

The Oxidation of Large Molecular Weight Hydrocarbons in a Pressurized Flow Reactor

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Abstract

The preignition behavior of several large molecular weight hydrocarbons, neat and binary mixtures, has been examined in a pressurized flow reactor in the low and intermediate temperature regime (600 – 800 K) at elevated pressures (8 atm). The hydrocarbons examined included n-dodecane, 2,2,4,4,6,8,8-heptamethyl-nonane (iso-cetane), methylcyclohexane, and 1-methylnaphthalene. For each experiment, gas-phase samples were extracted to identify and quantify the major oxidation products. All of the fuels exhibited a strong negative temperature coefficient (NTC) behavior at the conditions investigated. The quantification showed that the majority of the intermediates of n-dodecane and iso-cetane were fuel fragments less than half the original fuel size. Methylcyclohexane dehydrogenated instead of fragmenting. The results were compared to a lumped mechanism developed by Ranzi and Faravelli at Politecnico di Milano [1]. For n-dodecane and iso-cetane, the agreement between the mechanism and experiments were generally acceptable, but the model overestimated the formation of lower molecular weight fragments. The agreement for methylcyclohexane was considerably worse, as the mechanism improperly assumed that the fuel fragments instead of dehydrogenates. Several improvements to the mechanism are suggested based upon the experimental evidence.

Introduction

Both aviation and diesel fuels are complex mixtures formulated to meet general physical property specifications, not a specific composition. As a result, similarly specified fuels can be formulated by a virtually infinite variety of hydrocarbon mixtures. The relative proportion of the various hydrocarbon classes is constrained by the property requirements in the specifications. However, there are some fundamental differences between aviation and diesel fuels. Diesel fuels are generally either a distillate blend, a distillate and kerosene blend, or a kerosene blend depending on the grade of diesel; i.e., DF-2, DF-1, or arctic grade diesel fuel (DF-A). Whereas, aviation fuels, i.e. JP-8, Jet-A, or Jet A-1, are typically kerosene-type fuels. The fundamental difference between kerosene-type and distillate-type fuels is the temperature at which they are separated in a distillation column. The hydrocarbons in JP-8 are typically in the C₉- C₁₆ range, while, the hydrocarbons in DF-2, are typically in the C₁₀- C₂₂ range. As a result, JP-8 has a lower average empirical formula of C₁₁H₂₁ [2] as compared to DF-2 diesel at \approx C₁₄H₂₄.

Due to the complexity and variability of these full-boiling range fuels, researchers have developed simplified blends, or surrogates, to study the combustion processes [2]. Typically, the surrogate blends representative compounds from each of the major hydrocarbon classes, of appropriate molecular weight and relative fraction, such that the surrogate can mimic the desired behavior of the full boiling range fuel. For JP-8, which nominally consists of 60% alkanes, 20% naphthenes, 18% aromatics, and 2% alkenes [2], the surrogates include one or two representative compounds from each of these classes [3-5]. However, very few experimental investigations have examined the oxidation of these large hydrocarbons at elevated pressures, which is an important element in modeling combustion in engine systems, including autoignition, flame propagation, and pollutant emissions.

In the present work, the oxidation of neat n-dodecane, and binary mixtures of n-dodecane and 2,2,4,4,6,8,8-heptamethyl-nonane (iso-cetane), n-dodecane and methylcyclohexane, and n-dodecane and 1-methylnaphthalene were investigated in the low and intermediate temperature regime (600 – 800 K) at elevated pressures, 8 atm, in a flow reactor. The main objective was to develop a fundamental understanding of the preignition oxidation of large molecular weight hydrocarbons and to extend the previous experiments and modeling of Agosta et al. [1].

