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13. ABSTRACT (Maximum 200 words)

A research program to study the low temperature oxidation chemistry of JP-8 at high pressures has been conducted at Drexel University. The current program was initiated in June 2003 through a grant from the Army Research Office (Grant No. DAAD19-03-1-0070, Project No. 44458-EG) and was completed in July 2006. The objectives of this project were to determine the effects of fuel composition variations in JP-8 reactivity at low and intermediate temperatures (600 - 1000 K) and elevated pressures (2 - 20 atm), to develop a chemical surrogate for JP-8, and to obtain kinetic information of the JP-8 surrogate components neat and in blends. Fuels were oxidized in a pressurized flow reactor, with complimentary experiments conducted in a single cylinder research engine. Detailed kinetic information was obtained utilizing gas chromatography with flame ionization detection and coupling to a mass spectrometer. In addition, hydrocarbons similar to the JP-8 surrogate components but of lighter molecular weight were studied in detail to ascertain the fundamental branching pathways of hydrocarbons at low temperatures; several other potential surrogate components and blends, including for Fischer-Tropsch JP-8, were also examined.

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The Low Temperature Oxidation Chemistry of JP-8 and its Surrogates at High Pressure

FINAL PROGRESS REPORT

N.P. Cernansky and D.L. Miller

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I. FOREWORD

A research program to study the preignition oxidation chemistry of single and multiple component hydrocarbon fuels has been conducted at Drexel University. The current program was initiated in June 2003 through a grant from the U.S. Army Research Office (Grant No. DAAD19-03-1-0070, Project No. 44458-EG) and was completed in July 2006. The principal objectives were to (1) determine the effects of fuel composition variations on the oxidation process in the low and intermediate temperature ranges (600-1000 K) over a range of pressures (up to 20 atm) for JP-8, (2) participate in the development of a "standard" chemical surrogate to represent the complex combustion processes of the typical JP-8 fuel under compression ignition engine conditions, (3) obtain kinetic information in the low and intermediate temperature ranges over a range of pressures for the oxidation of distillate fuel components and their mixtures, and (4) develop detailed and reduced/skeletal mechanisms which can model the progress of these reactions for use in predicting ignition and emissions characteristics.

Experiments were conducted in the Pressurized Flow Reactor (PFR) facility at Drexel University, which operates at temperatures of 600 – 1000 K and pressures of 2 – 20 atm. The design of the PFR allows for the study of fuel preignition oxidation chemistry, without considering the additional complexities of fluid mechanics and temperature gradients. Online analysis of the data included CO and CO_2 measurements using a nondispersive infrared analyzer. Offline analysis, for identification and quantification of intermediate species, was performed using gas chromatography with flame ionization detection and coupling to a mass spectrometer. Additional experiments were conducted in a single cylinder research engine.

Samples of JP-8 and Jet A of varying composition were oxidized, and their reactivities were compared. A JP-8 surrogate composed of 43% n-dodecane / 27% iso-cetane / 15% methylcyclohexane / 15% 1-methylnaphthalene by volume was developed to mimic the average composition and low temperature reactivity of the jet fuels. Each of the surrogate components was also studied individually to determine their low temperature oxidation branching pathways. This information is valuable for the development of chemical kinetic models. Other tasks conducted under this project included follow-up speciation studies of a gasoline surrogate and components identified in the previous program, an investigation of the low temperature reactivity of Fischer-Tropsch JP-8 and a potential surrogate, and an exploration into possible diesel and jet fuel surrogates. The latter task was performed in conjunction with the recently-initiated Surrogate Fuel Working Groups on diesel, gasoline, and jet fuels – a collaborative effort (coordinated by AFOSR/ARO/NIST/NSF) involving industry, government, and university researchers.

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III. PROBLEM STATEMENT

DoD directive 4140.43 mandated JP-8 as the universal fuel for all military applications. Field testing of JP-8 in military specification compression ignition (CI) engines showed that benefits included reductions in combustion-related component wear, nozzle fouling/deposit problems, and exhaust emissions and thermal signatures, and in improvements in cold start performance. However, disadvantages included horsepower reduction due to lower volumetric heat content. Furthermore, wide variations in cetane index, aromatic content, and cycloalkane content were observed, and the impacts of these variations on CI engine operation are not well understood. A surrogate, a mixture of selected components at specified fractions, which can mimic the composition, properties, and reactivity of JP-8, will aid in studying the operation of JP-8 in current and advanced CI engines. However, due to the range of properties of JP-8, a surrogate must be tuned to a sample of average reactivity and composition. Therefore, the first task of this project was to identify an average JP-8 sample and to determine how the variability in composition and properties affects the reactivity of JP-8. The second task was to develop a JP-8 surrogate that mimics the composition and reactivity of average JP-8. Success in this task depends on the ability of a surrogate to match the behavior of the fuel in a variety of experimental settings, and thus cooperation with other laboratories was required. A suitable surrogate that matches the low and intermediate temperature reactivity was identified and collaborations have been developed to explore its ability to match the behavior of the fuel in other reaction regimes. The third task was to perform detailed species identification and quantification of the intermediates and products of the fuels during combustion. By performing mechanistic analysis using these data, the fourth task follows, which was to identify reaction mechanisms for inclusion in chemical kinetic models that predict ignition, combustion, and emissions characteristics.

IV. EXPERIMENTAL METHODOLOGY

The primary test facility in this program was the Pressurized Flow Reactor (PFR) in the Combustion and Fuels Laboratory at Drexel University. The PFR is designed to study the effects of temperature and pressure on the oxidation of hydrocarbon species at temperatures of 600 – 1000 K and pressures of 2 – 20 atm with relative isolation from fluid mechanics and temperature gradients (Koert et al., 1992). A schematic of the PFR is shown in Fig. 1. Synthetic air, free of contaminants, is formed by mixing high purity nitrogen and oxygen. The liquid fuel is injected from a syringe pump into a stream of nitrogen for vaporization. This vaporized fuel in nitrogen and the synthetic air enter the reactor through an opposed jet nozzle. The mixture then flows into a quartz reaction tube. A gas sampling probe is moved inside the reaction tube to collect oxidized samples from the reaction zone at selected probe positions, which correspond to specific reaction times. Two types of experiments can be conducted. In controlled cool down (CCD) experiments, the PFR is preheated to a specified temperature (typically > 800 K) and once the reaction stabilizes, the PFR is cooled at a rate of 2-5ºC/min and the sampling probe is moved to produce a constant residence time. During this cool down, CO and CO_2 are continuously monitored and samples can be collected for detailed analysis at any selected temperature to produce a reactivity map of sampled species concentrations as a function of reaction temperature for the experimental residence time. In constant inlet temperature (CIT) experiments, the inlet temperature is set and the probe is moved to extract samples at different locations along the axis of the reactor which allows generation of species evolution in time profiles. For analysis offline, after an experiment, 14 samples can be collected and stored in a multiple loop storage system, which is heated to 463 K in order to prevent condensation of the less volatile components of the sample. Species are then separated, identified, and quantified using gas chromatography (GC) with flame ionization detection (FID) and with coupling to a mass spectrometer (GC/MS). For separation, the GC used a fused silica capillary column (Supelco Petrocol DH 100 m length, 0.5 μm film thickness, and 0.25 mm OD). For identification, the spectra from the MS are compared with the NIST '02 database of 147,198 compounds.

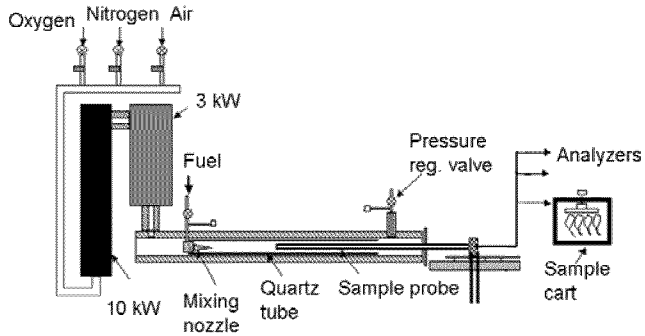

Figure 1: Schematic of the PFR

Some experiments in support of this program were also carried out in a research engine. For the engine experiments, the test facility consists of a single cylinder, Waukesha Motor Corporation Model 48D, Cooperative Fuels Research engine directly coupled to a motor dynamometer. A schematic of the engine is shown in Fig. 2. The engine has an 8.26 cm cylinder bore and a variable compression ratio. For our experiments, the compression ratio was set at 16:1, which corresponds to an 11 cm piston stroke and a 589 cm^3 displacement. Test fuel is injected into the air stream of the heated inlet manifold well upstream of the intake valve to assure complete vaporization and mixing. During a typical experiment, inlet manifold temperature is slowly increased and the reactivity behavior of the fuel is monitored. The autoignition behavior of the fuels is monitored by measuring the in-cylinder pressure with a water cooled, piezoelectric pressure transducer coupled to a charge amplifier.

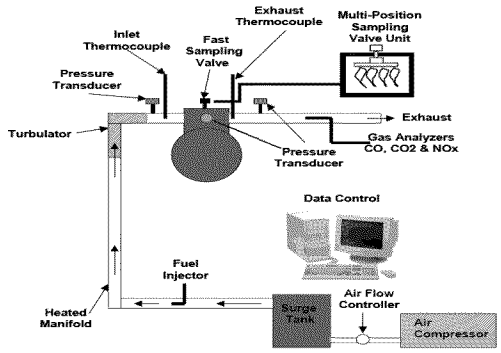

Figure 2: Schematic of the single cylinder research engine

V. SUMMARY OF RESULTS

Several subtasks were completed to achieve the program objectives. Samples of JP-8 and Jet A of varying composition were oxidized, and their reactivities were compared. A JP-8 surrogate composed of 43% n-dodecane / 27% iso-cetane / 15% methylcyclohexane / 15% 1-methylnaphthalene by volume was developed to mimic the composition and low temperature reactivity of the average jet fuel. Each of the surrogate components was also studied individually to determine their low temperature oxidation branching pathways. This information is valuable for the development of chemical kinetic models. Other subtasks conducted under this project included follow-up speciation studies of a gasoline surrogate and components identified in the previous program, an investigation of the low temperature reactivity of Fischer-Tropsch JP-8 and a potential surrogate, and an exploration into possible diesel and jet fuel surrogates. The latter task was performed in conjunction with the recently-initiated Surrogate Fuel Working Groups on diesel, gasoline, and jet fuels – a collaborative effort (coordinated by AFOSR/ARO/NIST/NSF) involving industry, government, and university researchers.

The significant findings from this work can be grouped and listed as follows:

(1) JP-8 characterization and surrogate development highlights:

- (a) Observed reactivity differences between JP-8 and Jet A in the low and intermediate temperature regimes are not significant enough to prevent the interchangeable use of Jet A and JP-8 for surrogate development.
- (b) The range of low and intermediate temperature reactivity is broad and in surrogate development an average sample must be used.
- (c) Of several JP-8 surrogates tested, a mixture of 43% n-dodecane / 27% iso-cetane / 15% methylcyclohexane / 15% 1-methylnaphthalene by volume stands out in its ability to mimic the low temperature reactivity of average JP-8.
- (d) The JP-8 surrogate mixture developed in the PFR closely matches the autoignition behavior of the corresponding JP-8 fuel in a single cylinder engine, at lean conditions.
- (e) Fischer-Tropsch JP-8 is more reactive than petroleum-derived JP-8 at low temperatures.
- (f) Jet fuel and diesel fuel surrogates proposed by the Surrogate Fuel Working Groups and consisting of 2:1:1 and 1:1:1 blends of n-decane:n-butylcyclohexane:n-butylbenzene are more reactive than JP-8.

(2) Key mechanistic observations during gasoline and diesel surrogate development, pertaining to low and intermediate temperatures:

(a) When n-dodecane oxidized, it favored the formation of C_6 and smaller hydrocarbons.

(b) When iso-cetane oxidized, it fragmented to C_8 and lower hydrocarbons.

(c) At lean stoichiometry, methylcyclohexane undergoes dehydrogenation, rather than ring rupture as reported for high temperature conditions.

(d) The preferred pathway of 1-pentene oxidation is HO_2 addition to the double bond, known as the "Waddington" mechanism.

(e) n-Heptane mainly reacts to form aldehydes, in addition to significant quantities of alkenes and ethers.

(f) iso-Octane mainly forms cyclic ethers.

(3) Suggestions for improving current kinetic models:

(a) A C_6 radical species should replace the C_7 radical species in the n-dodecane model.

(b) The iso-cetane model should be modified to produce smaller quantities of aldehydes and alkenes.

(c) Hydrogen abstraction from methylcyclohexane first occurs at the cyclohexane group at low temperatures, rather than at the methyl group as in the model.

(d) Increasing the importance of the "Waddington" mechanism may improve the 1-pentene model.

(e) Decreasing the extent of fuel conversation for n-heptane above 670 K may improve the model.

(f) The iso-octane model should predict a lower rate of reactivity at low temperatures.

(4) Fuel component synergies, pertaining to low and intermediate temperatures:

(a) Although neat toluene is not reactive, it becomes reactive when mixed with alkanes.

(b) Neat n-butylbenzene is not reactive and when mixed with aliphatics reduces overall reactivity.

(c) 1-Methylnaphthalene oxidation forms large quantities of naphthalene, 1-naphthaldehyde, and benzaldehyde when mixed with alkanes, though it is not reactive neat.

(d) At very lean conditions, methylcyclohexane is only reactive when mixed with alkanes, while n-butylcyclohexane is reactive when neat.

Details of the subtasks described above and work leading to the significant findings follow.

