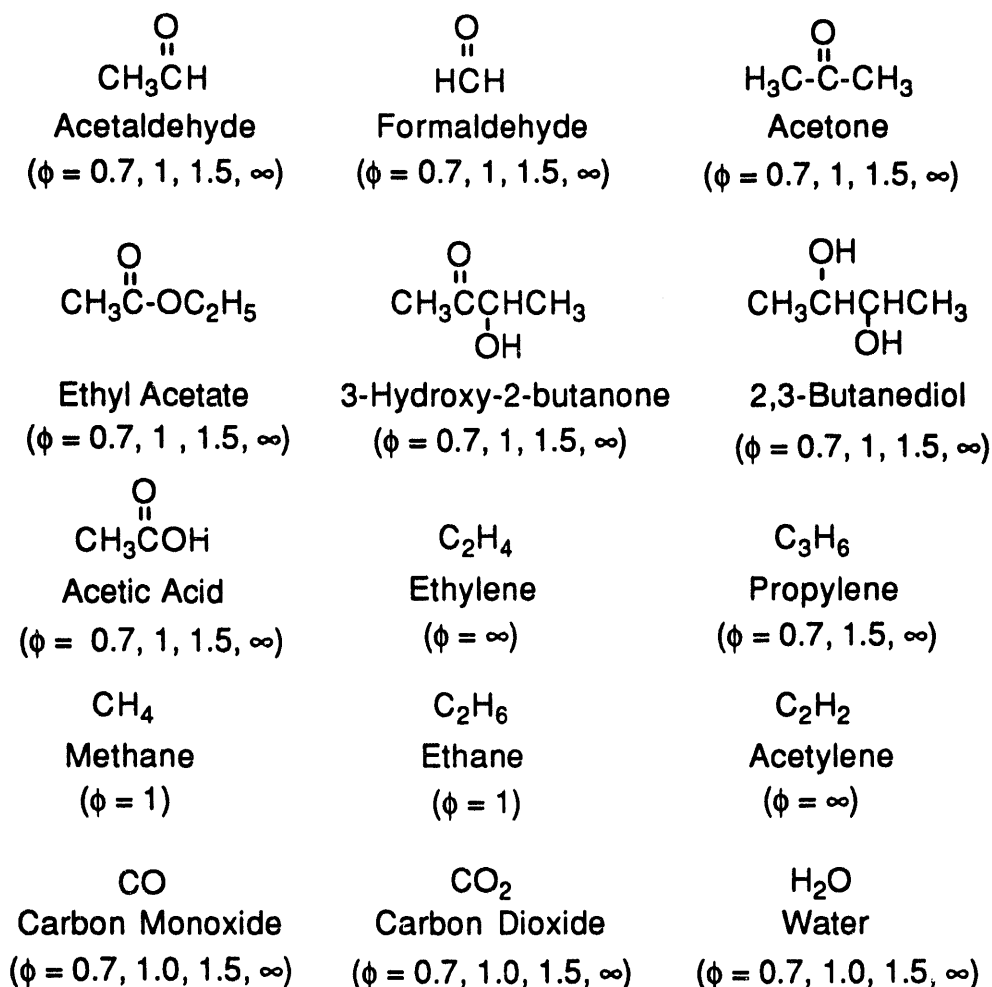
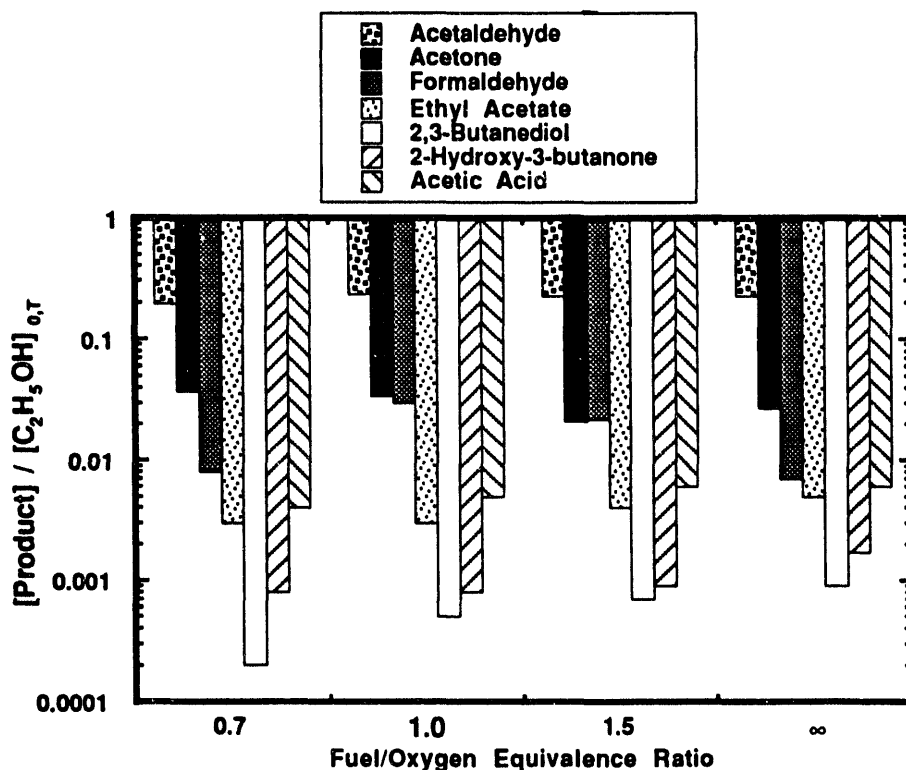


Figure 7. Ethanol oxidation and pyrolysis products.