Experimental Facility

All of the experiments to investigate the oxidation chemistry of large molecular weight hydrocarbons were carried out in Drexel's Pressurized Flow Reactor (PFR) facility over a range of temperatures (600-800 K), equivalence ratios, and diluent

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concentrations at 8 atm. Detailed descriptions of the experimental facility and experimental techniques have been reported earlier [6-8] and only the relevant information is presented here. The operating pressure and temperature regimes accessible for investigation are 2-20 atm and 500-1000 K. The key operational feature of the reactor is a quartz reactor tube (2.5 cm in diameter) within a pressure vessel. To achieve high reaction pressures the inside and the annulus between the quartz reactor and pressure vessel are maintained at the same pressure. Oxygen and nitrogen are metered through mass flow controllers (5% uncertainty) and heated before entering the reactor. Fuel was metered as a liquid by a high pressure syringe pump and vaporized by a heated nitrogen stream before entering the reactor. The vaporized fuel and oxidizer streams are mixed at the inlet of the reactor by an offset annular jet mixing nozzle. The pressure of the system was controlled by a stainless steel metering valve and was measured by pressure transducers placed at the entrance and exit of the reactor. Bead heaters wrapped around the circumference of the pressure vessel minimize the axial temperature variations to less than 5-10 °C along the axial length of the reactor.

During the experiments, samples of the reacting mixture were withdrawn from the reactor's centerline at selected axial locations with a glass-lined, water-cooled gas sampling probe with an integrated thermocouple for the measurement of the sample point temperature. Position of the probe was set by a computer controlled, stepper motor driven, linear positioning table. The quenched gas samples from the probe may be directed to a variety of permanent gas analyzers for CO and CO₂ measurements, to an online Fourier Transform Infrared Spectrometer (FT-IR), or to a heated sample storage unit for offline gas chromatography (GC) and gas chromatography with mass spectroscopy (GC/MS) analysis.

In order to obtain information on the reactivity behavior of the selected hydrocarbons and mixtures in the low and intermediate temperature regions, two types of experiments were conducted, a controlled cool down (CCD) and a constant inlet temperature (CIT) experiment.

For CCD experiments, the reactor was preheated using compressed air at atmospheric pressure flowing at the same bulk flow rate as the experiment. After heated to the desired temperature, the air flow was transitioned to only nitrogen and pressurized, after which the fuel stream was introduced and calibrated using the FT-IR. Following calibration, a portion of the nitrogen steam was replaced by oxygen. Once the system has stabilized, the reactor heating was discontinued which produces a cooldown rate of approximately 2 – 5 °C/min. As the reactor cools, the gas density increases, thereby increasing the residence time. In order to maintain constant residence time samples, the computer continuously adjusts the probe position. As the reactor cools, samples were extracted and analyzed. From a single CCD experiment, the reactivity behavior over a range of temperatures at a fixed pressure and residence time is obtained, creating the "reactivity map" of the fuel.

For CIT experiments, the same heating and fuel calibration procedure outlined for the CCD was followed, but the reactor was heated to a selected inlet temperature and heating was not discontinued at the start of the experiment. Instead, samples were extracted and analyzed at discrete axial locations, i.e. residence times. From a CIT experiment, the reaction intermediates can be determined over a range of residence times at a fixed pressure and temperature.

A Finnigan mass spectrometer (MS) coupled to a Finnigan gas chromatograph with flame ionization detector (FID) was used to analyze each offline sample. For chromatographic separation, a Supelco Petrocol DH column (100 meter, 0.5 μm film thickness, 0.25 mm OD, 1250 Phase Ratio (β)) was installed in the GC. To permit simultaneous identification and quantification, the flow at the end of the column was split between a FID and the MS. Two methods, retention time matching and/or mass spectrum matching, were utilized to identify of the unknowns. The spectra for the unknown compounds were compared to the NIST'02 database that contains spectra of 147,198 compounds. Quantification of the identified compounds was accomplished using the FID. Many of the compounds identified did not have associated calibration curves due to the inability to purchase standards. The lack of standards was especially prevalent for oxygenates and to a lesser extent for branched alkanes and alkenes. As a result, quantification of these compounds was accomplished employing the calibration curve of a structurally similar molecule.