A. Oxidation of Jet A and JP-8

Due to the intentionally broad specifications for JP-8, variations in cetane index, aromatic content, sulfur content, API gravity, and additive content are observed. The fundamental difference between JP-8 and U.S. commercial jet fuel Jet A is that JP-8 includes three additives: a lubricity improver/corrosion inhibitor, an anti-

static additive, and Fuel System Icing Inhibitor (FSII), with only the FSII being added in substantial quantities. To elucidate the impact of JP-8 compositional variations and the differences between JP-8 and Jet A, several well-characterized samples of JP-8 and Jet A from Wright-Patterson Air Force Base (WPAFB), one well-characterized sample of JP-7 from WPAFB, and one independently procured JP-8 sample from a refinery were oxidized in Drexel University's Pressurized Flow Reactor (PFR). The physical properties of the various samples of JP-8, Jet A and JP-7 used are shown in Tables 1-2.

Table 1: Physical Properties of the JP-8 Samples.

	JP-8 POSF-4177	JP-8 POSF-3684	JP-8 POSF-3804	JP-8 POSF-3773
Aromatics [% vol]	16.3	18.1	19.7	15.9
Alkenes [% vol]	0.9	1.3	0.5	0.7
Naphthalenes [% vol]	1.0	N/A	N/A	N/A
Hydrogen Content [% mass]	13.7	13.8	13.8	13.9
API Gravity	42.4	44.6	45.9	45.8
Total Sulfur [% mass]	0.14	0.04	0.08	0.07
FSII [% vol]	0.11	0.07	0.10	0.07

Table 2: Physical Properties of Jet A & JP-7 Samples.

	JET A POSF-3592	JET A POSF-3602	JET A POSF-3638	JP-7 POSF-3327
Aromatics [% vol]	19	24	12	0
Alkenes [% vol]	1.9	0.9	1.4	N/A
Naphthalenes [% vol]	N/A	N/A	N/A	N/A
Hydrogen Content [% mass]	N/A	N/A	N/A	14.64
API Gravity	42.9	41.1	46.1	46.9
Total Sulfur [% mass]	0.2	0.0	0.0	0.0
FSII [% vol]	0.00	0.00	0.00	0.05

Reactivity maps (CO production as a function of temperature) at 8 atm pressure, equivalence ratio of 0.3, nitrogen dilution of 80%, and residence time of 120 ms are shown in Figs. 3 and 4. CO formation has been shown to be a good measure of low and intermediate temperature reactivity, as in this temperature regime CO does not oxidize significantly to CO_2. In all cases, reactivity started at ~ 620 K and a clear Negative Temperature Coefficient (NTC) behavior was observed. While the reactivity level of each sample was significantly different, with the JP-7 sample having the most reactivity, the temperature of peak reactivity, referred to as the start of the NTC regime, is nearly identical for all of the samples and occurred around 690 K. This is consistent with previous work that had suggested increasing the overall aromatic content of a fuel would tend to decrease reactivity, but not significantly affect the start of the NTC region.

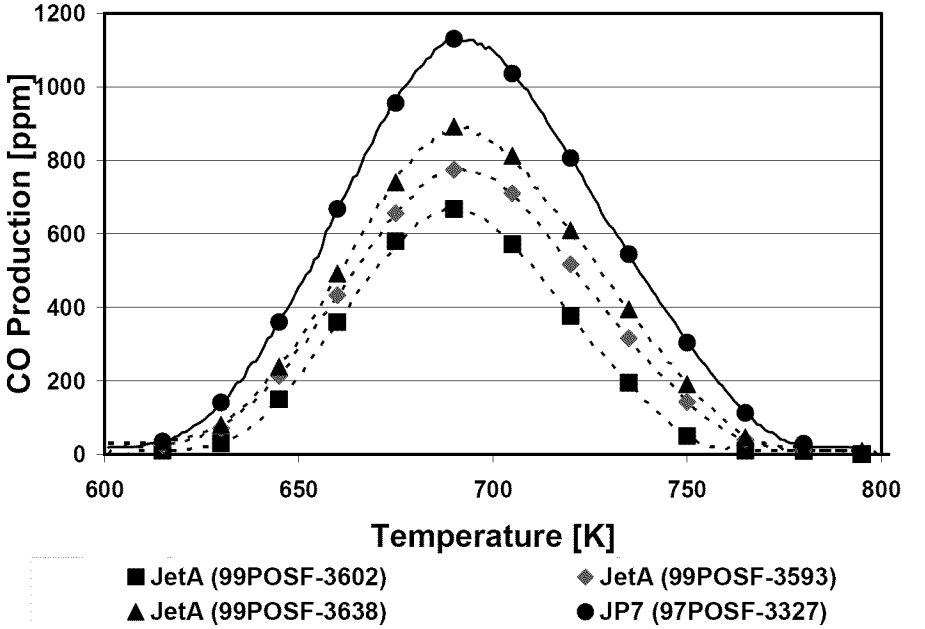

Figure 3: Reactivity map of Jet A and JP-7.

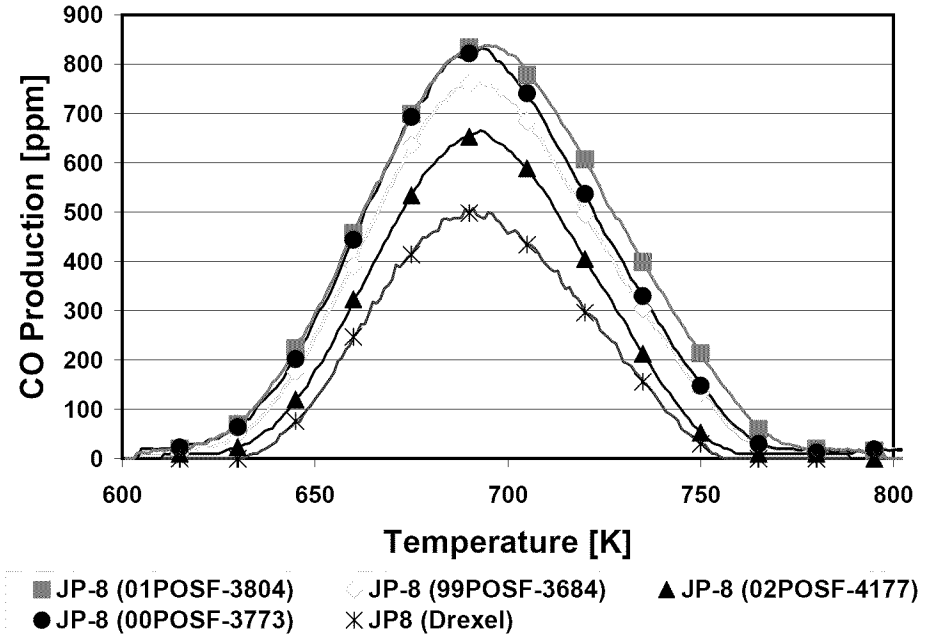

Figure 4: Reactivity map of JP-8.

Comparison of the physical and chemical properties and the overall reactivity of the samples identified some interesting relationships. First, due to the limited variation and overall low content of alkenes, < 2% by volume, no impact of the alkene content was observable. Secondly, the API gravity value of Jet A is consistently lower for a given maximum CO concentration compared to JP-8, Fig. 5. Thirdly, the relationship between maximum CO production and aromatic content is nearly linear for the Jet A and JP-7 samples, as

shown in Fig. 6. However, the strong linear relationship between aromatic content and maximum CO production is not as apparent for the JP-8 samples. Specifically, two of the JP-8 samples, POSF-3804 and POSF-4177, clearly deviate from a linear response. There is no readily apparent cause for the behavior of these samples. Due to the high concentrations of FSII additive (1000 to 1500 ppm by volume), a direct investigation of the effects of the additive was conducted. The FSII additive was mixed with a sample of Jet A, POSF-3593, at the maximum concentration permitted by the specifications. Figure 7 shows the comparison between the reactivity maps of the "neat" and FSII modified Jet A samples. The difference between the two reactivity maps was 30 ppm, which is within the experimental repeatability. This suggests that there is no significant effect of the FSII additive on the low and intermediate temperature chemistry. Consequently, the FSII additive would not need to be included in the surrogate formulations. Furthermore, both JP-8 and Jet A have considerable variation in sulfur content, Tables 1-2, yet the impact of sulfur on the overall reactivity and the linearity of the aromatic/CO production relationships does not appear to be significant, Fig. 8. However, additional investigation on the impact of sulfur, specifically sulfur oxides, on the oxidation process is necessary. Nevertheless, there does appear to be an "average" behavior at least in the domain of the low and intermediate temperature regime and using Jet A in place of JP-8 for the development of surrogates is feasible so long as the composition of the Jet A samples is near the average composition of JP-8. The key conclusion therefore is that for jet fuel experiments conducted in both military and civilian sectors, it is acceptable to acquire a Jet A sample of "average" composition from a local airport as an equivalent of JP-8. With respect to surrogate development, significant care should be taken when selecting either a Jet A or JP-8 reference sample to ensure that the composition of the samples is representative of the average fuel composition, most notably aromatic content, otherwise significant tuning of the surrogate to a specific sample will occur.

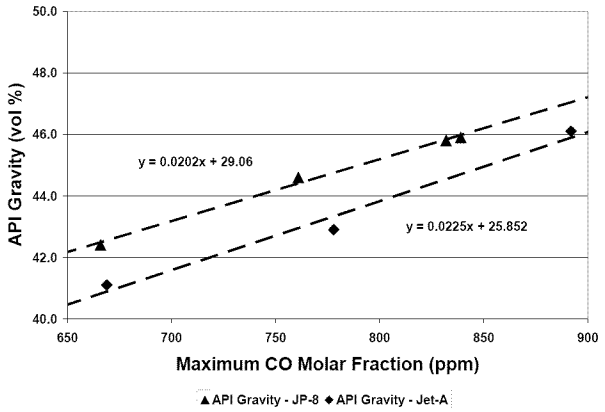

Figure 5: Relationship between API Gravity and maximum CO production for Jet A & JP-8.

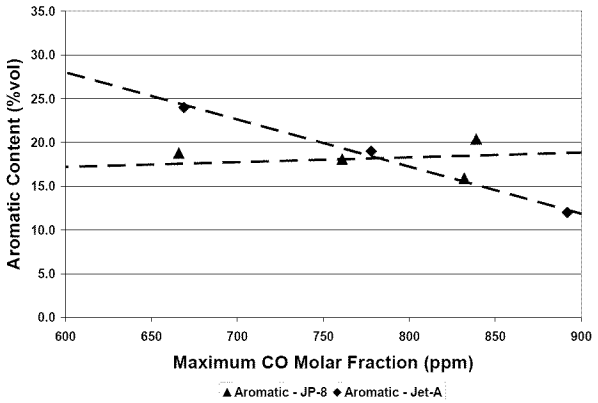

Figure 6: Relationship between aromatic content and maximum CO production for Jet A & JP-8.

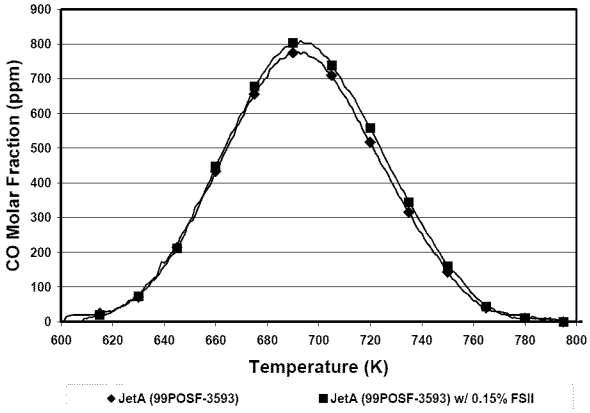

Figure 7: Relationship between Jet A and Jet A with the FSII additive.

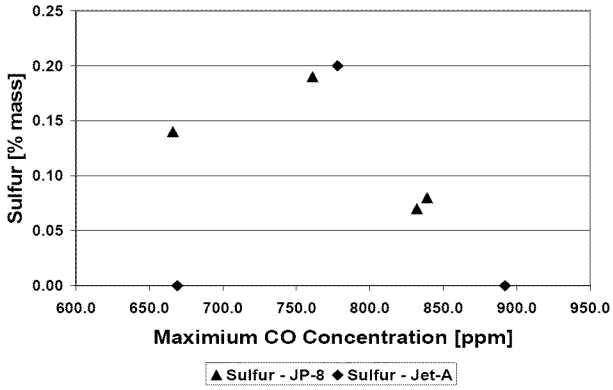

Figure 8: Relationship between sulfur content to maximum CO production for JP-8 and Jet-A.

B. Autoignition of Jet A and JP-8 in an Engine

To confirm the connection between flow reactor results and engine performance, tests were run in the single cylinder research engine facility. Three JP-8 samples and three Jet A samples, acquired from Wright-Patterson Air Force Base and described in Table 3, were stressed to the point of autoignition in the engine at equivalence ratios of 0.28, 0.35, 0.42, and 0.49. The low and intermediate temperature reactivity of the samples had been measured in the PFR facility, and these engine experiments were run to provide additional information relevant for modeling. Figures 9 and 10 show the pressure traces of the JP-8 and Jet A samples, respectively, as functions of the crank angle degree (CAD).

Table 3: Engine text matrix of jet fuel samples

Fuel	% Alkanes and Cycloalkanes	% Aromatics	% Alkenes	Cetane Index
*JP-8 #3684	80.6	18.1	1.3	44.8
JP-8 #3804	79.8	9.7	0.5	47.0
JP-8 #3773	83.4	15.9	0.7	46.0
*Jet A #3593	79.1	19.0	1.9	44.4
Jet A #3602	75.1	24.0	0.9	40.7
Jet A #3638	86.6	12.0	1.4	45.9

***Specific samples that matched the "average" composition and properties of JP-8 and Jet A**

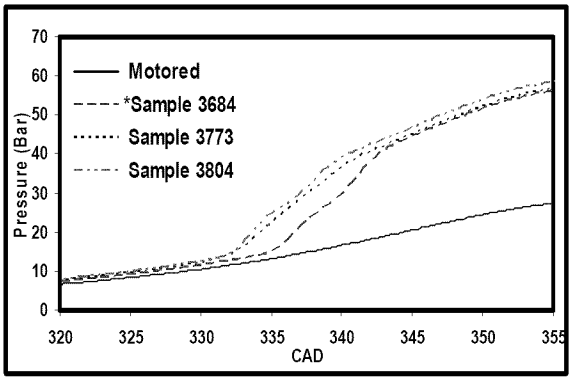

Figure 9: Autoignition of JP-8 samples at ϕ = 0.49, CR = 16, and T_{in} = 476 K.