The effect of equivalence ratio on the maximum relative response of intermediate by-products has been determined by normalizing by-product response to the initial, non-degradative ethanol response (at that temperature). The results are shown in Figure 8. Acetaldehyde was the highest-yield intermediate by-product with a relative response of  $0.21 \pm 0.02$ , independent of equivalence ratio. The relative response of formaldehyde varied significantly with equivalence ratio with a maximum response of 0.03 observed under stoichiometric conditions. The relative response of acetone, ethyl acetate, and acetic acid were generally independent of equivalence ratio. The very low responses of 2,3-butanediol and 3-hydroxy-2-butanone increased by a factor of 4 and a factor of 2, respectively, with increasing equivalence ratio. The relative response of the unburned hydrocarbons varied widely with changing equivalence ratio to the extent that some compounds were not detected for different conditions. With the exception of propylene, the relative response of these compounds was very low ( $<0.01$ ). All intermediate by-products exhibited maximum concentrations at relatively low temperature ( $650^{\circ}\text{C}$  to  $775^{\circ}\text{C}$ ).



**Figure 8. Normalized, semi-quantitative response of Intermediate ethanol thermal degradation by-products as a function of equivalence ratio.**

Semi-quantitative thermal degradation profiles as a function of equivalence ratio are presented in Figures 9 through 16. For fuel-lean, stoichiometric, and fuel-rich conditions, the thermal degradation of ethanol was largely insensitive to equivalence ratio, initiating at  $\sim 500^{\circ}\text{C}$  and with nearly complete degradation observed at  $775^{\circ}\text{C}$ . Under oxygen-free pyrolysis conditions, ethanol was observed to be somewhat more stable, as complete degradation required temperatures of  $825^{\circ}\text{C}$ . A much larger number of partially oxidized and unburned hydrocarbon by-products was observed for ethanol than for methanol thermal degradation. However, for all equivalence ratios, all of the organic intermediates were observed to be thermally fragile, degrading at temperatures at or below that required for the complete degradation of ethanol. An important result of the qualitative ethanol decomposition studies, as observed for methanol, was the lack of formation of stable, organic, intermediate reaction by-products at high temperature. Carbon monoxide, carbon dioxide, and water vapor were the only reaction by-products observed to be more stable than the parent fuel.



There are two additional observations worth noting in the initial ethanol thermal degradation experiments. First, the formation/destruction profiles of the intermediate by-products clearly indicate that acetaldehyde is the initial, primary organic decomposition by-product under all four equivalence ratios studied. Formaldehyde, acetone, and the much lower responding acetic acid, ethyl acetate, 2,3-butanediol and 3-hydroxy-2-butanone are secondary by-products. These secondary by-products appear to be formed to a significant extent from the degradation of acetaldehyde and to a lesser extent from the degradation of ethanol. A second point of interest is the formation profiles of the stable by-products carbon monoxide, carbon dioxide, and water vapor. An inflection is evident in these profiles for three of the four conditions tested, excluding the oxygen-free pyrolysis experiments. These inflections, which occur at temperatures between 700°C and 800°C and appear to shift to lower temperatures with increasing initial oxygen concentration, suggest that the degradation of ethanol involves two zones of distinctly different chemistry. In the first zone, ethanol is converted primarily to acetaldehyde and relatively low yields of carbon monoxide, carbon dioxide, and water vapor (and secondary by-products). In the second zone, acetaldehyde is rapidly converted (over a relatively short temperature window of ~50°C) to carbon monoxide, carbon dioxide, and water vapor. This two-zone behavior was not clearly observed in the methanol degradation experiments.