Neat n-Dodecane Oxidation

The oxidation of neat n-dodecane (99+%), C₁₂H₂₆, was studied from 600 to 800 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 120 ms (CCD experiment) and over a range or residence times (40 to 150 ms) at a temperature of 683 K and a pressure of 8 atm (CIT experiment). During the CCD experiments, a strong NTC behavior was observed to begin at 695 K.

For both of the CCD and CIT experiments, 15 gas samples were extracted and analyzed. The species identified and quantified included CO, CO₂, 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. Although these species only account for approximately half of the available carbon atoms, significant insight into the oxidation mechanism for n-dodecane can be achieved, as this is one of the first 'detailed' studies at these conditions.

During the oxidation, when n-dodecane fragmented to C₁ to C₁₁ hydrocarbons, it principally fragmented into significantly smaller hydrocarbons. In other words, most of the oxidation fragments (both alkenes and aldehydes) were in the C₁ to C₆ range, not the C₇ to C₁₁ range. Consequently, the major intermediates identified and quantified were acetaldehyde, ethane, 1-hexene, propanal, and 1-propene, respectively. 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. However, not all of the fuel fragmented to C_1 to C_6 intermediates, as shown by the significant concentrations of dodecene isomers. Furthermore, the research by Blin-Simiand et al. [9] has suggested that large alkanes, such as n-dodecane, easily isomerize and may form C_{12} species with one or more carbonyl groups. As these species would have very high boiling points, it is likely that they would have condensed during the sampling or storage processes. Although speculative in nature, this may account for the minor residue observed in the sampling lines after the n-dodecane experiments and part of the discrepancy in the closure of the carbon balance.

The speciation was compared to a lumped model by Ranzi and Faravelli [1]. The lumped mechanism included 7400 reactions among 276 species. Model predictions and experimental data were generally in passable agreement, given the significant simplifications made during the development of the model. The model does a reasonable job describing the decomposition of the fuel and the formation of CO. However, the model significantly overpredicts the formation of the smaller alkenes and aldehydes. The experimental results suggest that a C_6 radical species should replace the current C_7 radicals, due to the significantly larger formation of 1-hexene over 1-heptene. Secondly, the mechanism assumed that conjugate alkenes are not formed, yet, considerable formation was observed experimentally. Although not measured during these experiments, the very low carbon balance may suggest that C_{12} oxygenates were formed. Therefore, pathways for the formation of the C_{12} alkenes should be included in the mechanism and possibly some C_{12} oxygenate pathways. Nevertheless, the model is a noteworthy first step at developing mechanisms for higher molecular weight hydrocarbons. Several representative graphs of the intermediate species and associated model predictions are shown in Figure 1. The experimental data are shown as symbols and model (M) predictions as lines.