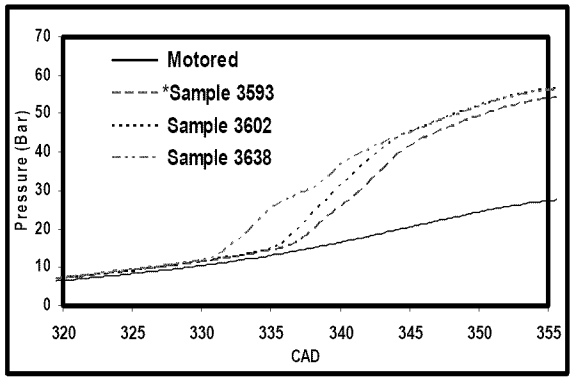

Figure 10: Autoignition of Jet A samples at ϕ =0.49, CR = 16, and T_{in} = 476 K.

The differences in autoignition behavior are due to differences in the preignition chemistry, as defined by fuel properties, such as aromatic content, cycloalkane content, and cetane index. The results showed that increasing aromatic content delayed ignition timing. For the JP-8 samples, increasing cetane index shortened ignition timing. However, the Jet A samples 3593 and 3602 had essentially the same ignition time with significantly different cetane index values (44.4 and 40.7) but similar aromatic content. This confirms our prior conclusion that the ASTM formula (D 976) used for calculating these cetane indices may not be valid for jet fuels. Nevertheless, in general the engine experiments matched the flow reactor results, whereby using the same set of fuels in both experiments, the ordering of maximum CO production from greatest to least in the PFR corresponded with the ordering of the CAD at ignition from least to greatest in the engine. Furthermore, comparison of results from the four equivalence ratios showed that increasing equivalence ratio to closer to 1 advanced the ignition timing, as expected.

n-Dodecane, iso-cetane, methylcyclohexane, and 1-methylnaphthalene (the JP-8 surrogate components) were tested in the engine as representative components for linear alkanes, branched alkanes, cycloalkanes, and aromatics, respectively. Methylcyclohexane and 1-methylnaphthalene showed no reactivity as neat fuels so they were run with n-dodecane as a reaction initiator. For comparison a mixture of n-dodecane and iso-cetane was also run. Figures 11 and 12 show the measured pressure traces. Mixes 1, 2, and 3 had cetane index values of 41.0, 42.2, and 40.8, respectively. Figure 11 shows that the difference in ignition time for Mixes 1 and 2, with a cetane index difference of 1.2, is very small. However, Mix 3, with almost the same cetane index as Mix 1, showed a significantly different ignition time. This demonstrates that the autoignition behavior of mixtures cannot simply be predicted by cetane index values.

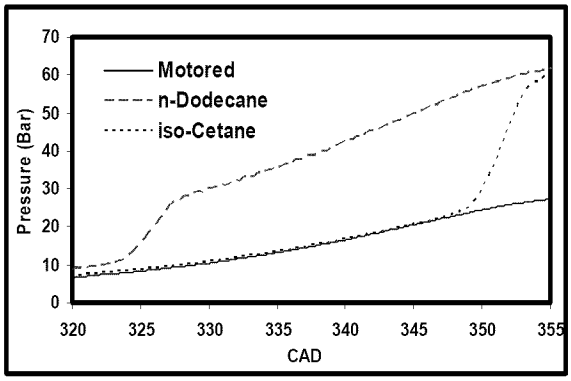

Figure 11: Autoignition of neat n-dodecane and neat iso-cetane at ϕ = 0.49, CR = 16, and T_{in} = 476 K

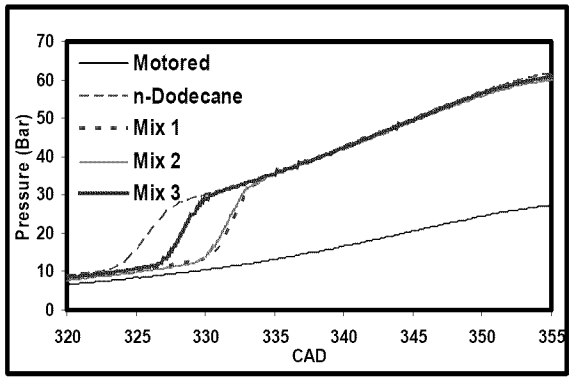

Figure 12: Autoignition of binary mixtures at ϕ = 0.49, CR = 16, and T_{in} = 476 K

Mix 1: 40 % n-dodecane, 60 % iso-cetane
Mix 2: 37 % n-dodecane, 63 % methylcyclohexane
Mix 3: 51 % n-dodecane, 49 % 1-methylnaphthalene

In our PFR experiments described in the next section, a mixture of 43% n-dodecane, 27% iso-cetane, 15% methylcyclohexane, and 15% 1-methylnaphthalene was shown to match the low and intermediate temperature reactivity of the average JP-8 sample, #3684. For further exploration of this mixture as a JP-8 surrogate, it was run in the engine test facility at equivalence ratios of 0.20, 0.32, and 0.35. Figures 13 and 14 show the pressure traces for the ϕ = 0.20 and 0.32 experiments, respectively; the ϕ = 0.35 data have slightly shorter ignition times than the ϕ = 0.32 data. The results with this mixture matched the average behavior of JP-8 and Jet A to within ~1.5 CAD, suggesting that a surrogate fuel developed in a pressurized flow reactor mimics the corresponding autoignition behavior in an engine.

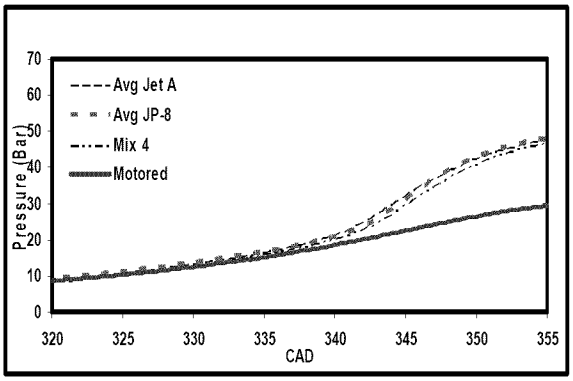

Figure 13: Comparison of the average JP-8 and Jet A samples and the surrogate mixture (Mix 4) at ϕ =0.20, CR = 16, and T_{in} = 476 K

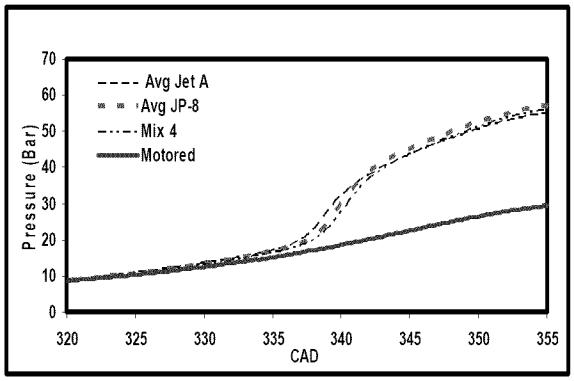

Figure 14: Comparison of the average JP-8 and Jet A samples and the surrogate mixture (Mix 4) at ϕ =0.32, CR = 16, and T_{in} = 476 K

C. Oxidation of JP-8 Surrogates

Utilizing the "average" JP-8 reactivity map previously identified, two surrogate mixtures developed at Drexel and one surrogate from Sarofim and coworkers at the University of Utah were investigated. Our previous work to develop a surrogate utilized the JP-8 sample procured directly from a refinery. However, this sample is considerably less reactive than the "average" behavior, Fig. 15. Therefore, the previous five component surrogate (S9) was "tuned" to match a lower than "average" reactivity. This illustrates the dangers of utilizing a non-average sample of JP-8 or Jet A. Of the developed surrogates, the mixture that matched the "average" JP-8 reactivity the closest was a four component mixture (S1) consisting of 43% n-dodecane, 27% iso-cetane, 15% methylcyclohexane, and 15% 1-methylnaphthalene. Although this surrogate reasonably matches the reactivity of JP-8, the peak of reactivity was shifted to a higher temperature by approximately 10 °C. The surrogate from Sarofim and coworkers was a mixture of 5% iso-octane, 5% methylcyclohexane, 20% toluene, 25% n-decane, 25% n-dodecane and 20% n-tetradecane (Violi et al., 2002). This surrogate was developed to simulate the volatility, sooting propensity, boiling-point curves, and compositional characteristics of JP-8. However, the reactivity mapping experiments show that the Sarofim surrogate, composed of 70% linear alkanes of C_{10} to C_{14}, is significantly more reactive than the JP-8 samples, which have an average concentration of 59% linear *and* branched alkanes (Edwards et al., 2006).

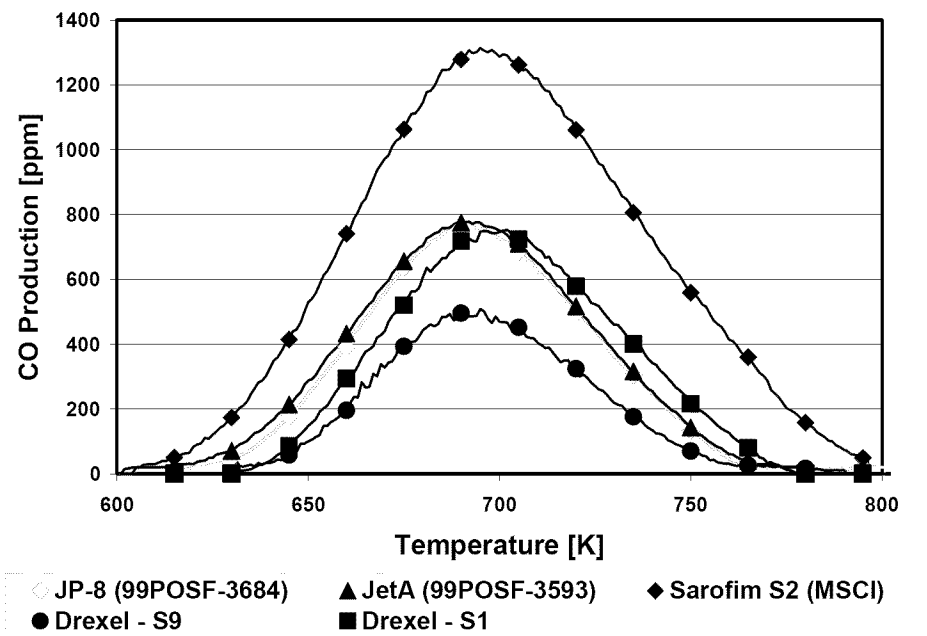

Figure 15: Surrogate comparison to "Average" JP-8 Reactivity Map.

D. Detailed Speciation of n-Dodecane Oxidation

n-Dodecane was studied from 600 to 800 K at 8 atm pressure for a residence time of 120 ms under 80.0% N_2 dilution and 0.25 equivalence ratio (CCD experiment). A CIT experiment was also run at 683 K inlet temperature at 8 atm pressure and samples were collected at residence times of 40 to 150 ms. In the CCD experiment, a strong NTC behavior started at 695 K, Figs. 16-17. Species identified and quantified included CO, CO_2, methane, ethene, 1-propene, acetaldehyde, 1-butene, 2-propenal, propanal, 3-buten-2-one, butanal, 1-pentene, pentanal, 1-hexene, hexanal, 1-heptene, heptanal, 1-octene, octanal, 1-nonene, 1-decene, several dodecene isomers, and n-dodecane, Figs. 18-19. When n-dodecane fragmented, it formed smaller hydrocarbons in the C_1 to C_6 range. The major intermediates identified were acetaldehyde, ethane, 1-hexene, propanal, and 1-propene. Formaldehyde was also a significant intermediate species, but was not quantified during this study. Mechanistic analysis indicated that the secondary hydrogen bonds were the first to be abstracted, specifically, the hydrogen from the second and third carbon atoms from each end of the linear chain, as noted by the *b* and *c* hydrogens, Fig. 20. The decomposition pathways of the $b\dot{C}_{12}H_{25}$ and $c\dot{C}_{12}H_{25}$ radicals were addition of molecular oxygen to form an alkylperoxy radical and β-scission to form a lower molecular weight alkene and an alkyl radical. However, as indicated by large concentrations of dodecene, not all of the fuel fragmented into smaller intermediates. The experiments were compared with a lumped model consisting of 7400 reactions among 276 species (Agosta et al., 2004). The model reasonably predicted the decomposition of the fuel and the formation of CO. However, the model overpredicted the formation of smaller alkenes and aldehydes. The experimental results suggest that a C_6 radical species should replace the current C_7 radicals in the mechanism, based on the measurement of a significantly higher concentration of 1-hexene than 1-heptene. Secondly, while the mechanism assumes that no conjugate alkenes are formed, the measured species distribution indicates that they should be included in the reaction set. The carbon balance data suggest that several groups of large hydrocarbons (including some oxygenates), that could not be quantified, are formed during the reaction.

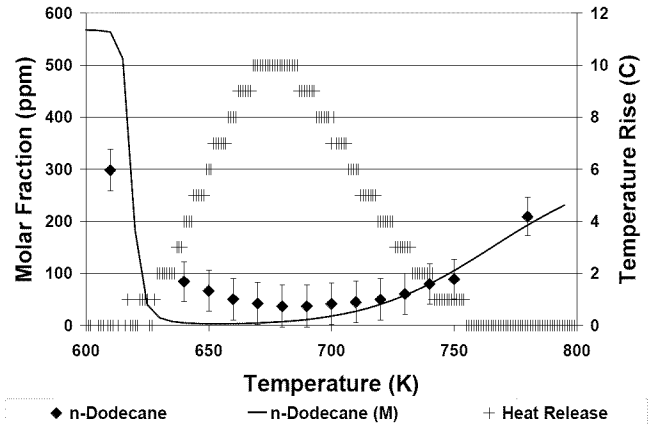

Figure 16: Experimental n-dodecane (points), model n-dodecane (line), and temperature rise during the n-dodecane CCD experiment at 120 ms.