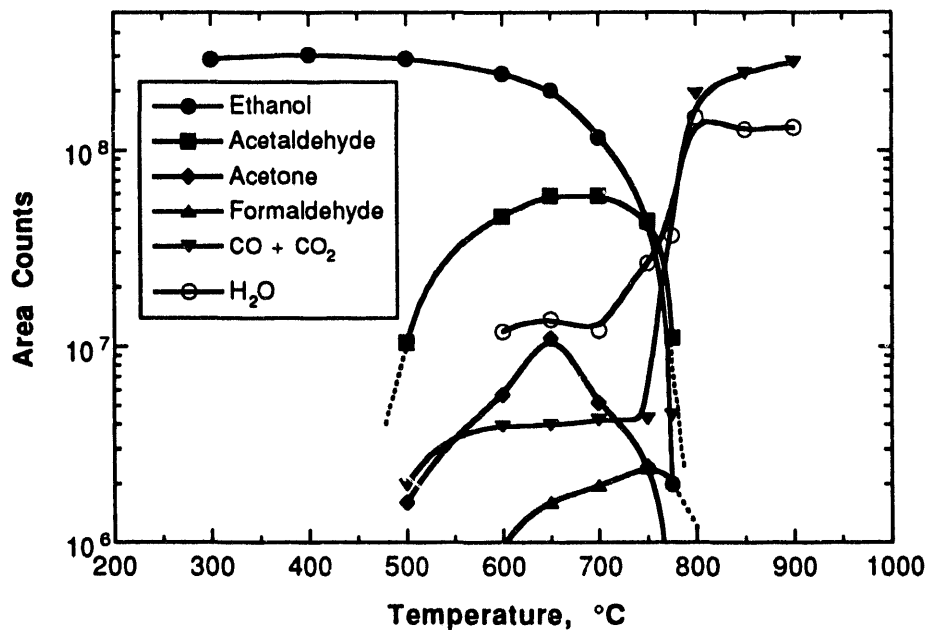


Figure 9. Semi-quantitative thermal decomposition profile (major products) for ethanol.  $\Phi = 0.7$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 540$  ppm.

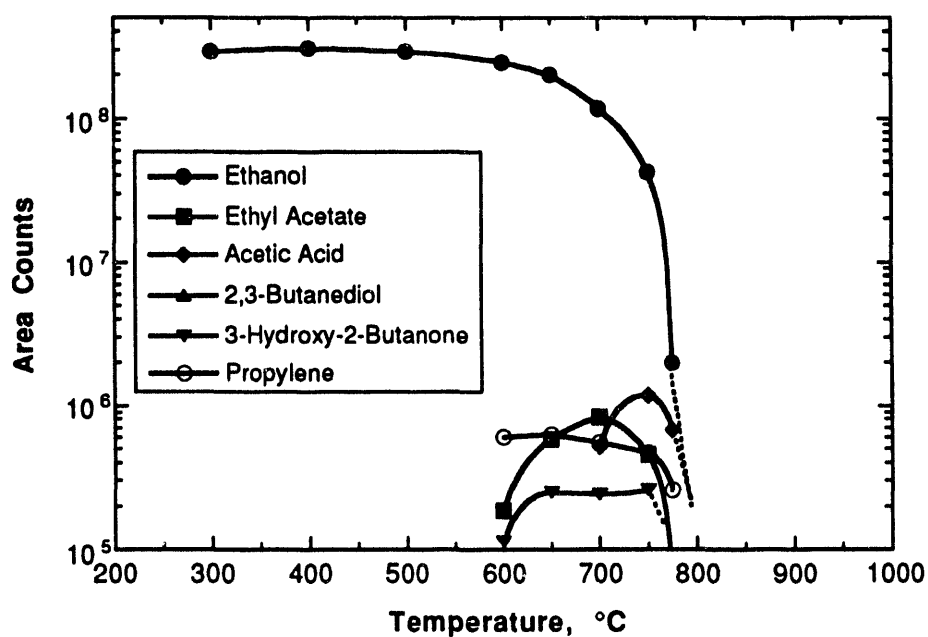


Figure 10. Semi-quantitative thermal decomposition profile (minor products) for ethanol.  $\Phi = 0.7$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 540$  ppm.

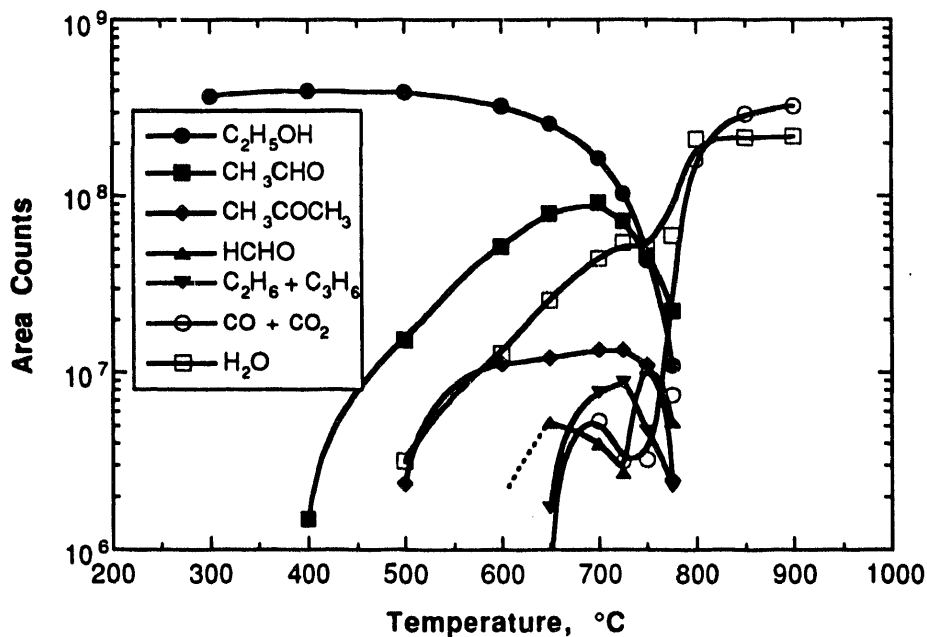


Figure 11. Semi-quantitative thermal decomposition profile (major products) for ethanol.  $\Phi = 1.0$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 770$  ppm.