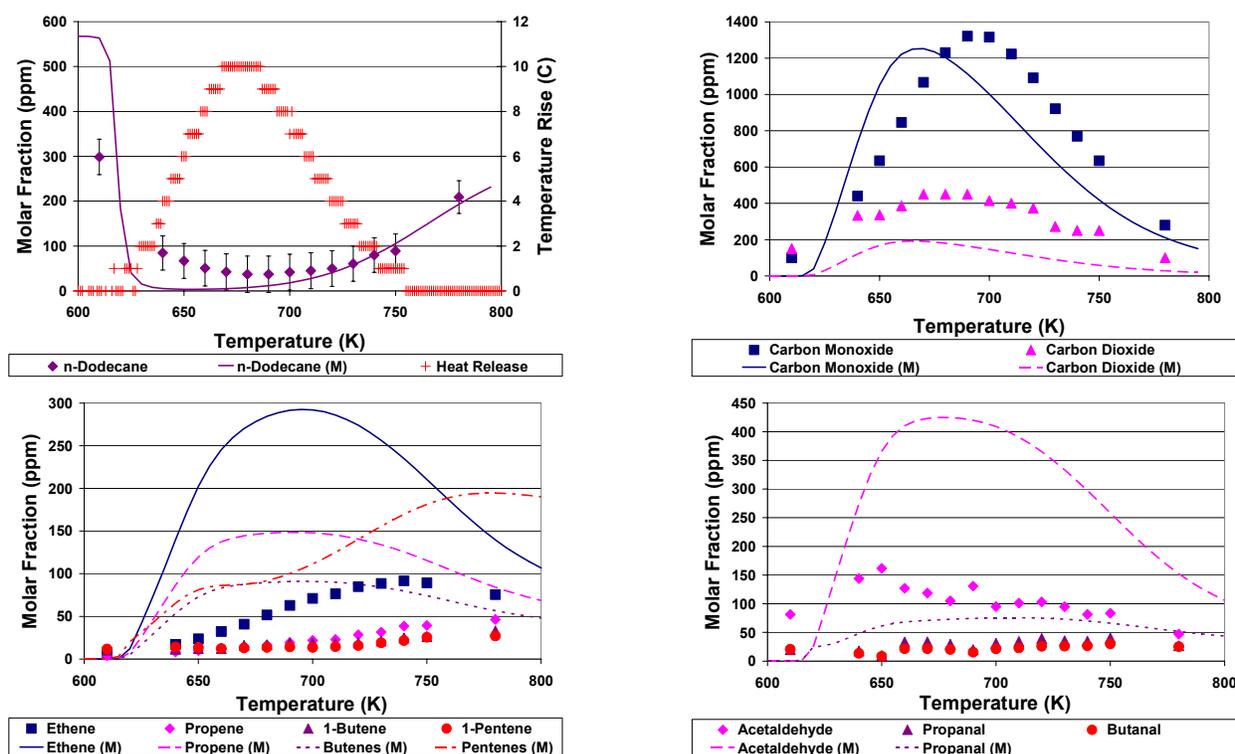


Figure 1: Concentration profiles and model predictions (M) for n-dodecane and a few of the intermediates plus the temperature rise during the n-dodecane CCD experiment.

iso-Cetane Mixture Oxidation

The oxidation of the volumetric blend of 40% n-dodecane and 60% iso-cetane (98+%), $C_{16}H_{32}$, was studied from 600 to 800 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 175 ms (CCD experiment) and over a range or residence times (65 to 220 ms) at a temperature of 687 K and a pressure of 8 atm (CIT experiment). During the CCD experiments, a strong NTC behavior was observed, the start of which occurred at 690 K.

Detailed speciation measurements were obtained during the CCD and CIT experiments. The 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-propenal, 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 ($C_{11}H_{22}$), 2,4,4,6,6-

pentamethyl-1-heptene, several dodecene isomers, several hexamethyl-nonene isomers ($C_{15}H_{30}$), n-dodecane, and iso-cetane. As with n-dodecane, when iso-cetane fragmented, it primarily formed significantly smaller hydrocarbon fragments. 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-pentenes (2,2,4-trimethyl-1-pentene and 2,2,4-trimethyl-2-pentene), and 4,4-dimethyl-2-pentanone. Mechanistic analysis showed that the primary hydrogen bonds at the ends of the iso-cetane molecule were the sites for the majority of the hydrogen abstractions.

One significant observation that can be made from the n-dodecane and iso-cetane experiments was that when the respective fuels fragmented they preferentially fragment to smaller hydrocarbons, and most of the fragments are half the original size of the molecule or smaller. A similar fragmentation mode was observed during the n-decane studies of Bales-Gueret et al. [10]. However, it is unclear how much of the original structure of the iso-cetane fuel molecule remains intact in the form of oxygenates and conjugate alkenes as no C_{16} intermediates were identified and quantified. As a result, it is difficult to conclusively suggest that fragmentation is the primary mode of decomposition. However, relating the iso-cetane results to that of neat n-dodecane would suggest that C_{16} intermediates are formed. Model predictions using the Ranzi and Faravelli [1] mechanism and experimental data were generally in reasonable agreement. However, the model significantly overpredicted decomposition of iso-cetane and the formation of the smaller alkenes and aldehydes. Several representative graphs of the intermediate species and associated model predictions are shown in Figure 2.

