

# Development of an Experimental Database and Kinetic Models for Surrogate Diesel Fuels

J.T. Farrell,<sup>\*</sup> N.P. Cernansky,<sup>†</sup> F.L. Dryer,<sup>‡</sup> D.G. Friend,<sup>§</sup> C.A. Hergart,<sup>\*\*</sup> C. K. Law,<sup>‡</sup>  
R.M. McDavid,<sup>\*\*</sup> C.J. Mueller,<sup>††</sup> A.K. Patel,<sup>\*\*</sup> and H. Pitsch<sup>‡‡</sup>

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## ABSTRACT

Computational fluid dynamic (CFD) simulations that include realistic combustion/emissions chemistry hold the promise of significantly shortening the development time for advanced high-efficiency, low-emission engines. However, significant challenges must be overcome to realize this potential. This paper discusses these challenges in the context of diesel combustion and outlines a technical program based on the use of surrogate fuels that sufficiently emulate the chemical complexity inherent in conventional diesel fuel. The essential components of such a program are discussed and include: (a) surrogate component selection; (b) the acquisition or estimation of requisite elementary chemical kinetic, thermochemical, and physical property data; (c) the development of accurate predictive chemical kinetic models, together with the measurement of the necessary fundamental laboratory data to validate these mechanisms; and (d) mechanism reduction tools to render the coupled chemistry/flow calculations feasible. In parallel to these efforts, the need exists to develop similarly robust models for fuel injection and spray processes involving multicomponent mixtures of wide distillation character, as well as methodologies to include all of these high fidelity submodels in computationally efficient CFD tools. Near- and longer-term research plans are proposed based on an application target of premixed diesel combustion. In the near term, the recommended surrogate components include n-decane, iso-octane, methylcyclohexane, and toluene. For the longer term, n-hexadecane, heptamethylnonane, n-decylbenzene, and 1-methylnaphthalene are proposed.

## INTRODUCTION

Significant improvements in diesel engine efficiency and emissions are required to meet future legislated targets. Conventional engine design approaches that rely on prototype development are too time-consuming and expensive to meet these challenges. The development of predictive and efficient computational tools that incorporate the relevant chemical kinetics, molecular transport, and turbulent flow would represent a significant step forward in the ability to rapidly design high efficiency, low emission engines. However, significant gaps and uncertainties exist in our knowledge of these fundamental processes and their coupling.

In recognition of this need, the National Institute of Standards and Technology (NIST) held a workshop on Combustion Simulation Databases for Real Transportation Fuels in September 2003 [1]. The overall goal was to develop the experimental database, chemical kinetics, and computational methodology necessary to simulate realistic combustion processes, with fuels representative of actual commercial gasoline, diesel, and aviation fuels. The present paper is an outgrowth of the original meeting and additional endeavors of a subsequently formed adhoc Surrogate Diesel Fuel Working Group over the past three years.

Because of the complexity of diesel fuel composition and reaction kinetics, studies focused on developing a molecular-level understanding of diesel combustion often employ surrogate fuels. Surrogate fuels are simpler representations of fully blended fuels which are comprised of selected species of known concentrations and that exhibit combustion characteristics similar to those of the real fuel. Experiments with surrogate fuels are particularly useful when it is desirable to limit the chemical and/or physical complexity of the fuel to generate insight and understanding of underlying processes such as vaporization, mixing, ignition, and pollutant formation.

<sup>\*</sup> ExxonMobil Research and Engineering

<sup>†</sup> Drexel University

<sup>‡</sup> Princeton University

<sup>§</sup> National Institute of Standards and Technology

<sup>\*\*</sup> Caterpillar Inc.

<sup>††</sup> Sandia National Laboratories

<sup>‡‡</sup> Stanford University

Most surrogate studies, particularly those involving more than one component and molecular weights that are characteristic of diesel fuel components, have been limited by the lack of well developed, validated, detailed chemical kinetic models of the multicomponent surrogate mixture, and by the paucity of experimental validation data needed to create accurate models. Of equal significance, there presently exist few dimensionally reduced versions of these kinetic models that are compatible for use in multi-dimensional, computational fluid dynamic (CFD) engine design codes.

Formulating surrogates that match conventional diesel fuel combustion parameters requires matching both the chemical and physical properties of the fuel, and will likely require more components than can be handled in current computational codes. Consequently, there are presently practical reasons to limit the number of pure components used to represent full blend diesel chemical kinetics. While the long-term goal of increasing the number of species considered should remain, near-term research should reflect a long-term desire to simultaneously describe both physical and chemical kinetic parameters of diesel fuel.