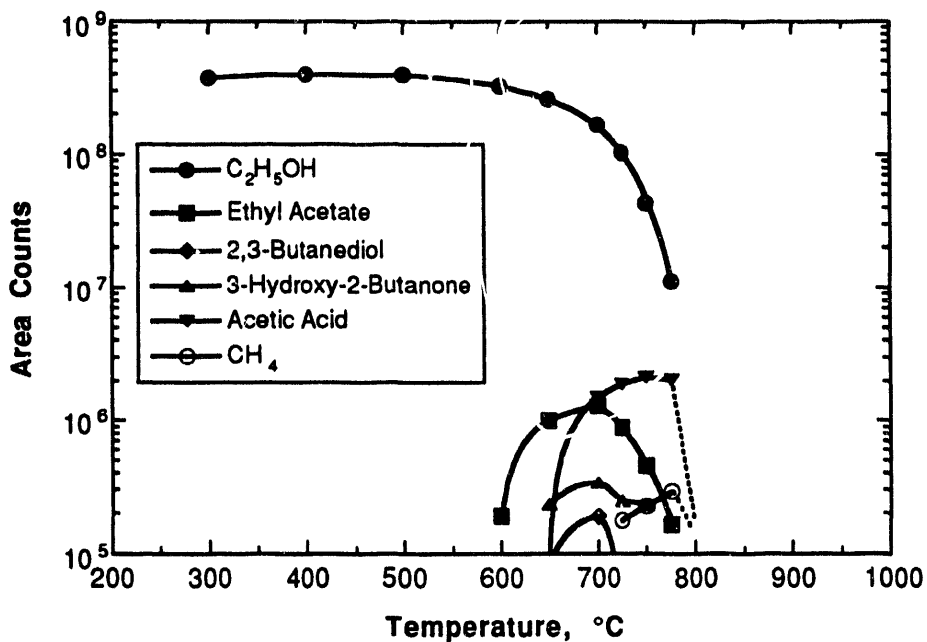


Figure 12. Semi-quantitative thermal decomposition profile (minor products) for ethanol.  $\Phi = 1.0$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 770$  ppm.

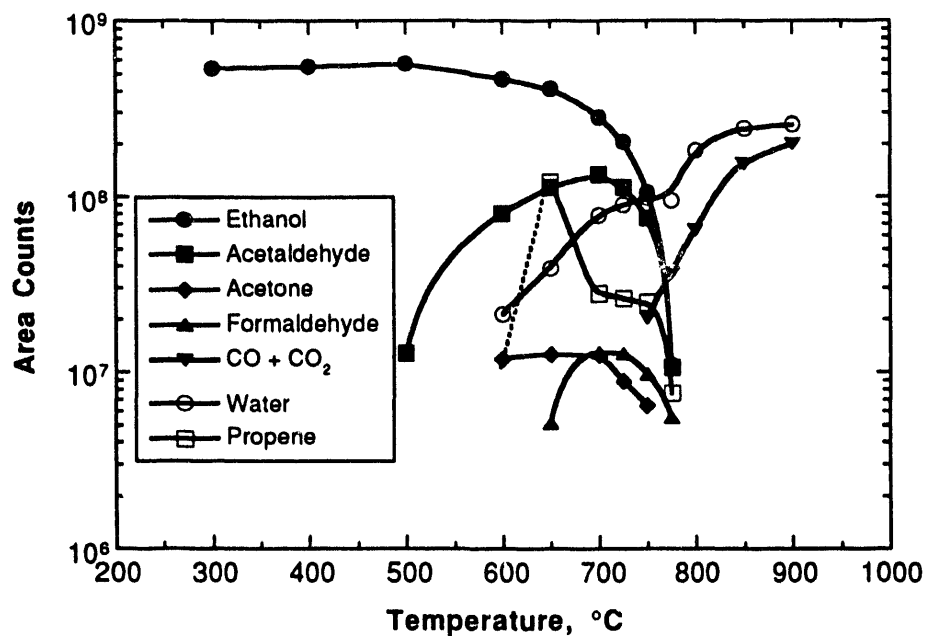


Figure 13. Semi-quantitative thermal decomposition profile (major products) for ethanol.  $\Phi = 1.5$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 1160$  ppm.