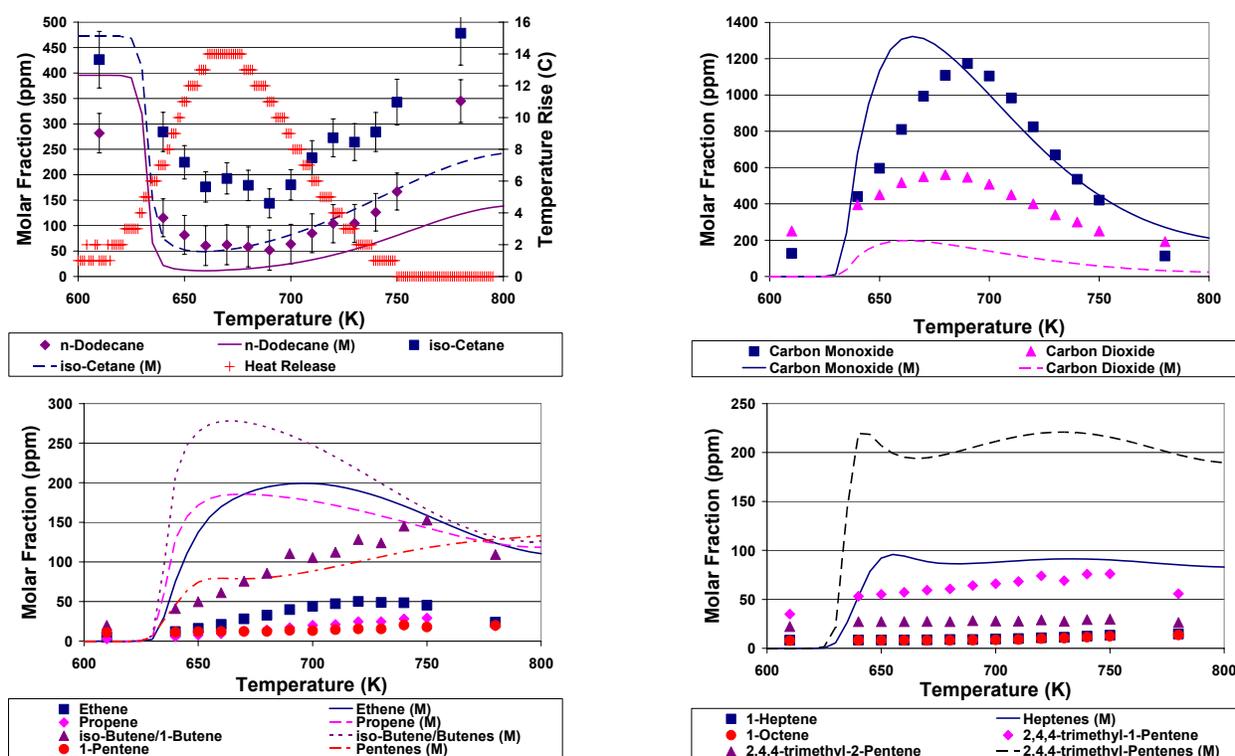


Figure 2: Concentration profiles and model predictions (M) for n-dodecane, iso-cetane, and a few of the intermediates plus the temperature rise during the n-dodecane/iso-cetane CCD experiment.

Methylcyclohexane Mixture Oxidation

The oxidation of the binary mixture of 37% n-dodecane and 63% methylcyclohexane (99+%), C_7H_{14} , was studied from 600 to 800 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 120 ms (CCD experiment) and over a range of residence times (40 to 150 ms) at a temperature of 668 K and a pressure of 8 atm (CIT experiment). During the CCD experiments, a strong NTC behavior was observed beginning at 695 K. However, compared to the other fuels, the reactivity map was significantly narrower.