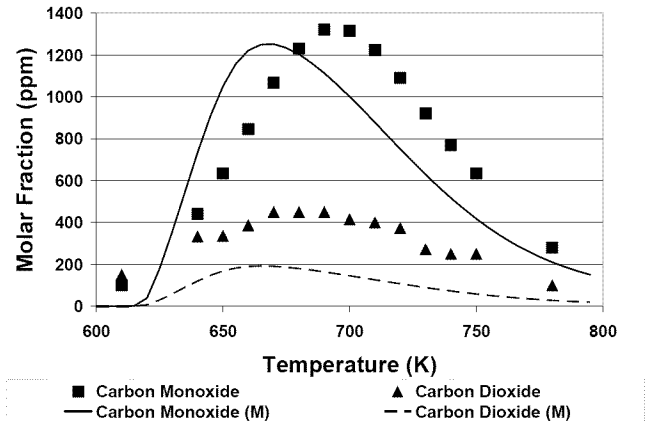

Figure 17: Experimental (points) and model (lines) for CO and CO_2 during the n-dodecane CCD experiment at 120 ms.

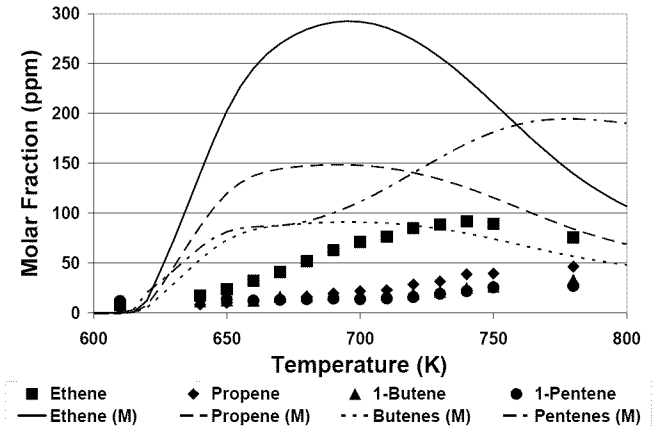

Figure 18: Major alkene intermediates during the n-dodecane CCD experiment at 120 ms.

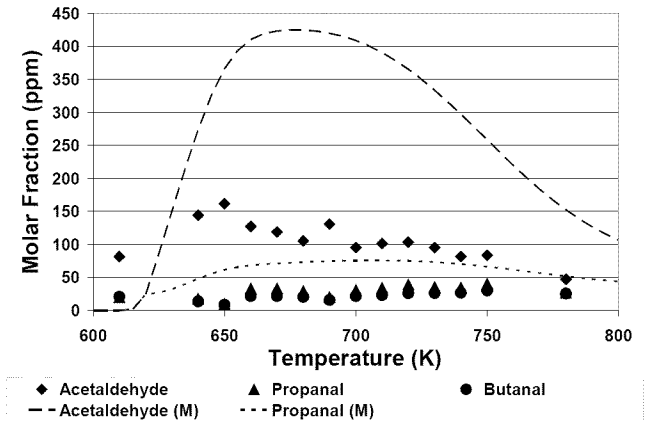

Figure 19: Major oxygenate intermediates during the n-dodecane CCD experiment at 120 ms.

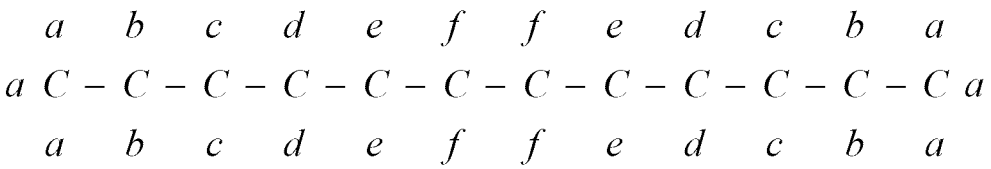

Figure 20: n-$C_{12}H_{26}$ chemical structure.

E. Detailed Speciation of iso-Cetane Oxidation

Due to a lack of reactivity using neat iso-cetane, a mixture of 60% 2,2,4,4,6,8,8-heptamethyl-nonane (iso-cetane) and 40% n-dodecane was examined, where the n-dodecane serves as a reaction initiator. The mixture was studied over the temperature range 600 to 800 K at 8 atm pressure at a residence time of 175 ms under 70.0% N_2 dilution and 0.30 equivalence ratio (CCD experiment) and at residence times of 65 to 220 ms at

8 atm pressure at a temperature of 687 K (CIT experiment). In the CCD experiment, a strong NTC behavior started at 690 K, Figs. 21-22. Species identified and quantified included CO, CO_2, methane, ethene, 1-propene, acetaldehyde, 1-butene, 2-methyl-1-propene, 2-propanone, 2-propenal, propanal, 2-methyl-propanal, 2-methyl-2-propanal, 3-buten-2-one, butanal, 1-pentene, pentanal, 1-hexene, hexanal, 4,4-dimethyl-1-pentene, 4,4-dimethyl-2-pentene, 4,4-dimethyl-2-pentanone, 1-heptene, heptanal, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 1-octene, octanal, 1-nonene, 1-decene, several tetramethyl-heptene isomers, 2,4,4,6,6-pentamethyl-1-heptene, several dodecene isomers, several hexamethyl-nonene isomers, n-dodecane, and iso-cetane. The major intermediates identified and quantified that can be attributed to iso-cetane oxidation were 2-propanone, 2-methyl-1-propene, 2,2,4-trimethyl-1-pentene, 2,2,4-trimethyl-2-pentene, and 4,4-dimethyl-2-pentanone. Based on the identification of intermediate species, it was proposed that in the iso-cetane/n-dodecane reaction half of the fragments were less than half of the size of the original molecule. However, it is unclear how much of the iso-cetane molecule remains intact in the form of oxygenates or smaller alkenes because no C_{16} intermediates were identified. However, a comparison of iso-cetane and n-dodecane results suggests that C_{16} intermediates are formed. The experimental results were compared with a lumped model consisting of 7400 reactions among 276 species (Agosta et al., 2004). Agreement between the data and model was good, but the model overpredicted the formation of smaller alkenes and aldehydes. Mechanistic analysis revealed that the *a* and *h* hydrogens (Fig. 23) were the first to be abstracted. Despite higher bond energies, the larger number of these hydrogen sites controls the reaction pathway.

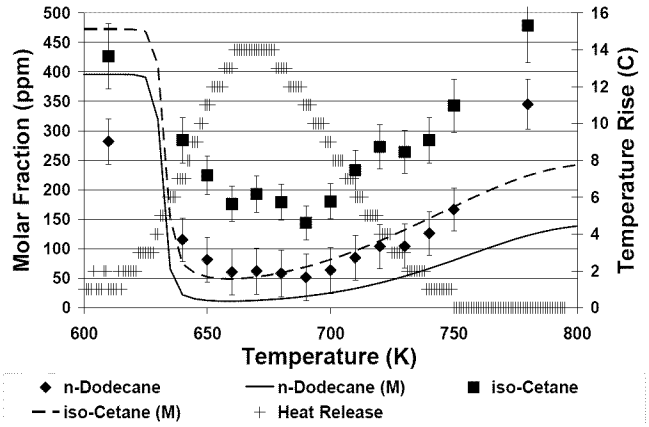

Figure 21: iso-Cetane, n-dodecane, and temperature rise during the iso-cetane / n-dodecane CCD experiment at 175 ms.

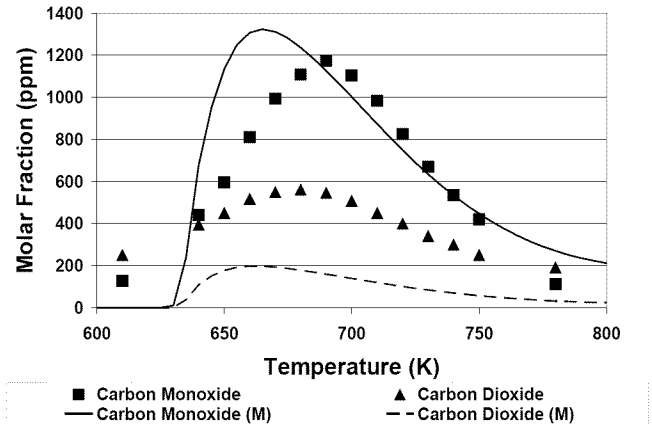

Figure 22: CO and CO_2 during the iso-cetane / n-dodecane CCD experiment at 175 ms.

```
                a                c                f                h
            a   C   a       c   C   c       f   C   f       h   C   h
        a       |       b       |       d       |       g       |       h
    a   C   –   C   –   C   –   C   –   C   –   C   –   C   –   C   –   C   h
        a           |       b       |       d       e       g       |       h
            a   C   a       c   C   c                           h   C   h
                a                c                                   h
```

Figure 23: iso-$C_{16}H_{34}$ chemical structure.

F. Detailed Speciation of Methylcyclohexane Oxidation

A mixture of 63% methylcyclohexane and 37% n-dodecane was studied in the PFR over the temperature range 600 to 800 K at a pressure of 8 atm at a residence time of 120 ms under 80.0% N_2 dilution and 0.30 equivalence ratio (CCD experiment), and at residence times of 40 to 150 ms at 8 atm pressure at a temperature of 668 K (CIT experiment). In the CCD experiment, a strong NTC behavior started at 695 K, Figs. 24-25. The species identified and quantified included CO, CO_2, ethene, 1-propene, acetaldehyde, 1-butene, 2-propenal, propanal, 3-buten-2-one, butanal, 1-pentene, pentanal, 1,3-cyclohexadiene, cyclohexene, benzene, cyclohexanone, cyclohex-2-en-1-one, 1-hexene, hexanal, several methyl-1-cyclohexene isomers, 1-methylenecyclohexane, several $C_7H_{10}O$ isomers, several $C_7H_{12}O$ isomers, toluene, 1-heptene, heptanal, 1-octene, octanal, 1-nonene, 1-decene, several dodecene isomers, n-dodecane, and methylcyclohexane. The results indicate that at low and intermediate temperatures and lean stoichiometry methylcyclohexane undergoes dehydrogenation, rather than the ring rupture observed in high temperature methylcyclohexane studies (Granata et al., 2003; Zeppieri et al., 1997). In addition, the model assumed that the *a* site (Fig. 26) was the first to be removed, followed by ring opening and fragmentation. Analysis of the partial oxidation products suggests that dehydrogenation is preferred via *b*, *c*, *d*, or *e* sites. Sites *c*, *d*, and *e* might be equally selected given that the three methyl-1-cyclohexene isomers were detected in similar quantities. A new set of reactions for methylcyclohexane (Fig. 27) in the low and intermediate temperatures regimes was proposed to reflect the product distribution. Decomposition is initiated by abstraction of hydrogen from the ring (N1, N2, and N3). This is followed by oxygen addition to the $cy\dot{C}_6H_{10}CH_3$ radical (N4). Additional steps include internal isomerization (N5 and N6) and the formation of conjugate alkenes (N7). The methyl-1-cyclohexene isomers decompose through hydrogen abstraction of allylic hydrogen (N8 and N9).

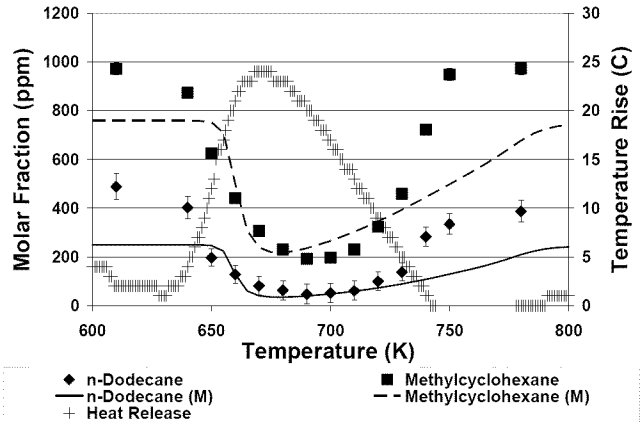

Figure 24: Methylcyclohexane, n-dodecane, and temperature rise during the methylcyclohexane / n-dodecane CCD experiment at 120 ms.

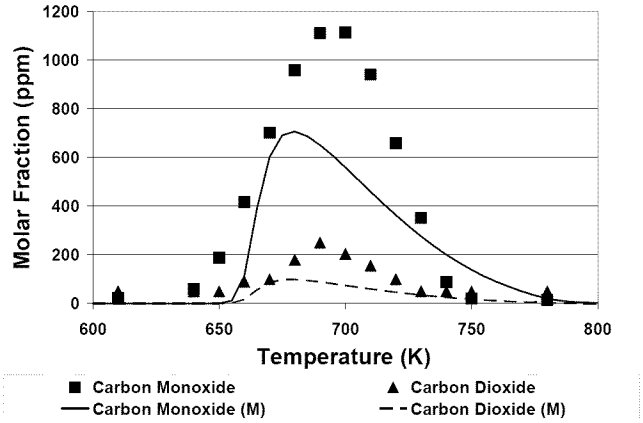

Figure 25: CO and CO_2 during the methylcyclohexane / n-dodecane CCD experiment at 120 ms.