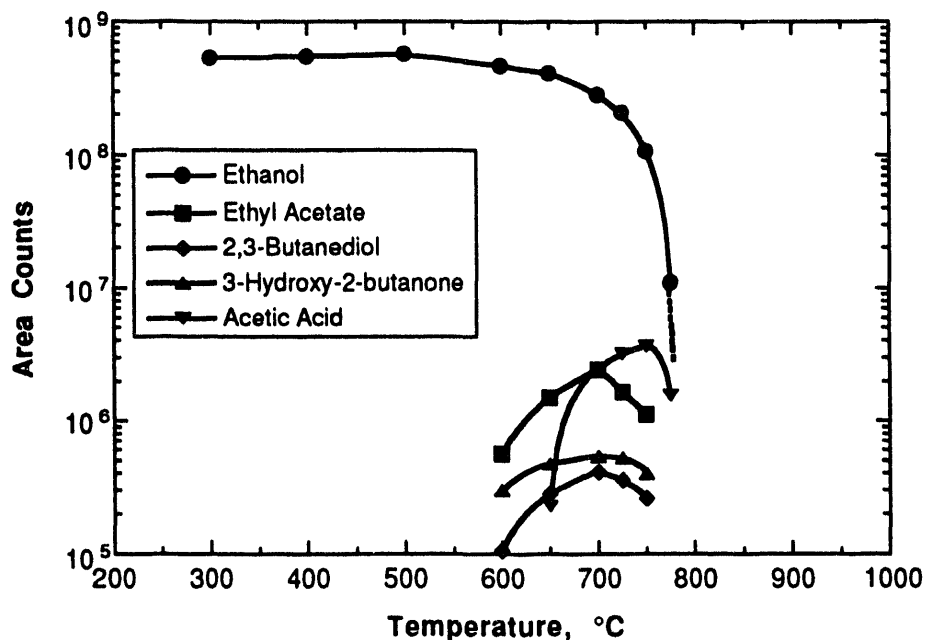


Figure 14. Semi-quantitative thermal decomposition profile (minor products) for ethanol.  $\Phi = 1.5$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 1160$  ppm.

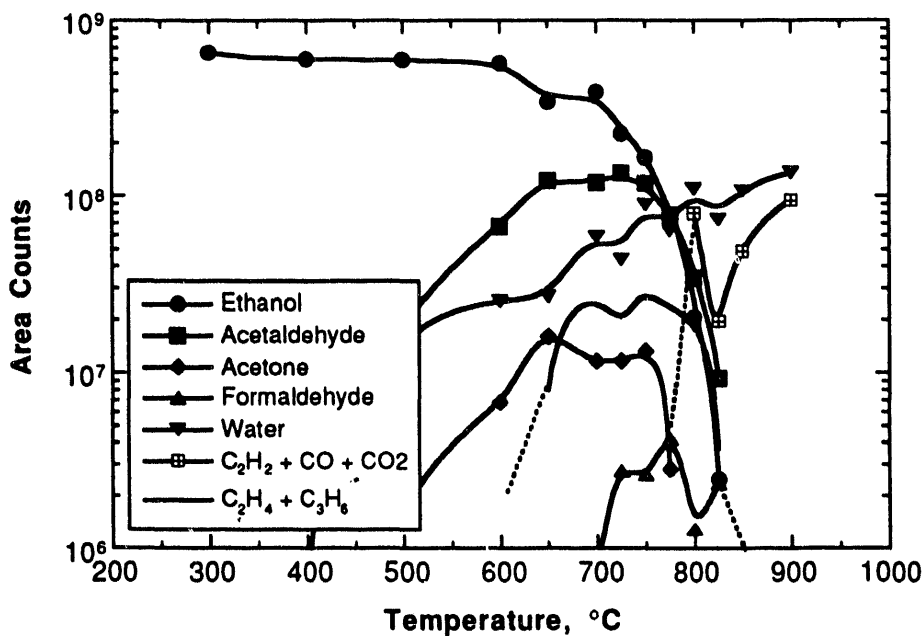


Figure 15. Semi-quantitative thermal decomposition profile (major products) for ethanol.  $\Phi = \infty$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 900$  ppm.