For the CCD and CIT experiments, 15 gas samples were extracted and analyzed. 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 methylcyclohexane undergoes dehydrogenation rather than ring rupture in the low and intermediate temperature regime, producing significant concentrations of the methyl-1-cyclohexene isomers and the $C_7H_{10}O$ oxygenates.

Mechanistic analysis could not conclusively establish the preferred abstraction site, which is not entirely surprising as the bond energy of the ring hydrogens is nearly identical. Species quantification was compared to the lumped mechanism by Ranzi and Faravelli [1]. Model predictions were extremely poor given that the model incorrectly assumes that methylcyclohexane fragments, instead of dehydrogenates. Several representative graphs of the intermediate species and associated model predictions are shown in Figure 3.

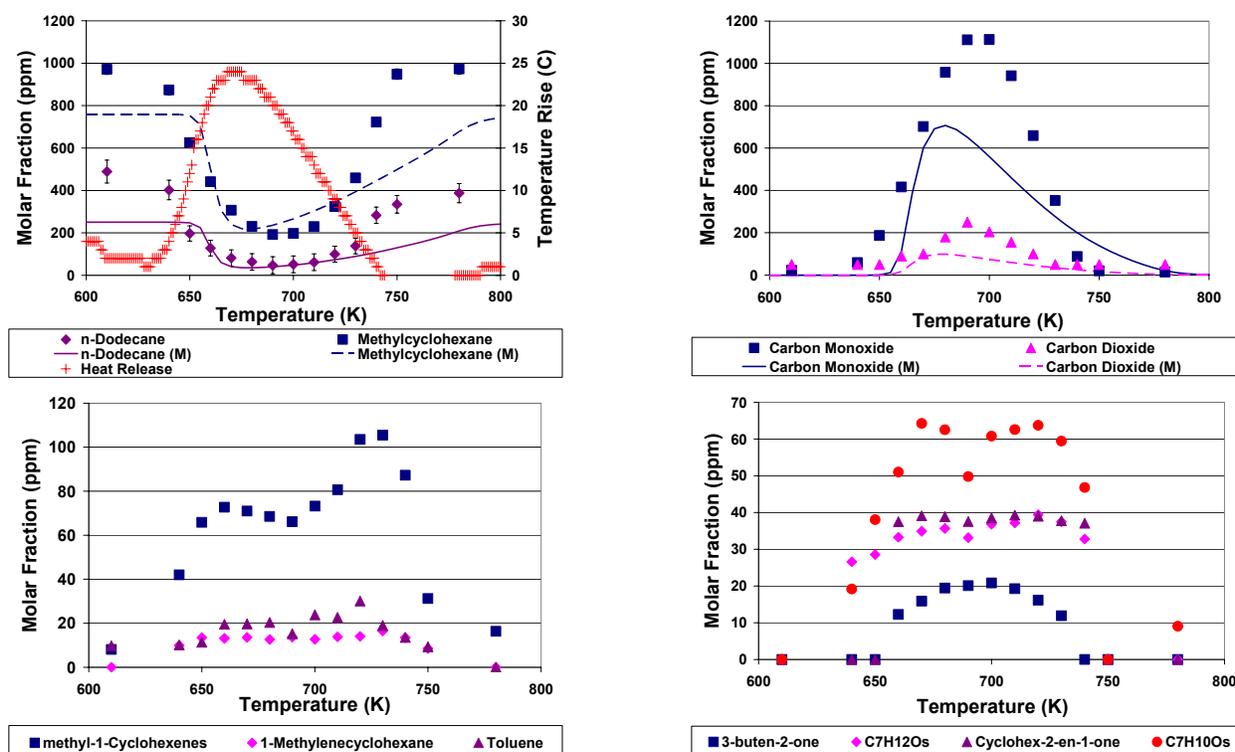


Figure 3 Concentration profiles and model predictions (M) for n-dodecane, methylcyclohexane, and a few of the intermediates plus the temperature rise during the n-dodecane/methylcyclohexane CCD experiment.