The goals of the present paper are to assess the current state of diesel surrogate fuel research and to outline a research program for the development of the experimental database and modeling tools necessary to adequately emulate the chemical complexity of real diesel fuel. The essential components of this research program are: (a) the identification of a suitable small number of fuel components representative of actual fuel composition that can be blended to mimic properties of commercial fuels, yet be sufficiently simple to permit detailed kinetic modeling; (b) acquisition or estimation of elementary chemical kinetic, thermochemical, and physical property data needed for the surrogate molecules and mixtures thereof; (c) the development of accurate, predictive chemical kinetic models, together with the measurement of the necessary fundamental laboratory data to validate these mechanisms; and (d) mechanism reduction tools to render feasible the coupled chemistry/flow calculations. In parallel to efforts to develop more robust physical and chemical kinetic models, there are needs to develop similarly robust models for fuel injection and spray processes involving multicomponent mixtures of wide distillation character, a rigorous description of turbulence-chemistry interactions in combustion, as well as methodologies to include all of these high-fidelity submodels in computationally efficient CFD tools. Ultimately, data acquired from well characterized engines will be required for final validation.

The paper is organized as follows. First, the physical and chemical properties of commercial diesel fuel are described in order to elucidate the necessary property targets for realistic surrogates. Second, the key targets desired for matching a surrogate fuel to a real fuel are discussed. Next, published work on surrogate diesel

components and fuels is reviewed to determine the extent to which existing data on surrogates can be used as a foundation for this activity. We then propose a research plan for developing the necessary experimental database and kinetic models for diesel surrogate fuels. We will distinguish the near-term (1-7 years) and longer-term (7+ years) time frames.

## OVERVIEW OF DIESEL FUEL COMPOSITION

Although a surrogate diesel fuel does not necessarily need to contain components that are representative of the molecules contained in diesel fuel to match the real fuel behavior, it is reasonable to expect that a compositional match may permit better agreement. Thus, we provide a brief overview of the composition of commercial diesel fuel.

Commercial diesel fuels are complex blends of several hundreds of individual species [2-4]. The primary chemical and physical property ranges of North American (U.S. and Canada) diesel fuels are given in Table 1 [5,6]. There is tremendous variability in diesel fuel properties not only internationally, but regionally and locally as well, which reflects the nature of the crude and the processes used at the refinery from which the fuel originates.

Table 1. Chemical and physical properties of typical North American diesel fuel [5,6]

Property	Value
Cetane Number	40-56
Carbon Number Range	C <sub>10</sub> -C <sub>24</sub>
Boiling Range (°C)	190-360
Composition:	
% normal, iso-paraffins	25-50
% cyclo-paraffins	20-40
% aromatics	15-40

The diesel-range molecules produced from distillation of crude oil (the first processing step) include paraffins, cyclo-paraffins, and aromatic molecules (see Figure 1). The paraffins include straight-chain (normal) and branched (iso) paraffins. The iso-paraffins in diesel fuel are very slightly branched, typically containing only one or two methyl substitutions on a long (C<sub>10</sub>-C<sub>24</sub>) chain. 2-methyl analogues are the most common, followed by 3-methyl, 4-methyl, etc. The cyclo-paraffins are primarily 1-ring cyclohexanes with multiple alkyl sidechains; 2-ring and larger cyclo-paraffins are usually present at levels less than 5 % of the total fuel. Aromatics, which constitute 20-40 % (30-35 % average) of commercial US diesel fuels [6], are primarily 1-ring analogues, *i.e.*, alkyl-benzenes (15 %), with 5 % substituted 2-ring aromatics (naphthalenes). Naphtho-aromatics and larger 3-ring cyclo-paraffins and aromatics can also be present in diesel, but the relative concentrations are small and likely to decrease in the future.