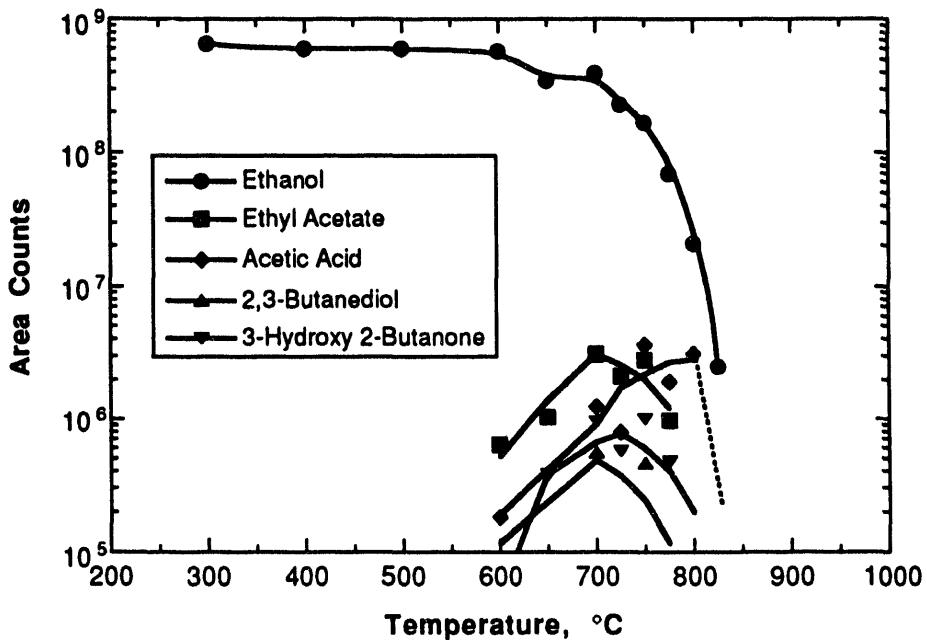


Figure 16. Semi-quantitative thermal decomposition profile (minor products) for ethanol.  $\Phi = \infty$ ,  $t_r = 2.0$  s.  $[C_2H_5OH]_0 = 900$  ppm.

## Discussion

In this section, we present a discussion of observed products from our flow reactor experiments with the limited available data from engine tests of these alternative fuels.

There have been a considerable number of engine studies performed to determine emission levels from the combustion of alternative fuels. We have attempted to conduct a detailed literature search to determine the extent of this data. The results are tabulated in Table 2. A review of the seven reported studies indicates that the analytical capabilities were limited. A very limited number of specific emissions were reported, ranging from CO and CO<sub>2</sub> [2,3], unburned methanol [3,4,8], formaldehyde [3,4,8], nitric oxide [2,5], methyl nitrite [6], unburned hydrocarbons [7], and specific unburned hydrocarbons (alkanes, alkenes, acetylene). Unfortunately, experimental conditions were generally not reported. The reported data for methyl nitrite is now believed to be an analytical artifact. The available data for ethanol tests were very sparse. We located only one study [8] where emissions from the combustion of an ethanol blend was compared to gasoline. In this study, only unburned hydrocarbon and CO emissions were reported.

To provide a straightforward, qualitative comparison of the results of this study with previous engine tests, we have tabulated the reported combustion by-products for the two alcohol fuels. The results are shown in Table 3.

For methanol, the only organic product in common with both sets of data was formaldehyde. Of course, both CO and CO<sub>2</sub> were observed at stable combustion by-products in both sets of data. The previous engine tests also reported significant levels of unburned hydrocarbons and nitric oxide. We did not observe even trace levels of unburned hydrocarbons from the thermal degradation of methanol. Nitric oxide was not measured in our studies as there is no source of nitrogen in the fuel or oxidizer.

We could not locate reports of emission levels from engine studies of pure ethanol. In contrast to methanol, our studies indicated that significant levels of unburned hydrocarbons were produced, particularly under stoichiometric and fuel-rich conditions. This is somewhat similar to the one previous engine test of a 20% ethanol-gasoline blend where unburned hydrocarbon emissions were reported [8]. In our tests, a much larger number of partially oxygenated organic combustion by-products were observed from the thermal degradation of ethanol as compared to methanol. The one previous engine test also reported emissions of aldehydes, although no speciation data were provided [8]. The fact that formaldehyde was observed in both flow reactor and engine tests from methanol leads one to believe that partially oxygenated organic combustion by-products may also be observed in engine tests of ethanol combustion.

As this report was being prepared, we have received a series of papers from Southwest Research Institute describing emission measurements from engine tests with methanol-fueled vehicles [9-11]. These studies are generally consistent with those in Table 2 in that reported emissions include unburned hydrocarbons, CO, NO<sub>x</sub>, and total aldehydes. In one study of a GMC bus burning methanol fuel [11], methane was reported as the predominant hydrocarbon emission. In this same study, formaldehyde accounted for 90% to 97% of the total aldehyde emissions. Acetaldehyde was also observed with lesser levels of acetone, benzaldehyde, isobutyraldehyde, and methyl ethyl ketone as a group.

The UDRI study appears to correlate quite well with the methanol engine tests, in particular the study of Ullman et al. [11], where formaldehyde and acetone emissions were reported. The major inconsistency in this comparison is the lack of detectable unburned hydrocarbons in the UDRI experiments. Our initial focus in the quantitative methanol degradation experiments will be to further vary our experimental conditions with the goal of obtaining unburned hydrocarbon yields. Temperature may be an important variable, and measurements will be reported up to temperatures of 1100°C.