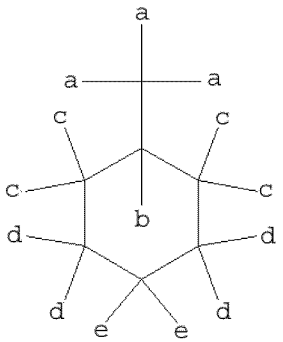

Figure 26: C_7H_{14} chemical structure.

$$cyC_6H_{11}CH_3 + O_2 + M \longleftrightarrow cy\dot{C}_6H_{10}CH_3 + H\dot{O}_2 + M \quad \text{(N1)}$$

$$cyC_6H_{11}CH_3 + \dot{O}H \longleftrightarrow cy\dot{C}_6H_{10}CH_3 + H_2O \quad \text{(N2)}$$

$$cyC_6H_{11}CH_3 + H\dot{O}_2 \longleftrightarrow cy\dot{C}_6H_{10}CH_3 + H_2O_2 \quad \text{(N3)}$$

$$cy\dot{C}_6H_{10}CH_3 + O_2 \longleftrightarrow cyC_6H_{10}(O\dot{O})CH_3 \quad \text{(N4)}$$

$$cyC_6H_{10}(O\dot{O})CH_3 \longleftrightarrow cy\dot{C}_6H_9(OOH)CH_3 \quad \text{(N5)}$$

$$cy\dot{C}_6H_9(OOH)CH_3 \longleftrightarrow cyC_6H_9(O)CH_3 + \dot{O}H \quad \text{(N6)}$$

$$cy\dot{C}_6H_9(OOH)CH_3 \longleftrightarrow cyC_6H_9CH_3 + H\dot{O}_2 \quad \text{(N7)}$$

$$cyC_6H_9CH_3 + \dot{O}H \longleftrightarrow cy\dot{C}_6H_8CH_3 + H_2O \quad \text{(N8)}$$

$$cyC_6H_9CH_3 + H\dot{O}_2 \longleftrightarrow cy\dot{C}_6H_8CH_3 + H_2O_2 \quad \text{(N9)}$$

$$cy\dot{C}_6H_8CH_3 + O_2 \longleftrightarrow cyC_6H_8(O\dot{O})CH_3 \quad \text{(N10)}$$

$$cyC_6H_8(O\dot{O})CH_3 \longleftrightarrow cy\dot{C}_6H_7(OOH)CH_3 \quad \text{(N11)}$$

$$cy\dot{C}_6H_7(OOH)CH_3 \longleftrightarrow cyC_6H_7(O)CH_3 \quad \text{(N12)}$$

Figure 27: Steps for C_7H_{14} reaction mechanism in low and intermediate temperature regimes.

G. Detailed Speciation of 1-Methylnaphthalene Oxidation

A mixture of 49% 1-methylnaphthalene and 51% n-dodecane was studied in the PFR over the temperature range 600 to 800 K at 8 atm pressure at a residence time of 175 ms under 70.0% N_2 dilution and 0.30 equivalence ratio (CCD experiment). Due to excessive sooting in the sampling probe, species quantification and CIT experiments were not conducted. Species that were identified and attributed to the 1-methylnaphthalene included benzene, toluene, benzaldehyde, ethyl-benzene, acetophenone, indene, naphthalene, and 1-naphthaldehyde. The most abundant species were naphthalene, 1-naphthaldehyde, and benzaldehyde. Previous studies showed that the major intermediates produced by the monocyclic aromatic toluene were benzene, benzaldehyde, phenol, and ethyl-benzene, with no appreciable ring scission or growth (Ellis et al., 2003; Emdee et al., 1992). Furthermore, previous high temperature 1-methylnaphthalene studies showed that 1-methylnaphthalene decomposition is similar to that of toluene (Shaddix et al., 1992; Shaddix et al., 1997). However, from our measurements, a significant fraction of 1-methylnaphthalene formed soot or benzaldehyde, indicating that bicyclic aromatics such as 1-methylnaphthalene are considerably less stable than monocyclic aromatics in the low and intermediate temperature regimes.

H. Detailed Speciation of JP-8 Surrogate Oxidation

The oxidation of JP-8 surrogate S1, consisting of 43% n-dodecane, 27% iso-cetane, 15% methylcyclohexane, and 15% 1-methylnaphthalene by volume, was studied in the PFR over the temperature range 600 to 800 K at 8 atm pressure at a residence time of 175 ms under 70.0% N_2 dilution and 0.30 equivalence ratio (CCD experiment), and at residence times of 60 to 170 ms at 8 atm pressure at a temperature of 672 K (CIT experiment), Figs. 28-29. Detailed species measurements were made during both types of experiment, Figs. 30-31. Experimental results were compared to a lumped model and model predictions were good, however the model deficiencies identified during the binary mixture analysis were also evident for the more complex mixture. One major conclusion drawn from the JP-8 surrogate studies is that a relatively simple surrogate mixture can adequately reproduce the complex behavior of full boiling range fuels like JP-8.

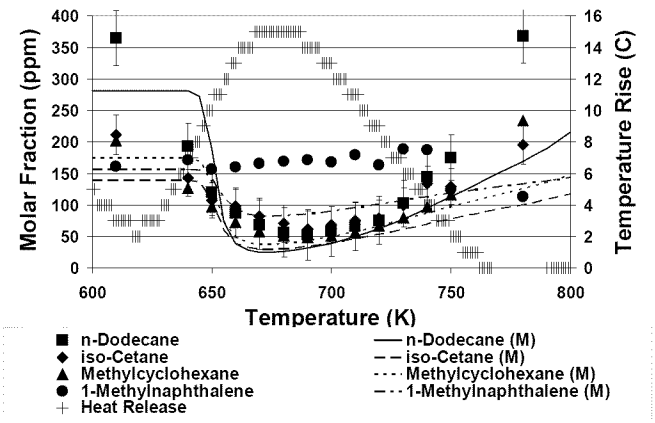

Figure 28: n-Dodecane, iso-cetane, methylcyclohexane, 1-methylnaphthalene, and temperature rise during the S1 surrogate CCD experiment at 175 ms.

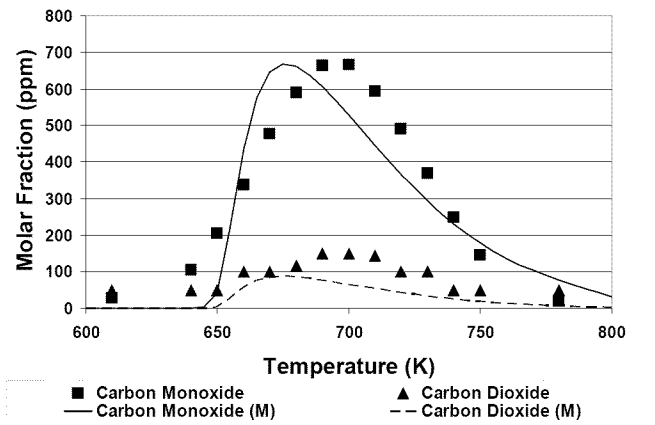

Figure 29: CO and CO_2 during the S1 surrogate CCD experiment at 175 ms.

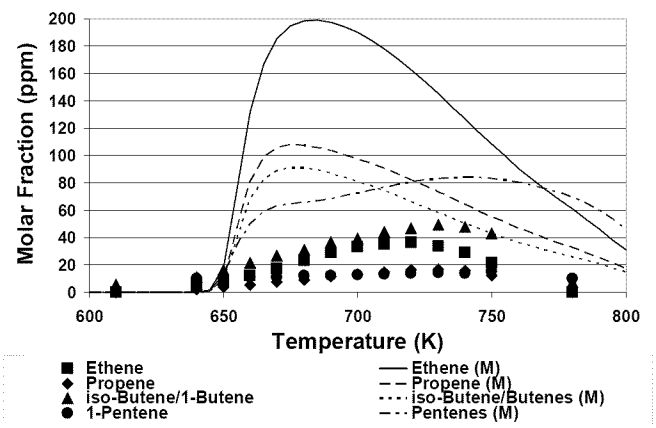

Figure 30: Major alkene intermediate during the S1 surrogate CCD experiment at 175 ms.

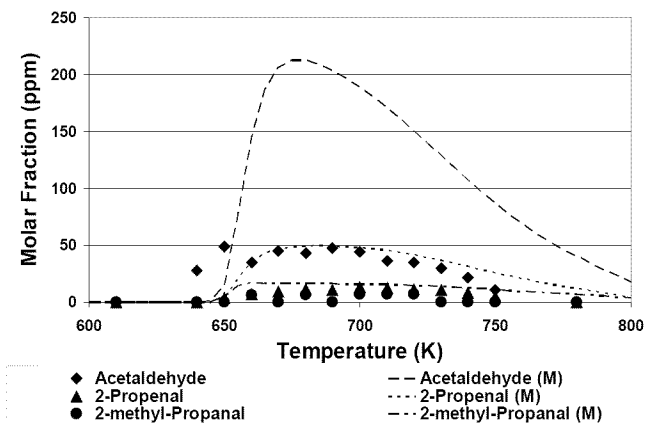

Figure 31: Major oxygenate intermediates during the S1 surrogate CCD experiment at 175 ms

I. Detailed Speciation of 1-Pentene Oxidation

Though 1-pentene is not a component of the JP-8 surrogate S1, it is a major alkene intermediate of many larger hydrocarbons and provides insight into the reactivity of larger alkenes that could be JP-8 surrogate components. The oxidation of 1-pentene was studied in the PFR from 610 to 800 K at a pressure of 8 atm under stoichiometric and dilute conditions at a residence time of 175 ms (CCD experiment). A clear NTC behavior was observed at 8 atm, equivalence ratio of 0.51, nitrogen dilution of 70%, and residence time of 175 ms. The start of NTC occurred at 710 K. Slightly more than 40% of the initial fuel concentration was converted to intermediate species near the start of the NTC region, Fig. 32. The species identified and quantified included CO, CO_2, ethene, formaldehyde, 1-propene, acetaldehyde, 1-butene, 1,3-butadiene, 2-propenal, 2-butanone, propanal, 1-pentene, n-pentane, 2-pentene (cis & trans), 1,3-pentadiene (cis & trans), cyclopentene, 3-buten-2-one, butanal, 2-methyl-furan, 2-propyl-oxiran, 2-pentenal, and 1-penten-3-ol. The most abundant of the hydrocarbon intermediates were formaldehyde, butanal, acetaldehyde, 2-propenal, ethene, and 1-propene. Representative results from the CCD experiment are presented in Figs. 33-35. Since formaldehyde was a major combustion intermediate and is not detectable with the FID, the MS signal was used to estimate its concentration. As a result, significant errors and scatter were observed in the estimated concentrations. For the other intermediate species, analysis of variance (ANOVA) and regression analysis were employed in an effort to quantify the errors associated with their quantification. The results of this analysis are included in the quantification graphs. Due to the lower sensitivity of the FID to oxygenated hydrocarbons, the errors associated with these compounds are larger than for non-oxygenated hydrocarbons. The identified intermediates accounted for 85% of the available carbon atoms (21380 C atoms). Note that this carbon balance only includes the carbon from positively identified compounds and does not include unidentified peaks of known molecular weight. Including these unidentified peaks, which based on MS fragmentation patterns should be mainly C_5 oxygenates, would increase the carbon balance to above 90%. It is also important to note that this analysis does not include other sources of errors, such as sample extraction errors, variations in reactor flow rates, possible decay of the samples prior to analysis, or errors resulting from carbon number correction factors. Nonetheless, the intermediate species were compared to an existing detailed kinetic model containing 3385 reactions and 837 species (Touchard et al, 2005). In general, the comparisons between the model and experimental results were good. However, the formation of CO, 1-propene, and butanal were under predicted while 1,3-butadiene was over predicted.

The results of a mechanistic analysis showed that 1-pentene decomposition occurs through both alkane and alkene type pathways. The preferred alkene type pathway was through HO_2 addition to the double bond, the

so-called "Waddington" mechanism, which is responsible for the formation of significant quantities of butanal and formaldehyde. The preferred alkane type pathways were through the decomposition of $\dot{C}_5H_8OOH$ to form 2-propenal and ethene and through the decomposition of $HOO\dot{C}_5H_7OOH$ to form acetaldehyde. Overall, the "Waddington" mechanism was the dominant pathway for the decomposition of 1-pentene. However, as the alkene molecules become larger and more like those present in kerosene and diesel fuels, it is reasonable to assume that radical addition to the double bond would become less important and should not be considered the only decomposition pathway.

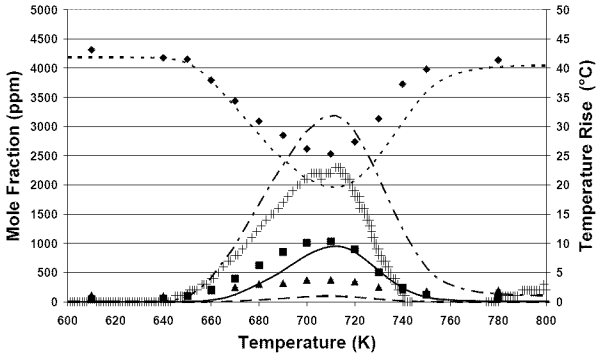

Figure 32: Species profiles and temperature rise as a function of reactor temperature for 1-pentene CCD experiment at 175 ms: (■,——) CO; (▲,— —) CO_2;(◆ ,.....) 1-Pentene; (+,— .) ΔT. Symbols are experimental results; lines are model predictions.

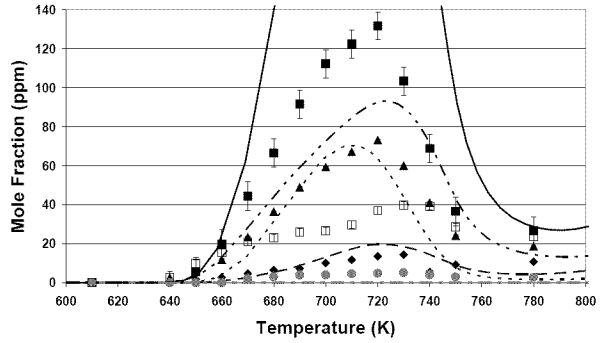

Figure 33: Alkene species profiles as a function of reactor temperature for 1-pentene CCD experiment at 175 ms:): (■,——) Ethene; (▲,— —) 1-Propene; (◆ ,.....) 1,3-Butadiene; (●,— .) 2-Pentene; (□,— . .) cis- & trans-1,3-Pentadiene. Symbols are experimental results; lines are model predictions.