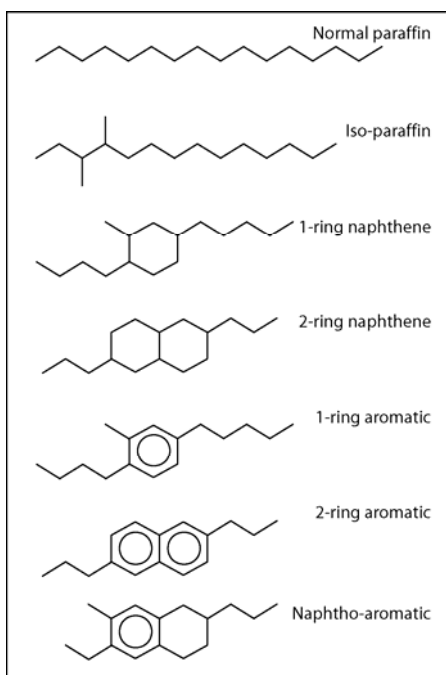


Figure 1. Representative examples of the major classes of molecules contained in diesel fuel. Commercial fuels contain a very large number of isomers of each class, and the specific C<sub>16</sub> isomers shown are representative only. Adapted from Sato et al. [7].

Figure 2 shows a breakdown of molecular type vs. carbon number based on detailed analytical characterization of three commercially available diesel fuels. The large compositional differences between various market fuels is evident. The figure shows that Fuel B contains a significantly higher level of cyclo-paraffins than Fuels A and C, and that Fuel C contains significantly more aromatics. These differences underscore an important point, *i.e.*, that a surrogate fuel that matches the combustion properties of a specific real diesel fuel may not be broadly applicable to other market fuels.

Diesel fuels from nonconventional resources are projected to augment the petroleum-derived fuels increasingly in the future [8]. Biodiesel, *i.e.*, fatty acid esters produced via transesterification with methanol or ethanol of either vegetable oil or animal fat has been used in Europe for several years, and is currently finding increased use in the United States [9]. As biodiesel will be available in relatively small quantities, it will be utilized primarily as a blending stock at levels up to 20 %. The molecular structure of biodiesel is much different from that of petroleum-derived diesel fuel, with a more homogeneous distribution. For example, soy-derived biodiesel typically consists of five methyl esters, with methyl linoleate being the dominant component (~67 %) [10].

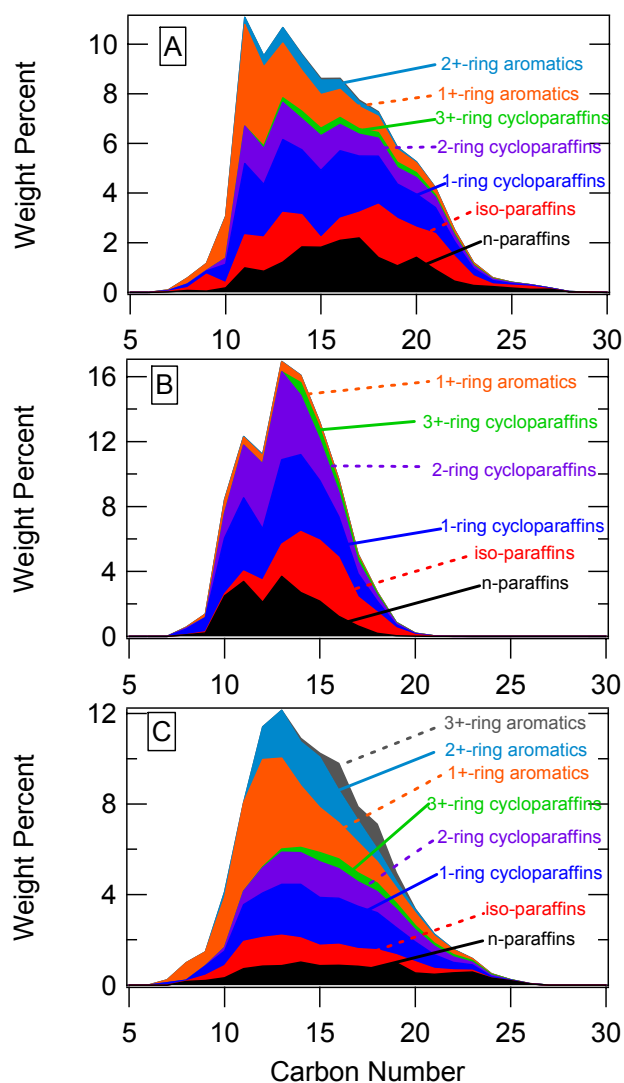


Figure 2. Detailed hydrocarbon analysis of three commercial diesel fuels as a function of molecule type and carbon number. Significant compositional variability is evident.