**Table 2. Reported Emissions from Engine Studies of Methanol Combustion**

Compounds Emitted	Concentration		Experimental Conditions			
			Peak Pressure		Peak Temperature	
	$\phi$	ppm	$\phi$	$P_m(\text{atm})$	$\phi$	$T_m(^{\circ}\text{K})$
CO [2]	0.8	3.1	0.6	5.8	0.8	2460
	1.0	3.8	0.8	6.0	1.0	2600
	1.2	4.2	1.0	6.5	1.2	2620
	1.4	4.5	1.2	6.8	1.4	2580
				1.4	6.5	
CO <sub>2</sub> [3]	$\phi$	ppm (x 10 <sup>-4</sup> )	Experimental conditions were not reported in Reference 3.			
	0.6	6.5				
	0.8	8.1				
	1.0	9.6				
	1.2	9.2				
Formaldehyde [4]	$\phi$	ppm	$\phi$	$P_m(\text{atm})$		
	0.6	56	0.6	5.5		
	0.8	42	0.8	6.4		
	1.0	32	1.0	7.1		
	1.2	40	1.2	7.3		
	1.4	72	1.4	7.2		
[3]	1.6	40				
	1.8	55				
	2.0	75				
	2.25	100				
Methanol (Data sources in brackets)	$\phi$	ppm [4]	[3]	$f_r(\%)$	[4]	
	0.6	3000			6	
	0.75		0.41			
	0.8	2000			2.8	
	1.0		0.38		1.5	
	1.1		0.35			
	1.2	1800			2.0	
	1.4	3800			3.5	
	1.5		0.42			
[8]	cold start	1580 ppm				Experimental conditions were not reported in Reference 8.
	hot start	810 ppm				

**Table 2. Reported Emissions from Engine Studies of Methanol Combustion  
(continued)**

Compounds Emitted	Concentration			Experimental Conditions
	$\phi$	ppm [2]	ppm (10 <sup>-3</sup> ) [5]	
NO (Data sources in brackets)				Experimental conditions were not reported in Reference 5.
	0.8	3.9	0.4	
	0.9		0.8	
	1.0	3.7	1.8	
	1.1		1.1	
	1.2	3.2	0.5	
	1.4	2.8		
Methyl Nitrite [6]	$\phi$	ppm		Experimental conditions were not reported in Reference 6
	0.6	1000		
	0.8	3200		
	0.9	5200		
	1.0	4500		
Hydro- carbons [7]	$\phi$	ppm (liquid injection)	ppm (vapor injection)	Experimental conditions were not reported in References 7 and 8.
	0.7	~700		
	0.8	700		
	0.9	900	650	
	1.0	1400	750	
	1.1	2400	750	
	1.2	3000	800	
	ppm (cold start)	ppm (hot start)		
Paraffins [8]:				
Methane	7.8	Not		
Ethane	trace	measured		
N-Pentane	0.02	trace		
Isobutane	0.02	trace		
Isopentane	0	0.10		
		0		
Olefins:				
Ethylene	2.1	2.5		
Propylene	trace	0.07		
Butene	0.12	0.07		
Acetylene	0.86	0.58		
Formaldehyde	146.5	131.5		
Total aldehydes	155.0	144.8		



**Table 3. Emissions Comparison of Flow Reactor and Engine Tests of Methanol and Ethanol Fuels**

Emission By-product	UDRI Flow Reactor		Engine Tests <sup>[2-11]</sup>	
	Methanol	Ethanol	Methanol	Ethanol
HCHO	X	X	X	X <sup>1</sup>
1,3,5-Trioxane	X			
CH <sub>3</sub> COCH <sub>3</sub>	X	X	X	
CH <sub>3</sub> CHO		X		X <sup>1</sup>
CH <sub>3</sub> COOH		X		
CH <sub>3</sub> COOC <sub>2</sub> H <sub>5</sub>		X		
2,3-Butanediol		X		
2-Hydroxy-butanone		X		
CH <sub>4</sub>		X	X	X <sup>1</sup>
C <sub>2</sub> H <sub>6</sub>		X	X	X <sup>1</sup>
C <sub>2</sub> H <sub>4</sub>		X	X	X <sup>1</sup>
C <sub>2</sub> H <sub>2</sub>		X	X	X <sup>1</sup>
C <sub>3</sub> H <sub>6</sub>		X	X	X <sup>1</sup>

<sup>1</sup> Hagey, et al. reported unburned hydrocarbons, carbon monoxide, NO<sub>x</sub> and total aldehydes from a series of engine tests of various ethanol/gasoline blends (0-20 vol%).

## Conclusions

The initial year of study of the thermal degradation under highly controlled conditions of two alternative fuels, methanol and ethanol, has produced several important findings. They are briefly summarized below.

The thermal degradation of ethanol has produced a substantially larger number of intermediate organic by-products than the similar thermal degradation of methanol. Ethanol degradation by-products, which were firmly identified using GC-MS analysis, were acetaldehyde, formaldehyde, acetone, acetic acid and several light hydrocarbons, including methane, ethane, ethylene, acetylene and propylene. Methanol degradation by-products, firmly identified using GC-MS analysis, were formaldehyde, 1,2,3-trioxane, and acetone (the latter observed under fuel-lean conditions).