1-Methylnaphthalene Mixture Oxidation

The oxidation of the binary mixture of 51% n-dodecane and 49% 1-methylnaphthalene (97+%), $C_{11}H_{10}$, was studied from 600 to 800 K at a pressure of 8 atm under lean and dilute conditions at a residence time of 175 ms (CCD experiment). During the CCD experiments, a strong NTC behavior started at 695 K. However, due to the high sooting propensity of the mixture (sufficient to partially block the sampling orifice), only qualitative measurements were completed during the CCD experiment and no CIT experiment was attempted. Several unique species attributable to 1-methylnaphthalene were identified, including, benzene, toluene, benzaldehyde, ethyl-benzene, acetophenone, indene, naphthalene, and 1-naphthaldehyde, Figure 4. The most abundant of these compounds were naphthalene, 1-naphthaldehyde, and benzaldehyde.

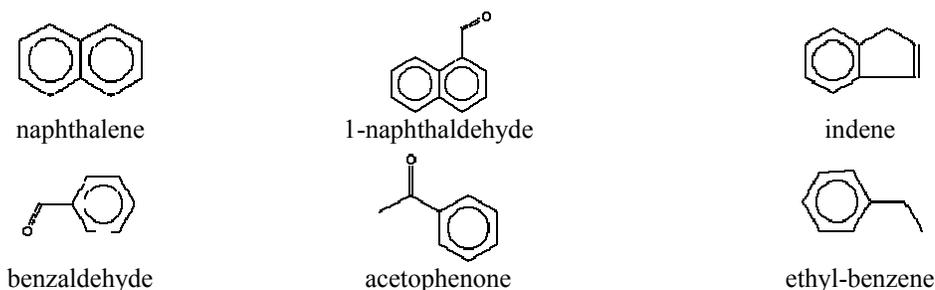


Figure 4: Structure of the species identified during 1-methylnaphthalene oxidation.

Shaddix and coworkers [11] have suggested that bicyclic aromatics follow the same chemical reaction pathways as monocyclics, based upon their high temperature studies with 1-methylnaphthalene and toluene. However, this appears to only be in part true for the low and intermediate temperature range. During previous toluene studies [12, 13], the major toluene intermediates were benzene, benzaldehyde, phenol, and ethyl-benzene with no appreciable ring scission or growth.

Correlating these species to 1-methylnaphthalene would indicate the major intermediates should have been naphthalene, 1-naphthaldehyde, 1-naphthalenol, and 1-ethyl-naphthalene. However, a significant fraction of 1-methylnaphthalene either increased (i.e. large soot concentrations) or decreased (i.e. benzaldehyde) in ring size, indicating that the ring structure of 1-methylnaphthalene is considerably less stable than toluene.

Summary and Conclusions

In this work, the preignition behavior of neat n-dodecane, and binary mixtures of n-dodecane and iso-cetane, n-dodecane and methylcyclohexane, and n-dodecane and 1-methylnaphthalene was explored in the low and intermediate temperature regime (600 – 800 K) at 8 atm. Gas phase samples were extracted during each experiment to identify and quantify the major intermediates. The results were compared to an existing lumped mechanism developed by Ranzi and Faravelli at Politecnico di Milano.

The oxidation of n-dodecane formed a large number of intermediates, most of the identified intermediates were lower molecular weight alkenes and aldehydes, mostly C₆ and smaller. The model predictions agreed reasonably well, but did not predict the observed formation of the C₁₂ alkene intermediates. The iso-cetane mixture experiments also produced large concentrations of lower molecular weight fragments, mostly C₃ and smaller. Methylcyclohexane principally dehydrogenated, rather than fragment as was assumed in the model. As a result, the model predictions were less than satisfactory. The oxidation of the 1-methylnaphthalene mixture produced copious quantities of soot sufficient to block the sampling orifice. However several intermediates attributable to 1-methylnaphthalene were identified, namely; naphthalene, 1-naphthaldehyde, and benzaldehyde. The experiments presented here represent some of the first detailed experiments of these fuels at elevated pressures, and will provide important information for model development and refinement.

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