Diesel fuels will also increasingly be derived from resources such as natural gas, oil sands, shale, coal, and petroleum coke. Commercial fuels produced from blending these materials will be required to meet performance, physical properties, and emissions regulations. The molecular structure distributions overall and within the distillation curve associated with many of these materials are also different from those characteristic of conventional petroleum-derived diesel fuel. For example, fuels derived from tar sands may have higher cyclo-paraffin content than conventional diesel [11], and fuels produced from coal via present direct coal liquefaction processes are predominantly cyclo-paraffinic [12]. Additionally, diesel-range fuels produced from natural gas, biomass, coal, and petroleum coke via the Fischer-Tropsch (FT) process are comprised almost entirely of normal and iso-paraffins. Like the iso-paraffins naturally present in

petroleum-derived diesel, the iso-paraffins are predominantly mono- and di-methyl paraffins, with the methyl substituent located on a carbon near the end of the molecule.

Since the vast majority of the commercial diesel fuel in the near future will be petroleum-derived and will be the baseline against which blends and/or complete petroleum-derived fuel substitutions are evaluated, this paper is constrained to discuss the petroleum derived problem in depth. However, it is expected that the program developed around petroleum-derived diesel fuels will be readily extendable to non-petroleum-derived fuels.

## TARGETS FOR SURROGATE DIESEL FUELS

Surrogate fuels are used to mimic the behavior of real diesel fuel in various combustion devices, and the definition and complexity of the surrogate fuel formulation depends on the intended application. The quantities used to compare the performance of a surrogate fuel to real diesel are often termed “targets.” We will distinguish here amongst three different types of targets: property targets, development targets, and application targets.

The term *property targets* refers to fundamental physical and chemical fuel properties. Common property targets such as density and hydrogen/carbon (H/C) ratio can be readily matched with a single-component surrogate, though doing so obviously does not guarantee a good match to diesel fuel combustion behavior. Other properties of the real fuel such as gross chemical composition, phase behavior (e.g., vapor-liquid equilibrium and distillation characteristics), and molecular transport properties may require many more components to match well. Because the physical and chemical complexity of a surrogate fuel will be reduced compared to that of a commercial diesel fuel, it will in general not be possible (nor necessarily desirable) to match a wide range of properties such as viscosity, chemical composition (e.g., percent aromatics), surface tension, etc. with a single surrogate formulation.

*Development targets* refers to kinetic and fluid dynamic processes that are important for validating surrogate mixture behavior, and that are typically evaluated in devices with better controlled conditions than those in real engines. Exemplar development targets include: kinetically-related phenomena (autoignition delay, burn rate, species evolution histories, emissions, etc.), with and without molecular-level transport coupling, measured in fundamental laboratory experimental devices; multi-component spray vaporization, droplet size distribution, and liquid penetration length experiments and model validations in combustion bombs; and elementary kinetic studies to define specific reaction pathways. As with property targets, it is likely

that several few-component surrogates will be required to match a broad range of development targets.

*Application targets* refers to results obtained from engine experiments. Exemplar application targets include engine operating characteristics such as combustion phasing and duration (timing and duration of cool flame and main heat release), combustion efficiency, and primary emissions (NO<sub>x</sub>, soot, CO, and unburned hydrocarbons). In addition to steady-state behavior, desirable application targets may include combustion properties during transient operation.

In many instances, developing surrogate fuels that match application targets will be the ultimate research goal. However, it is important to recognize that application targets for conventional diesel combustion cannot be used to assess the quality of a surrogate fuel unless all relevant physical and chemical properties are matched. This is because many processes, e.g., ignition, soot formation, etc., depend both on mixing and kinetically controlled processes. The definition of surrogates that match both physical and chemical properties of real fuel will likely require a larger number of components than necessary to match development targets, and thus constitutes a longer-term (7+ years) goal.

In the interim, it is desirable to identify application targets for which the coupling of kinetic- and mixing-controlled processes is much reduced compared to that of conventional diesel combustion. In the present paper, we have chosen premixed diesel combustion as the appropriate relevant application target. Preliminary experimental results with premixed charge compression ignition (PCCI) operation suggest that to first order, the decoupling of kinetic and physical processes is a good approximation.

## GENERAL CONSIDERATIONS AND PREVIOUS RESULTS FOR SURROGATE DIESEL FUELS

Depending on the application target chosen, a single component surrogate may suffice. For example, n-heptane is a gasoline-range molecule that has been utilized heavily as a single component surrogate for diesel fuel ignition. This frequent use reflects a cetane number (CN) for n-heptane (~55) that is comparable to that for current European and Japanese diesel fuel. Additionally, detailed chemical-kinetic mechanisms for low-, intermediate-, and high-temperature n-heptane oxidation are available, e.g., [13,14], and several models exist that have sufficiently reduced dimensionality (number of species and reactions) to enable their use in CFD simulations.