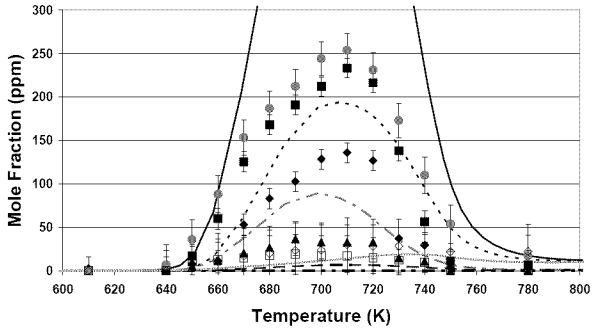

Figure 34: Aldehyde and ether species profiles as a function of reactor temperature for 1-pentene CCD experiment at 175 ms: (■,——) Acetaldehyde; (▲,— —) Propanal; (◆ ,.....) 2-Propenal; (●,— .) Butanal; (□,— . .) 2-Pentenal; (◇,.....) 2-propyl-Oxirane. Symbols are experimental results; lines are model predictions.

J. Detailed Speciation of n-Heptane Oxidation

n-Heptane was studied prior to n-dodecane so as to follow a logical progression in developing an understanding of the low temperature oxidation chemistry of high molecular weight straight chain alkanes. The oxidation of n-heptane was studied in the PFR from 600 - 800 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 100 ms (CCD experiment) and over a range of residence times (45 to 120 ms) at a temperature of 727 K and a pressure of 8 atm (CIT experiment). During the CCD experiments, a strong NTC behavior was observed to start at 703 K. During both CCD and CIT experiments, identification and quantification of the intermediate combustion species was completed for 14 samples taken throughout the low and intermediate temperature regime. Over 80% of the initial fuel concentration was converted to intermediate species near the start of the NTC region, Fig. 35. The species identified and quantified during these experiments included CO, CO_2, methane, ethene, formaldehyde, 1-propene, acetaldehyde, 1-butene, 1,3-butadiene, 2-propenal, propanal, 1-pentene, 3-buten-2-one, butanal, 1-hexene, 2-methyl-furan, 2-butenal, 1-Penten-3-one, pentanal, 1-heptene, trans-3-heptene, n-heptane, 2-heptene (cis & trans), 2-pentenal, 2-methyl-5-ethyl-tetrahydrofuran (cis & trans), 2-methyl-4-propyl-oxetan, 2-ethyl-3-propyl-oxiran, 2-methyl-3-butyl-oxiran, 2-propyl-tetrahydrofuran, 3-heptanone, and 2-heptanone. The major species identified were formaldehyde, acetaldehyde, 2-methyl-5-ethyl-tetrahydrofuran, propanal, ethene, and butanal. Since the species concentration profiles during the CCD and CIT experiments will be used for refinement of current n-heptane models, all of the measured species were compared to an existing detailed chemical model (Curran et al., 1998a). The detailed reaction mechanism included 2450 elementary reactions among 550 chemical species. The mechanisms had been updated with new chemical rate parameters and thermodynamic parameters by Curran, Pitz, and Westbrook since being published; the version used in this study was mechanism version 2b and thermodynamics version 2c. Representative results are presented in Figs. 36 – 38. In all of the graphs, (E) indicates experimental results and (M) indicates the model predictions. In general, the model predictions and experimental data were in good agreement.

The experimental results show that n-heptane mainly reacts to form aldehydes at these conditions before NTC. The major pathway identified for the formation of the aldehydes was the decomposition of the dihydroperoxyheptyl radical ($\dot{O}OC_7H_{14}OOH$). Furthermore, as the temperature increased beyond the start of the NTC region, the formation of the alkenes and ethers rapidly increased. This was due to the backward shift of the addition of O_2 to heptyl ($\dot{C}_7H_{15}$) and heptylhydroperoxy ($\dot{C}_7H_{14}OOH$) radicals, resulting in a larger

fraction of $\dot{C}_7H_{15}$ and $\dot{C}_7H_{14}OOH$ radicals being available for the formation of the conjugate alkenes and cyclic ethers.

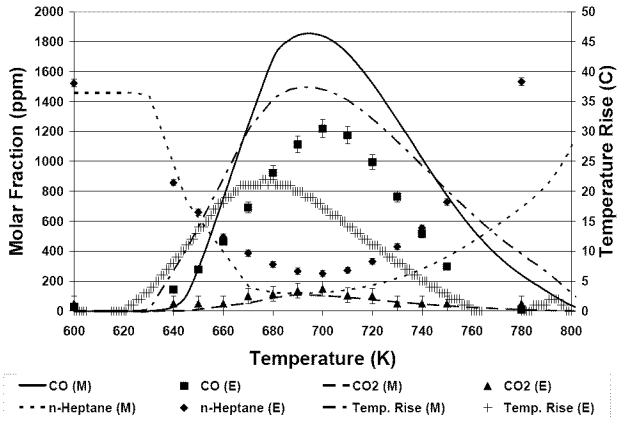

Figure 35: CO, CO_2, n-heptane, and temperature rise during the n-heptane CCD experiment at 100 ms.

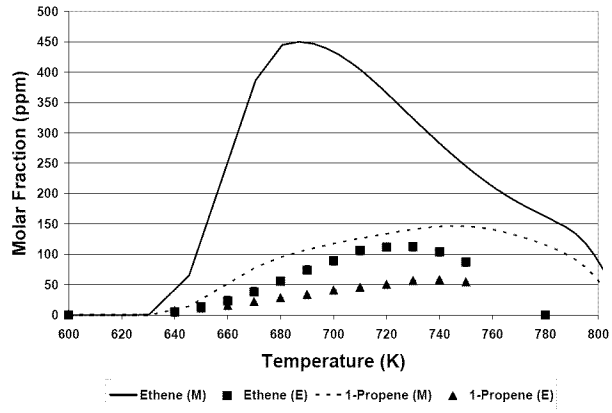

Figure 36: Major alkene intermediates during the n-heptane CCD at 100 ms.

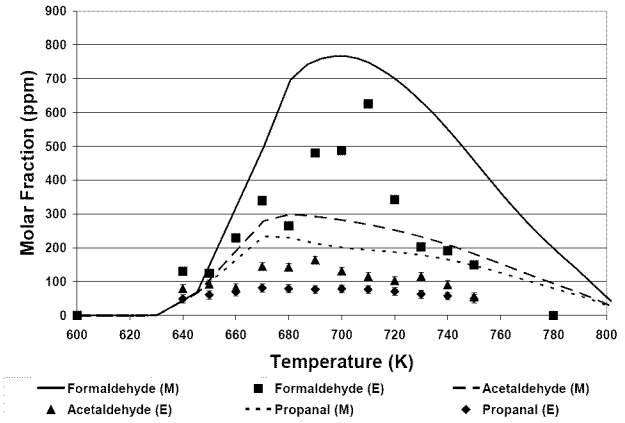

Figure 37: Major aldehydes intermediates during the n-heptane CCD at 100 ms.

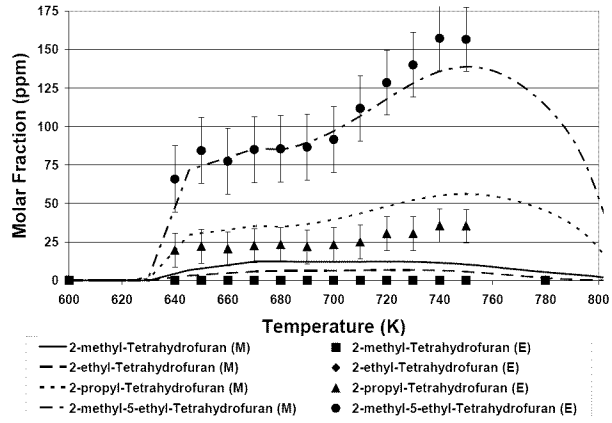

Figure 38: Major ether intermediates during the n-heptane CCD at 100 ms.

K. Detailed Speciation of iso-Octane Oxidation

In order to follow a logical progression to higher molecular weight iso-paraffins, iso-octane was studied prior to undertaking the iso-cetane experiments. The oxidation of 2,2,4-trimethyl-pentane (iso-octane) was studied in the PFR from 600 to 765 K at a pressure of 8 atm under stoichiometric and dilute conditions at a residence time of 250 ms (CCD Experiment) and over a range of residence times (125 to 330 ms) at a temperature of 676 K and a pressure of 8 atm (CIT Experiment). During the CCD experiments, a NTC behavior was observed to start at 665 K after minimal reactivity. During both CCD and CIT experiments, identification and quantification of the intermediate combustion species was completed for 13 samples taken throughout the low and intermediate temperature regime. Only 20% of the initial fuel concentration was

converted to intermediate species near the start of the NTC region, Figure 39. The species identified and quantified during these experiments included CO, CO_2, formaldehyde, 1-propene, acetaldehyde, 2-methyl-1-propene, 2-butanone, propanal, 2-propanone, 2-methyl-propanal, 2-methyl-2-propenal, 2,2-dimethyl-propanal, 4,4-dimethyl-1-pentene, 4,4-dimethyl-2-pentene (cis & trans), 2,4-dimethyl-1-pentene, 2,4-dimethyl-2-pentene, 2,2,4-trimethyl-pentane, 2,4-dimethyl-1,3-pentadiene, 2,4-dimethyl-furan, 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 4,4-dimethyl-2-pentanone, 2,2,4,4-tetramethyl-tetrahydrofuran, 2-tert-butyl-3-methyl-oxetan, 2,2,4-trimethyl-3-pentanone, 2-isopropyl-3,3-dimethyl-oxetan, and 2,2-dimethyl-hexanal. The major species identified were 2,2,4,4-tetramethyl-tetrahydrofuran, 2-isopropyl-3,3-dimethyl-oxetan, formaldehyde, 2-methyl-1-propene, 2-propanone, and 2-methyl-propanal. The species concentration profiles during the CCD and CIT experiments were compared to an existing detailed chemical model (Curran et al., 2002). The detailed reaction mechanism included 3600 elementary reactions among 860 chemical species. The mechanisms had been updated with new chemical rate parameters and thermodynamic parameters by Curran, Pitz, and Westbrook since being published; the version used in this study was mechanism version 2 and thermodynamics version 2b. Representative results are presented in Figures 39-42. In general, the model predictions and experimental data were in poor agreement, as the model significantly overpredicted the reactivity of iso-octane.

The experimental results showed that iso-octane mainly reacts to form cyclic ethers. The major pathway identified for the formation of the ethers was through the isooctylhydroperoxy ($i\dot{C}_8H_{16}OOH$) radical resulting in the formation of 2-isopropyl-3,3-dimethyl-oxetane and 2,2,4,4-tetramethyl-tetrahydrofuran.

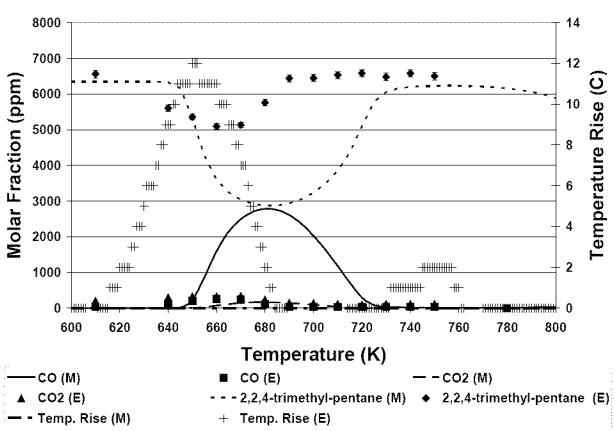

Figure 39: CO, CO_2, and fuel trends during the iso-octane CCD experiment at 250 ms.

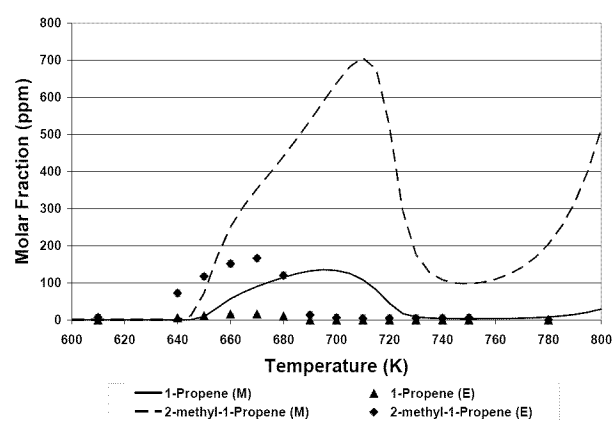

Figure 40: Major alkene intermediates during the iso-octane CCD at 250 ms.

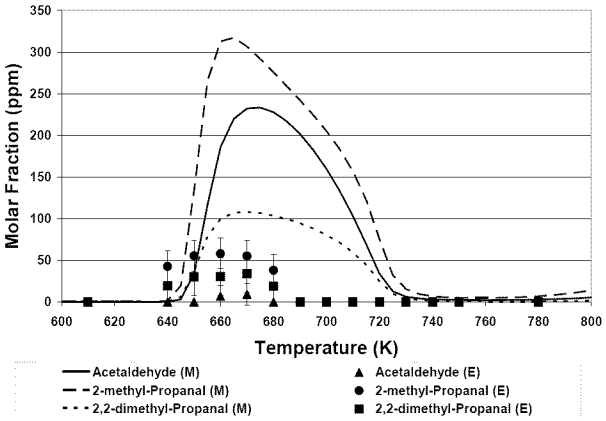

Figure 41: Aldehyde intermediates during the iso-octane CCD at 250 ms.