A second important finding from this initial work was the lack of stability of the organic intermediate by-products. The only by-products observed at temperatures where complete destruction of the parent fuel was observed were carbon monoxide, carbon dioxide, and water vapor. This highly significant result suggests that these two alcohol fuels do not have a propensity to form higher molecular weight by-products, even under oxygen-free pyrolysis conditions. The propensity to form higher molecular weight by-products is an important characteristic of hydrocarbon fuels.

A qualitative comparison of the UDRI flow reactor data with previous engine tests yielded some positive results. For methanol, organic by-products observed in both types of tests were formaldehyde and acetone. The UDRI study did not detect measurable quantities of methane or other unburned hydrocarbons, as observed in the engine tests. For ethanol, there are apparently very limited data. Organic by-products observed in both tests included unburned hydrocarbons and aldehydes. The one available engine test did not report speciated data for comparison with the UDRI results. We are unaware of any additional ethanol engine test data.

## References

1. Graham, J.L., Berman, J.M., and Dellinger, B. (1993). *J. Photobiol. A: Chem.* (71); pp. 65-74.
2. El-Eman, S.H. and Desoky, A.A. (1985). *Int. J. Hydrogen Energy* (10); pp. 497-504.
3. Okada, J., Koda, S. and Akita, K. (1985). *Fuel* (64); pp. 553-557.
4. Koda, S., Oda, K., Hirano, M., Hirano, T. and Akita, K. (1982). *Combust. Flame* (46); pp. 17-28.
5. Rubin, M.B. and McClean, W.J. (1978). *Combust. Sci. Technol.* (18); pp. 199-206.
6. Jonsson, A. and Bertilson, B.M. (1982). *Environ. Sci. Technol.* (16); pp. 106-110.
7. Baker, R.E. (1978). *International Symposium on Alcohol Fuel Technology*, pp. 2-7(1) - 2-7(8).
8. Hagey, G., Parker, A.J., Jr., Timbario, T.J., and Raley, D.L. (1978). *International Symposium on Alcohol Fuel Technology*, pp. 8-2(1) - 8-2(7).
9. Ullman, T.L., Hare, C.T., and Baines, T.M. (1982). *SAE Technical Paper Series*, #820966.
10. Smith, L.R., Urban, C.M. and Baines, T.M. (1982). *SAE Technical Paper Series*, #820967.
11. Ullman, T.L., Hare, C.T., and Baines, T.M. (1986). *SAE Technical Paper Series*, #860305.

## Bibliography

- Westbrook, C.K. and Dryer, F.L. (1980). *Combust. Flame* (37); pp. 171-192.
- Spindler, K. and Wagner, H. Gg. (1982). *Ber. Bunsenges Phys. Chem.* (86); pp. 2-13.
- Dove, J.E. and Warnatz, J. (1983). *Ber. Bunsenges Phys. Chem.* (87); pp. 1040-1044.
- Westbrook, C.K. and Dryer, F.L. (1984). *Prog. Energy Combust. Sci.* (10); pp. 1-157.
- Olsson, J.O., Olssen I.B.M., and Andersson, L.L. (1987). *J. Phys. Chem.* (91); pp. 4160-4165.
- Norton, T.S. and Dryer, F.L. (1990). *Intern. J. Chem. Kinet.* (22); pp. 219-241.
- Grotheer, H.-H., Kelm, S., Driver, H.S.T., Hutcheon, R.J., Lockett, R.D., and Robertson, G.N. (1992). *Ber. Bunsenges Phys. Chem.* (96); pp. 1360-1376.
- Driver, H.S.T., Hutcheon, R.J., Lockett, R.D., Robertson, G.N., Grotheer, H.-H. and Kelm, S. (1992). *Ber. Bunsenges Phys. Chem.* (96); pp. 1376-1387.
- Cribb, P.H., Dove, J.E., and Yamazaki, S. (1992). *Combust. Flame* (88); pp. 169-186 and 186-200 .
- Dryer, F.L. and Yetter, R.A. (1993). *Comprehensive Mechanisms for Combustion Chemistry: An Experimental and Numerical Study with Emphasis on Applied Sensitivity Analysis June 15, 1990 - February 1, 1993*. DOE Grant No. DE-FG02-86ER13503. Mechanical and Aerospace Engineering Department, Princeton University.
- Dobe, S. Otting, M., Temps, F., Wagner, H. Gg. and Ziemer, H. (1993). *Ber. Bunsenges Phys. Chem.* (97); pp. 877-884.
- E. A. Irdam, J. H. Kiefer, L. B. Harding, and A.F. Wagner (1993). *Intern. J. Chem. Kinet.* (25); pp. 285-303.
- Hidaka, Y., Taniguchi, T., Kamesawa, T., Masaoka, H., Inami, K., and Kawano, H. (1993). *Intern. J. Chem. Kinet.* (25); pp. 305-322.

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