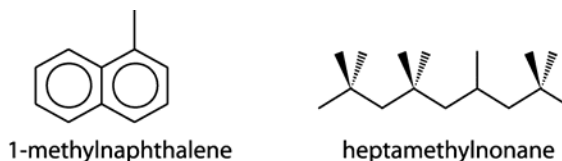
Even in instances when n-heptane and a real diesel fuel have comparable cetane numbers, the ignition behavior of the two fuels likely will not match over a wide

speed/load range. This is particularly true if the ignition is dominated by mixing-controlled processes, since the significantly higher volatility of n-heptane will lead to large differences in liquid spray penetration and vaporization, and consequently, in local fuel/air ratios. Because of this, CFD simulations that incorporate n-heptane kinetics to predict real diesel combustion behavior typically utilize physical properties for the real diesel to provide realistic injection, break-up, collision, and evaporation behavior.

However, even under conditions where the fuel/air distribution matches, the ignition behavior of n-heptane and real diesel may differ. This is because the first stage (low temperature) heat release of n-heptane and real diesel will likely exhibit a different dependence on temperature and pressure, which will vary as the speed and load change. This difference reflects the fact that the oxidation and pyrolysis kinetics of n-heptane do not describe those of real diesel fuel. More specifically, the potentially strong effects on ignition of aromatics, cyclo-paraffins, and iso-paraffins are not described well by n-heptane kinetics. This greatly reduced chemical complexity also impacts the ability of n-heptane to reproduce the pollutant formation processes of real diesel fuel. Moreover, the C/H ratio of the fuel departs significantly from that of diesel, and thus local mixing phenomena cannot be represented accurately in terms of stoichiometries in diesel fuel applications. As a consequence, while engine experiments with n-heptane are capable of providing much insight, they may not accurately reflect the combustion behavior of real diesel fuel. Similar limitations are expected to hold for any single component surrogate.

In recognition of this limitation, binary, ternary, and larger blends have also been extensively employed as surrogates. Table 2 lists components that either have been extensively studied as surrogate fuel components, or are suitable for inclusion in future studies. Included in the table are qualitative assessments (denoted by the labels A, B, C, D and F, which are defined in the legend at the bottom) of how well (in relative terms, compared to n-heptane) the kinetic and property information is known for each component. Under the “Understanding of Mechanism” heading, separate assessments are provided for the relative level of understanding of the low- and intermediate-temperature vs. high temperature kinetics. Similarly, qualitative evaluations are provided for the thermophysical vs. transport properties under the “Property Information” heading. It is important to note that an “A” rating does not indicate that the detailed mechanisms that exist for these components have been fully validated over all relevant conditions or are precisely defined at the elementary kinetic level. Select references for both mechanism development and experimental validation data are also provided in the table.

It is worth noting that many of the species included in Table 2 fall in the boiling range of gasoline or jet fuel. As will be discussed in a later section, the inclusion of these species reflects the limited availability of validation data and kinetic models for diesel-range components, which is evident from the small number of entries in the References columns. Of those studies that have used diesel-range molecules, several have been carried out with binary blends of the cetane reference scale components, *i.e.*, n-hexadecane (or n-cetane, CN=100) and either 1-methylnaphthalene (CN=0) or 2,2,4,4,6,8,8-heptamethylnonane (HMN, CN=15; also referred to as iso-cetane or iso-hexadecane).



Similarly, a significant amount of work with binary surrogate fuels has also been carried out for jet fuel applications (see [15] and references therein). Many of the components utilized fall in the front end of the diesel boiling range. Of particular note, a coordinated industry/academia European Union effort called “Computational Fluid Dynamics for Combustion” (CFD4C) was initiated in 2000 with the goal of developing surrogates for jet fuel combustion properties and emissions [16]. Several binary surrogate fuels involving n-decane and an aromatic species (toluene, n-propylbenzene, 1,2,4-trimethylbenzene) were evaluated, and a mixture of 80 vol % n-decane + 20 vol % n-propylbenzene was defined as the fuel with the best match to the application and design targets.