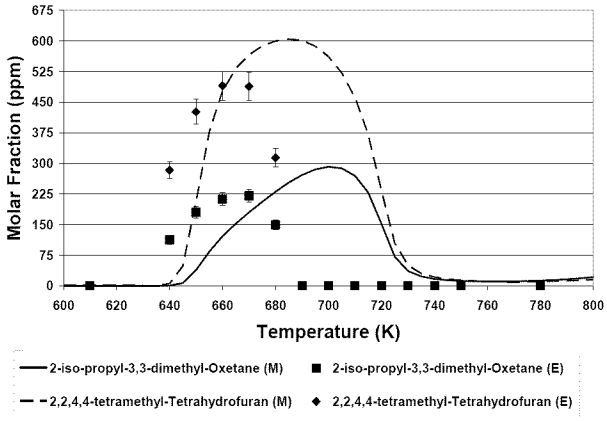

Figure 42: Major ether intermediates during the iso-octane CCD at 250 ms.

L. Detailed Speciation of Gasoline Surrogate Oxidation

A detailed study of a gasoline surrogate developed under an earlier ARO research program (Grant No. DAAG55-98-1-0286, Project No. 37699-EG) was conducted. The oxidation of the gasoline surrogate, GS4c-1, a mixture of 4.6% 1-pentene, 14% n-heptane, 49.6% iso-octane, and 31.8% toluene, was studied in the PFR from 600 to 780 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 225 ms (CCD Experiment) and over a range of residence times (110 to 280 ms) at a temperature of 722 K and a pressure of 8 atm (CIT Experiment). This mixture was formulated to have similar ratios of hydrocarbon functional groups, octane rating, and low and intermediate temperature reactivity as several industry standard full boiling range fuels, specifically RFA (Reference Fuel A) from the Auto/Oil Air Quality Improvement Research Program and a standard Ford test fuel (Khan, 1998). During the CCD experiment, a strong NTC behavior started at 693 K. This NTC region began approximately 15 °C lower than 1-pentene, and 10 °C lower than n-heptane, but considerably higher than iso-octane. The extent of fuel conversion varied for each of the constituents but the degree of conversion ranked according to the octane number of the fuel. For example, over 60% of the n-heptane (RON = 0) was consumed, but only 10% of the toluene (RON = 120) was consumed, Fig. 44. The species identified and quantified included CO, CO_2, ethene, formaldehyde, 1-propene, acetaldehyde, 2-methyl-1-propene,1,3-butadiene, 2-propenal, propanal, 2-propanone,1-pentene, 1,3-pentadiene (cis & trans), 2-methyl-propanal, 2-methyl-2-propenal, 3-buten-2-one, butanal, 2,2-dimethyl-propanal, 1-hexene, 4,4-dimethyl-1-pentene, 4,4-dimethyl-2-pentene (cis & trans), 2,4-dimethyl-1-pentene, 2,4-dimethyl-2-pentene, benzene, 1-penten-3-one, pentanal, 2,2,4-trimethyl-pentane, trans-3-heptene, n-heptane, 2-heptene (cis & trans), 2,4,4-trimethyl-1-pentene, 2,4,4-trimethyl-2-pentene, 2-pentenal, toluene, 4,4-dimethyl-2-pentanone, 2-methyl-5-ethyl-tetrahydrofuran (cis & trans), 2,2,4,4-tetramethyl-tetrahydrofuran, 2-tert-butyl-3-methyl-oxetan, 2-methyl-

4-propyl-oxetan, 2,2,4-trimethyl-3-pentanone, 2-isopropyl-3,3-dimethyl-oxetan, 2-propyl-tetrahydrofuran, 2,2-dimethyl-hexanal, benzaldehyde, and phenol. The major species identified were formaldehyde, 2,2,4,4-tetramethyl-tetrahydrofuran, 2-methyl-1-propene, 2-isopropyl-3,3-dimethyl-oxetan, benzaldehyde, and acetaldehyde. The results of the experiments were compared to a current detailed n-heptane/iso-octane model (Curran et al., 1998b). The detailed reaction mechanism included 4200 elementary reactions among 1050 chemical species. As before, the mechanisms had been updated with new chemical rate parameters and thermodynamic parameters by Curran, Pitz, and Westbrook since being published; the version used in this study was mechanism version 2 and thermodynamics version 2b. Model predictions and experimental data were generally in good agreement, particularly given the fact that no toluene submechanism was included and an abbreviated 1-pentene decomposition submechanism was used. Representative results are presented in Figs. 45 – 49.

During the oxidation of the surrogate, four major species were identified and associated with the oxidation of toluene: benzaldehyde, benzene, phenol, and ethyl-benzene that had not been previously measured. Analysis of the results indicated that all of the available toluene carbon was accounted for in these four species and that the benzene ring remains intact in the low and intermediate temperature regime. The mechanism forwarded by (Ciajolo et al., 1993) for the reaction of toluene in the low temperature regime does not predict the formation of phenol and ethyl-benzene. Therefore, three new pathways have been suggested to account for their formation, where ϕ indicates the phenyl group, as shown in Fig. 43.

$$\phi\dot{C}H_2 + \dot{C}H_3 \longleftrightarrow \phi CH_2CH_3$$

$$\dot{\phi} + \dot{O}H \longleftrightarrow \phi OH$$

$$\dot{\phi} + ROOH \longleftrightarrow \phi OH + R\dot{O}$$

Figure 43: Phenyl radical pathways.

Although not observed in our study, it has been suggested that interaction between the phenyl radicals formed during toluene oxidation and large hydrocarbon radicals may occur (Vanhove et al., 2004). Nevertheless, it appears that in the low and intermediate temperature regimes, toluene does actively react with the radical pool generated by the other compounds. The addition of toluene and 1-pentene also significantly increased the formation of lower molecular weight alkenes of n-heptane and iso-octane.

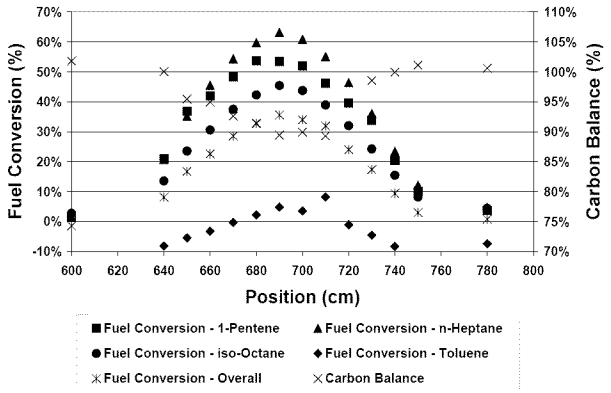

Figure 44: Carbon balance and fuel conversion calculations during the GS4c-1 CCD at 225 ms.

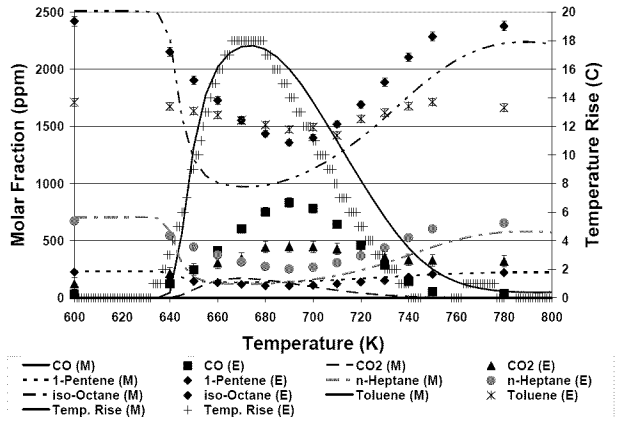

Figure 45: CO, CO_2, and GS4c-1 components and temperature rise during the GS4c-1 CCD at 225 ms.

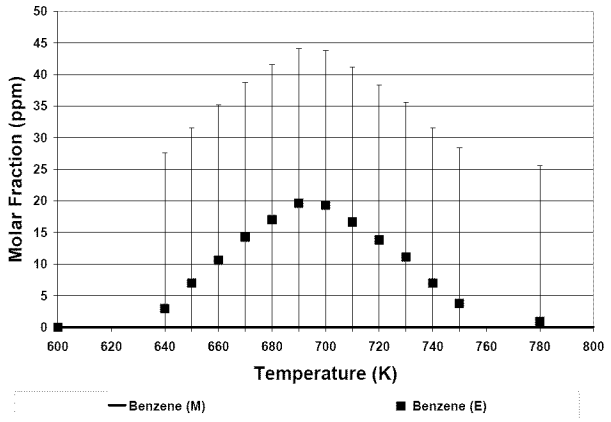

Figure 46: Major aromatic intermediate from the toluene fuel component during the GS4c-1 CCD at 225 ms.

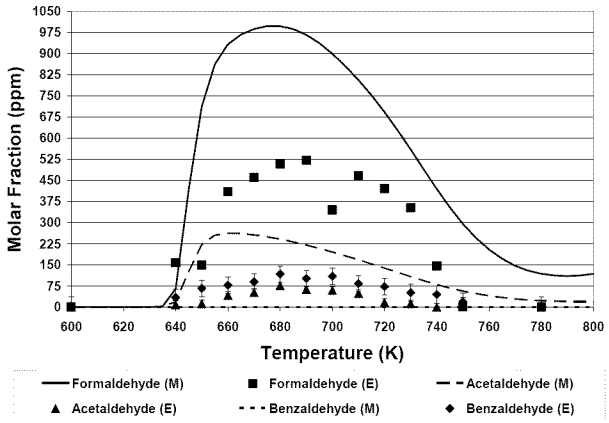

Figure 47: Major aldehyde intermediates during the GS4c-1 CCD at 225 ms.

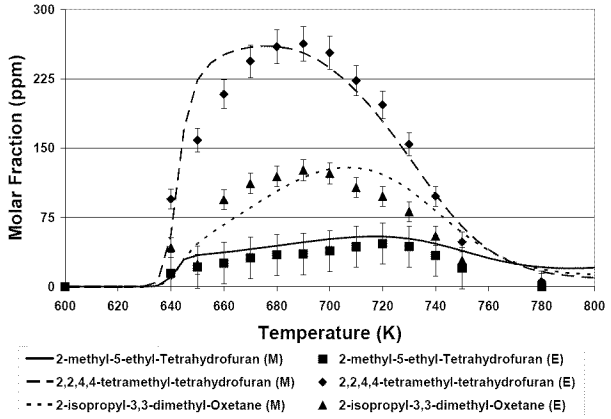

Figure 48: Major ether intermediates during the GS4c-1 CCD at 225 ms.

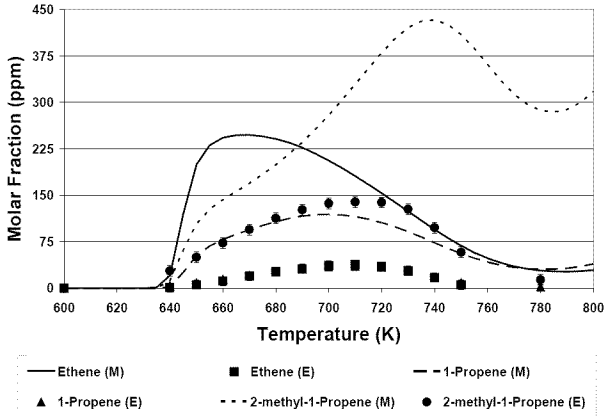

Figure 49: Major alkene intermediates during the GS4c-1 CCD at 225 ms.

M. Oxidation of Fischer-Tropsch JP-8 and a Fischer-Tropsch JP-8 Surrogate

Fischer-Tropsch JP-8 and two mixtures of n-decane and iso-octane were oxidized in the PFR in CCD experiments over the temperature range of 600 to 800 K at 8 atm pressure, 0.30 equivalence ratio, 120 ms residence time, and 80.0% N_2 dilution in the fuel. Figures 50 and 51 show the CO and CO_2, respectively, produced by the "average" petroleum-derived JP-8 (#3684) and Fischer-Tropsch JP-8 (#4734) samples. The NTC region for petroleum-derived JP-8 started at 692 K, where it produced 600 ppm CO. The NTC region for Fischer-Tropsch JP-8 started at approximately the same temperature, 690 K, yet it produced much more CO, 890 ppm.

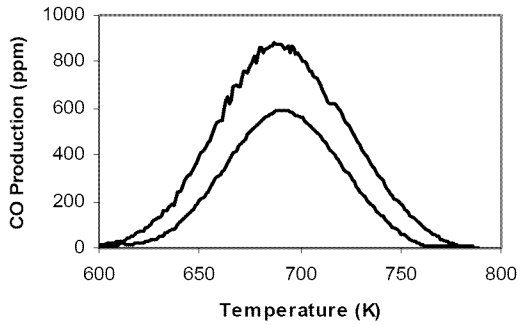

Figure 50: CO production of Fischer-Tropsch (upper) and petroleum-derived (lower) JP-8's in the PFR.

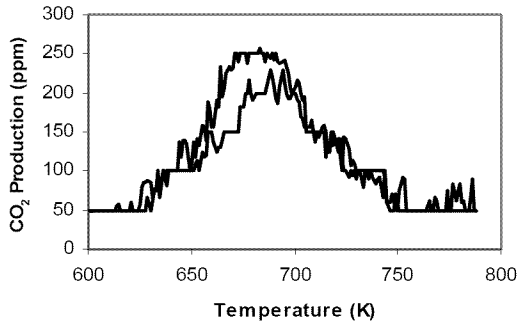

Figure 51: CO_2 production of Fischer-Tropsch (upper) and petroleum-derived (lower) JP-8's in the PFR.

While petroleum-derived JP-8 consists of approximately 60% alkanes, 20% cycloalkanes, and 20% aromatics, Fischer-Tropsch JP-8 consists of 100% alkanes. The petroleum-derived JP-8 formed significantly less CO because the addition of 40% cycloalkanes and aromatics produce a fuel with much lower cetane index and also because the aromatics may act as radical scavengers. This implies that different surrogates may be necessary for petroleum-derived and Fischer-Tropsch JP-8's. Thus, while our 4-component JP-8 surrogate, as defined above, may be appropriate for petroleum-derived JP-8, the development of an alternative surrogate for Fischer-Tropsch JP-8 is necessary.

As a first step, the low temperature reactivity of the linear and branched alkanes n-decane and iso-octane, respectively, was investigated to evaluate these potential components of a surrogate. Figure 52 shows two different binary blends, a 59.4% n-decane / 40.6% iso-octane blend developed to target the cetane index of Fischer-Tropsch JP-8 and a 53.1% n-decane / 46.9% iso-octane blend developed to target the low and intermediate temperature reactivity of Fischer-Tropsch JP-8. Figure 53 shows the latter blend compared to the Fischer-Tropsch JP-8.

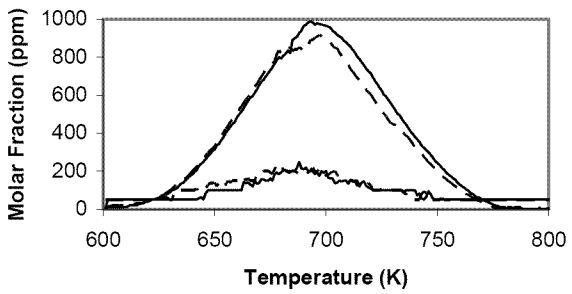

Figure 52: CO (upper 2 lines) and CO_2 (lower 2 lines) production of 59.4% n-decane / 40.6% iso-octane (—) and 53.1% n-decane / 46.9% iso-octane (- -).

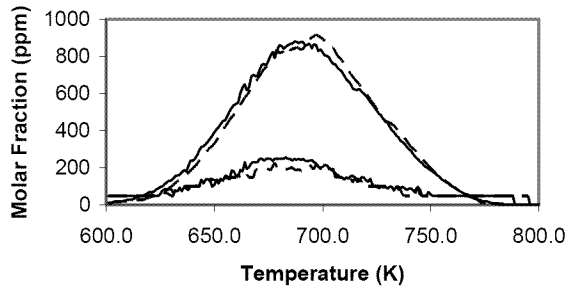

Figure 53: CO (upper 2 lines) and CO_2 (lower 2 lines) production of 53.1% n-decane / 46.9% iso-octane (- -) and F-T JP-8 (—).

N. Oxidation of Other Proposed Fuel Surrogates

In cooperation with the Surrogate Fuel Working Groups on diesel and jet fuels (a collaboration of university, industry, and national laboratory researchers), experiments were conducted in the PFR and the engine to examine several other potential surrogate fuel components and blends. Figure 54 compares four such experiments. The 1:1:1 mixture of n-decane, n-butylcyclohexane, and n-butylbenzene was initially suggested as a potential diesel fuel surrogate to mimic the composition and properties of diesel fuel, and a 2:1:1 mixture was suggested as a possible jet fuel surrogate. However, both mixtures were significantly more reactive than JP-8. Furthermore, there is currently no n-butylcyclohexane kinetic model and only an underdeveloped model for n-butylbenzene, so those components were replaced with methylcyclohexane and toluene, respectively, to produce a surrogate for immediate testing and possible modeling. After further examining mixtures of n-decane / n-butylcyclohexane / toluene and n-decane / methylcyclohexane / n-butylbenzene, each at a 1:1:1 ratio, it was observed that of the four cycloalkanes and aromatics, n-butylcyclohexane was the most reactive. Figure 55 shows neat runs of n-decane and n-butylcyclohexane. The high reactivity of neat n-butylcyclohexane contrasts with neat methylcyclohexane, which is not reactive at the same conditions. n-Butylbenzene was also run in the PFR, but produced no CO or CO_2. Furthermore, by comparing the CO production of neat n-decane and neat n-butylcyclohexane with the 1:1:1 mixtures of n-decane / n-butylcyclohexane / n-butylbenzene and n-decane / n-butylcyclohexane / toluene, it was observed that the CO productions of the mixtures was less than the neat runs would predict if it were assumed that the aromatics produced no CO. Thus, the aromatics reduce the CO production in mixtures with aliphatics, by approximately 100 ppm CO at these conditions. The high levels of reactivity shown by the n-decane/n-butylcyclohexane/n-butylbenzene mixtures may be due in part by the reactivity of n-butylcyclohexane, which had not been studied previously and did not show behavior similar to

methylcyclohexane. Overall, these experiments are aiding the Surrogate Fuel Working Groups in refining the selection of surrogate components and mixtures.

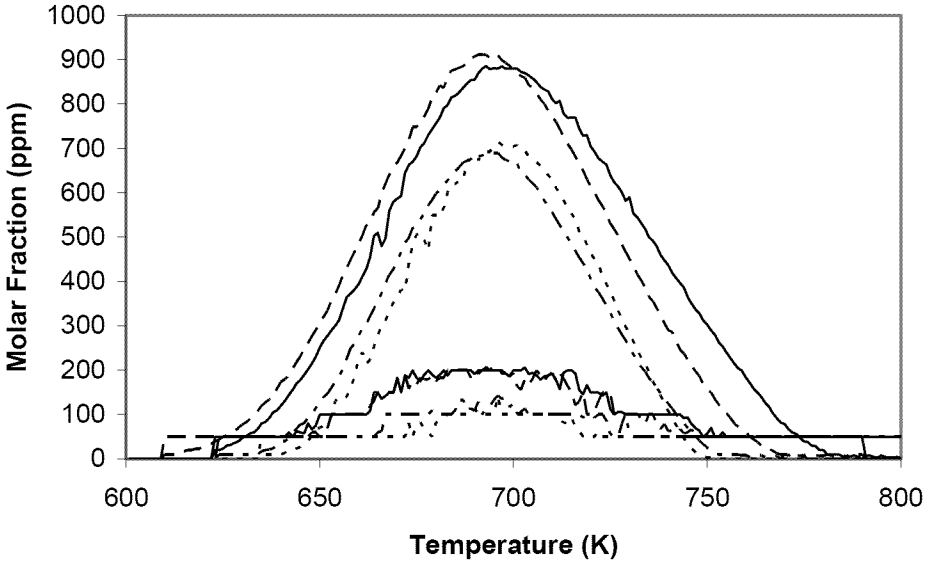

Figure 54: CO (upper 4 lines) and CO_2 (lower 4 lines) for 1:1:1 mixtures of n-decane / n-butylcyclohexane / n-butylbenzene (dashed line), n-decane / n-butylcyclohexane / toluene (solid line), n-decane / methylcyclohexane / n-butylbenzene (dotted line), and n-decane / methylcyclohexane / toluene (dot-dash line).

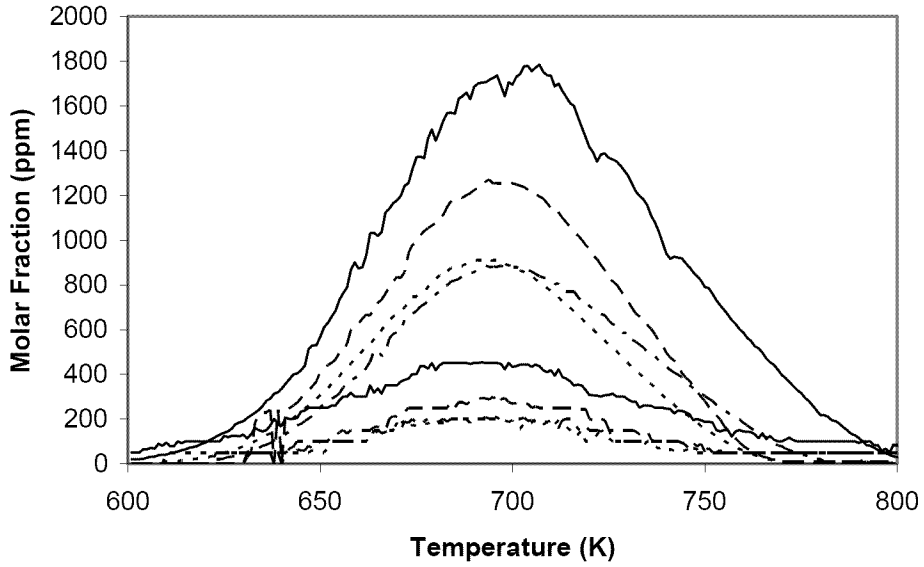

Figure 55: CO (upper 4 lines) and CO_2 (lower 4 lines) of n-decane (solid line), n-butylcyclohexane (dashed line), 1:1:1 n-decane / n-butylcyclohexane / n-butylbenzene (dotted line), and 1:1:1 n-decane / n-butylcyclohexane / toluene (dot-dash line).

VI. PUBLICATIONS AND TECHNICAL REPORTS

a) Papers Published in Peer-reviewed Journals

Agosta, A., N. P. Cernansky, D. L. Miller, T. Faravelli, and E. Ranzi. "Reference components of jet fuel: kinetic modeling and experimental results." *Experimental Thermal and Fluid Science* 28:701-708, 2004.

Lenhert, D.B. "The oxidation of a gasoline fuel surrogate in the negative temperature coefficient region." Master of Science Thesis, Drexel University, Philadelphia, PA, 2004.

Lenhert, D.B. "The oxidation of JP-8 and its surrogates in the low and intermediate temperature regime." Doctor of Philosophy Thesis, Drexel University, Philadelphia, PA, 2004.

Zheng, J., D.L. Miller, and N.P. Cernansky. "A global reaction model for the HCCI combustion process." Paper No. SAE 2004-01-2950, *SAE Transactions, Journal of Engines*, 2004.

Zheng, J., D.L. Miller, and N.P. Cernansky. "Two types of autoignition and their engine applications." Paper No. SAE 2005-01-0178, 2005 SAE Congress, 2005.

Lenhert, D.B., D.L. Miller, and N.P. Cernansky. "The oxidation of JP-8, Jet-A, and their surrogates in the low and intermediate temperature regime at elevated pressures." *Combustion Science and Technology*, 2006, in press.

b) Papers Published in Non-peer-reviewed Journals or in Conference Proceedings

Agosta, A., D.B. Lenhert, D.L. Miller, and N.P. Cernansky. "Development and evaluation of a JP-8 surrogate that models preignition behavior in a pressurized flow reactor." Paper No.USSCI-03-E07, 3rd Joint Meeting of the U.S. Sections of the Combustion Institute, Chicago, Illinois, March 16-19, 2003.

Lenhert, D.B., A.R. Khan, N.P. Cernansky, D.L. Miller, and K.G. Owens. "The oxidation of an ISF surrogate and its components in the negative temperature coefficient region." Paper No. USSCI-03-B16, 3rd Joint Meeting of the U.S. Sections of the Combustion Institute, Chicago, Illinois, March 16-19, 2003.

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Lenhert, D.B., N.P. Cernansky, and D.L. Miller. "The oxidation of large molecular weight hydrocarbons in a pressurized flow reactor." Paper No. USSCI-05-A22, 4th Joint Meeting of the U.S. Sections of the Combustion Institute, Philadelphia, PA, March 21-23, 2005.

Johnson, R., R. Natelson, M. Kurman, D.L. Miller, and N.P. Cernansky. "The auto-ignition of JP-8, Jet A, and selected fuel components in a single cylinder engine." Paper No. WSSCI-05F-55, Fall Meeting of the Western States Section of the Combustion Institute, Stanford, CA, October 17-18, 2005.

Kurman, M.S., R.H. Natelson, N.P. Cernansky, and D.L. Miller. "Oxidation of Fischer-Tropsch JP-8 in the low and intermediate temperature regimes." Paper No. CSSCI-06S-21, Spring Technical Meeting of the Central States Section of the Combustion Institute, Cleveland, OH, May 21-23, 2006.

c) Papers Presented at Meetings, but not Published in Conference Proceedings

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Lenhert, D.B., N.P. Cernansky, D.L. Miller, and K.G. Owens. "The oxidation and interaction of a gasoline surrogate and its components in the low and intermediate temperature regime." WIPP 4F1-06, 30th International Symposium on Combustion, Chicago, IL, July 25-30, 2004.

Zheng, J., D.L. Miller, and N.P. Cernansky. "A global reaction model for the HCCI combustion process." WIPP 4F1-18, 30th International Symposium on Combustion, Chicago, IL, July 25-30, 2004.

Lenhert, D.B., D.L. Miller, and N.P. Cernansky. "n-Dodecane/methylcyclohexane oxidation in the low and intermediate temperature regime." WIPP 2D-28, 31st International Symposium on Combustion, Heidelberg, Germany, August 6-11, 2006.

d) Manuscripts Submitted, but not Published

Lenhert, D.B., A.R. Khan, S.K. Prabhu, D.L. Miller, and N.P. Cernansky. "The oxidation of gasoline and gasoline surrogates in the negative temperature coefficient region." Submitted to *Combustion and Flame*, presently under revision.

Lenhert, D.B., D.L. Miller, N.P. Cernansky, and K.G. Owens. "The oxidation of a gasoline surrogate in the negative temperature coefficient region: Part I: Neat surrogate components." Submitted to *Combustion and Flame*, under review.

Lenhert, D.B., D.L. Miller, N.P. Cernansky, and K.G. Owens. "The oxidation of a gasoline surrogate in the negative temperature coefficient region: Part II: Surrogate mixture." Submitted to *Combustion and Flame*, under review.

e) Technical Reports submitted to ARO

None.

VII. ALL PARTICIPATING SCIENTIFIC PERSONNEL

N.P. Cernansky – Co-Principal Investigator
D.L. Miller – Co-Principal Investigator

D.B. Lenhert – Research Assistant, M.S. / Ph.D. (July 2004 / December 2004)
X. Gong – Research Assistant, Ph.D. (August 2005)
J. Zheng – Research Assistant, Ph.D. (August 2005)
M.S. Kurman – Research Assistant, M.S. / Ph.D. (M.S. expected August 2007)
R.H. Natelson – Research Assistant, M.S. / Ph.D. (M.S. expected August 2007)

VIII. REPORT OF INVENTIONS

None.

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