A diesel-boiling-range binary mixture of particular relevance is comprised of 70 vol % n-decane + 30 vol % 1-methylnaphthalene. This fuel was formulated as part of the Integrated Diesel European Action (IDEA) program [17], which was a concerted effort undertaken in the 1990s to specify a surrogate diesel fuel comprised of C<sub>10</sub> and heavier compounds to facilitate comparisons between experimental application targets and numerical simulations. The IDEA fuel has a CN (55), normal density (817 kg/m<sup>3</sup>), and hydrogen-to-carbon ratio (1.7) similar to those of European #2 diesel fuel [18,19].

Experiments in an optical direct injection (DI) diesel engine showed that the ignition delay and heat-release rate of the IDEA fuel and the chosen reference diesel fuel closely matched. The IDEA fuel also showed emissions trends similar to those of the real diesel fuel as engine output torque was varied, although NO<sub>x</sub> and soot emissions for the IDEA fuel were typically 3-7 % and 10-30 % lower, respectively, [18,19]. The reasonable agreement in emissions levels is interesting given that the liquid-phase penetration was considerably shorter for the IDEA fuel than for diesel, as determined from

Fuels	Understanding of Mechanism		Property Information		Selected References	
	Low & Intermediate Temperatures	High Temperatures	Thermo-physical	Transport	Mechanism	Experimental
<i>Straight-chain Alkanes</i>						
n-heptane	A	A	A	A-	[81,91,112,180-182,190]	[60,89,97,147,162,164,165,170,171,177,183-189]
n-decane	B	A-	A	A	[54-56,84-86,155,156]	[55,56,156,54]
n-dodecane	B	B	A	A	[63,157,190]	[60,63,158,159]
n-hexadecane (n-cetane)	C	C	B+	B	[62,87,160]	[62]
<i>Branched-chain Alkanes</i>						
2,2,4-trimethyl-pentane (iso-octane)	A-	A	B+	B	[79,91,96]	[89,91,96,97,147,161-168,170,171,177]
2,2,4,4,6,8,8-heptamethylnonane (iso-cetane)	C	C	B-	C+	[63]	[60,63,158,159]
<i>Cycloalkanes</i>						
methylcyclohexane	C	C	B+	B	[92,169]	[60,63,64,92,93,158,159,170]
ethyl/propyl/butyl cyclohexane	D	D	B	C		[64]
decahydronaphthalene (decalin)	D	D	B	B-		[63]
<i>Single Ring Aromatics</i>						
toluene	C	C	A	B+	[94,96,98,172-176]	[60,69,93,94,96-99,170-172,177]
ethyl/propyl/butylbenzene	C	C	B	B	[71]	[69-71,100,178]
n-decylbenzene	D	D	D	D		
<i>Multi-ring Aromatics</i>						
tetralin	D	C	B+	B-		
1-methylnaphthalene	C	C	B	C	[129,179]	[60,63,158,159]

<b>Legend</b>						
	A	B	C	D	F	
Understanding of Mechanism	Detailed mechanism(s) validated over wide range	Mechanism(s) reported, but with modest discrepancies or limitations	Mechanism(s) reported, but with major discrepancies or limitations	No mechanism reported		
Thermo-physical Properties (Information on species as component of mixture may be highly uncertain)	Equation of state available (density to 0.3%)	Sufficient data for model (density to 3%)	Limited data only	Extremely limited/no experimental data, predictive model feasible	No data or predictive model available	
Transport Properties (Information on species as component of mixture may be highly uncertain)	Correlations available for viscosity and thermal conductivity (5%)	Data available for models (5-10%)	Limited viscosity and/or thermal conductivity data	Extremely limited/no experimental data, predictive model feasible	No data or predictive model available	

measurements conducted using a high-pressure, high-temperature spray chamber [20]. By comparison, n-decane, which was also tested in the engine, produced only ~ 10 % of the soot emissions of real diesel. Development of the chemical-kinetic mechanism for the IDEA fuel was discussed, though the final mechanism has not been published in the open literature. Validation of the mechanism against development targets has been limited by the lack of requisite experimental validation data. The efforts in Europe with the IDEA fuel have been the most focused in defining and evaluating a surrogate fuel for the validation of numerical simulations of diesel combustion. Numerous other experimental investigations have employed surrogate diesel fuels to match application targets for conventional diesel combustion [21-25]. However, none of these studies compared surrogate fuel results with those for real diesel using experimental or computational approaches that could isolate kinetic and/or physical effects. Even in the few studies where measured (surrogate and real diesel) and computed (surrogate only) results have been compared, the selection methodology for the surrogate constituent compounds and the measures taken to validate the chemical kinetic models are not discussed, and the range of operating conditions used is small. Thus, it is difficult to discern the extent to which the level of agreement reported reflects a good match between the chemical kinetics of the surrogate and real diesel fuel, or whether the comparisons include compensating differences in chemical and physical property differences.

## PHYSICAL PROPERTIES

### *Previous Diesel Spray Surrogate Research*

Many experimental studies on surrogate diesel fuels have been conducted with constant-volume combustion vessels. Most of this work has been carried out to identify a surrogate to simulate only the vaporization of #2 diesel fuel, not its ignition, combustion, or emissions characteristics. However, since fuel vaporization will be important to model in-cylinder fuel/air distribution in direct-injection premixed diesel operation, we briefly review the status of the development of diesel spray surrogates.

Siebers has conducted a large parametric study using a high-pressure common-rail fuel injector to determine how the liquid length varies with ambient-gas conditions, injection parameters, and fuel volatility for n-hexadecane, HMN, and #2 diesel [26]. Measurements of liquid- and vapor-penetration rates and liquid-spray spreading angle have also been reported for n-dodecane, n-heptane, and the IDEA fuel [27]. The facility used in Reference 26 was later used to compare liquid lengths of n-hexadecane and HMN to those for #2 diesel, Fischer-Tropsch diesel, biodiesel, and several gasolines for ambient-gas temperatures from 700 to 1300 K and densities from 3.6 to 59 kg/m<sup>3</sup> at an injection pressure of 140 MPa [28]. A

follow-up study presented a model for predicting the liquid length if the physical properties of the surrogate compound and certain fuel-injection parameters are known [29]. The study provides criteria for a good vaporization surrogate, namely, that the liquid length, density, and T90 (temperature at atmospheric pressure for 90 % distillation recovery) of the real and surrogate fuels match. Based on these criteria, n-heptadecane was recommended as a good vaporization surrogate for #2 diesel fuel [29]. It is clear, however, that this choice is only based on physical properties, and thus is inappropriate for matching chemical kinetic targets.

Measurements of 1-methylnaphthalene fuel vapor concentration, droplet density, and mixture temperature have also been reported [30]. Results presented in Reference 31 provide vapor- and liquid-fuel penetration measurements over a range of ambient-gas and injection conditions as well as comparisons to the results of Siebers [29]. Additionally, experimental measurements of axial and radial penetration rates and wall heat transfer have been presented for the IDEA fuel and Swedish Class 1 diesel for single and split injections [32]. However, the matched-density criterion mentioned above precludes 1-methylnaphthalene from being a suitable vaporization surrogate for #2 diesel.

### ***Thermophysical Property Modeling and Experiments***

The development of computational models for processes such as fuel injection, atomization, vaporization, *etc.*, requires detailed fundamental physics models as well as accurate physical properties for the fuel. In addition to the distillation curve, it is important to predict properties such as the liquid density, liquid and vapor heat capacities, surface tension, and viscosity over a large range of temperatures and with pressures to more than 5 MPa. Low-temperature properties may be important for cold-start models. A thermodynamically consistent set of properties over the range of conditions encountered—possibly including those of the pure components and of mixtures with intermediates and air—would allow the most flexible possibilities for system modeling. However, representing such thermophysical properties of a complex mixture such as diesel fuel with a few-component surrogate is a major challenge, and the variety of fuels encountered in the current and future marketplace will require additional efforts to translate the knowledge learned from surrogates to an understanding of more realistic engine situations.

More generally, CFD and computational combustion modeling require consistent property information to maintain fidelity between the model and the system to be simulated. As noted earlier, the inclusion of both accurate property models and extensive kinetic information within a combustion code is clearly prohibitive with today's computational resources: the number of coupled kinetic equations itself is unwieldy, and when combined with accurate spatial- and time-



dependent density, heat capacity, viscosity, *etc.*, fields, detailed numerical simulations are not feasible at this time. In addition, studies have shown that ideal-gas approximations or incompressible fluid approximations within CFD codes can lead to problems [33].

The first step in studying the properties of a surrogate mixture is an analysis of data available for each potential constituent. With a potential slate of candidates, there are a variety of sources of data that can be consulted. For instance, the AIChE DIPPR database provides recommended data for many important compounds, and has predictive capabilities [34]; the NIST Chemistry WebBook [35] provides many types of data on-line; the NIST REFPROP database [36] incorporates consistent sets of equations for more common fluids and their mixtures; and the NIST ThermoDataEngine [37] can provide evaluated properties based on a huge and growing collection of experimental data and a library of predictive models.

For the present paper, we have not compiled a complete list of property references. There are excellent standard reference correlations for the lower alkanes, and we note that considerable information is available for n-decane: a validated equation of state from Lemmon and Span [38] gives saturated liquid densities with an uncertainty of 0.05 %, with compressed liquid densities somewhat higher and all thermodynamic properties calculable through a consistent Helmholtz energy formulation. A standard correlation for n-decane viscosity was described by Huber et al. [39], and for n-decane thermal conductivity, an equation by Huber and Perkins [40] can be recommended. Thus n-decane can serve as a good starting point for alkane property models, although the amount and reliability of the available data decreases as the carbon number increases. The thermophysical property models for normal dodecane have also been well established, and extrapolations beyond this carbon number—certainly to n-cetane—would be reasonable. Typically, the information on the transport properties for all of the higher alkanes is less reliable than that for the equilibrium properties.

For the iso-paraffins, the sheer number of isomers as the carbon number increases limits the possibility and desirability of extensive experimental study for all candidates. Although there is certainly property information available for some of the important iso-octane molecules, the largest molecule in this family considered among the standard reference property surfaces within the NIST REFPROP database [36] is iso-pentane (2-methylbutane). The uncertainty in the density of iso-octane might be on the order of 3 % in the range of temperatures and pressures of interest. For the larger species with only a few short side chains, such as those typically encountered in real diesel fuels, models that basically extrapolate from the normal alkane backbone often give reasonable property results. When

the side chains are larger, or with multiple longer chains, the ability to predict properties deteriorates, and basic experimental property studies on the fluid would be warranted.

There are considerably fewer data and the models are less reliable for both the cyclo-paraffins and the aromatic species. Evaluated models for cyclohexane have been considered in the REFPROP database. When the methyl side chain is attached (methylcyclohexane), uncertainties in density of 3 % again might be expected. Toluene has been extensively studied and serves as a standard in several applications, but data for the larger aromatics and those with side chains are generally sparse. The existing data, coupled with predictive models, might allow estimates of properties at the 5 % level of uncertainty for density. As with the alkanes, both data and the reliability of predictive models for the transport properties are worse than those for the equilibrium properties. New experimental data may be required for the larger cyclic and aromatic species important for surrogate diesel fuels.

Mixture property models generally require some information about the binary interactions in the system. For many diesel-range systems, information on the binary pairs is not available; for some of these, predictive models may be adequate. Such models are appropriately developed and validated by some experimental data for pairs chosen within and across the classes of interest (*e.g.*, n-paraffins, iso-paraffins, cyclo-paraffins, and aromatics). Sufficiently accurate quantum calculations are not currently feasible for most of the binary pairs under consideration; for low pressure properties, of primary importance here, the generation of pair potentials from *ab initio* calculations could allow a determination of the lowest-order corrections to the ideal-gas assumptions.

It has been recognized that it is difficult to match the details of a real diesel distillation curve with a few-component surrogate. The introduction of newer diesel blend-stocks (biodiesel, coal-derived diesel, *etc.*, as discussed above) will require surrogates to follow the trends in the new distillation curves. Recent work on advanced distillation curve measurements [41] allows a better connection between the distillation curve and the other phase behavior properties, and it may be possible to match specific features of the curve by varying surrogate composition.

### ***Spray/Multicomponent Vaporization Models***

Various approaches to handling multi-component evaporation have been described. Lippert et al. [42] promote an approach that employs a continuous probability density function to accurately capture the entire range of fuel components. However, this will lead to an inconsistency once the fuel evaporates if the gas



phase chemistry is subsequently represented by a discrete set of components.

The vaporization of an ideal, miscible multicomponent droplet is controlled by two factors, namely the relative volatilities of the components and the liquid-phase mass diffusion. Earlier studies have assumed that the vaporization sequence is controlled solely by the volatility differentials, and as such resembles the distillation process. However, fundamental droplet vaporization studies show [43-45] that the excessively small liquid-phase mass diffusion can limit the rates with which species can be transported to the surface and vaporized. In the limit of vanishing mass diffusivity the vaporization process would assume a so-called onion-skin mode, in which the fractional vaporization rate of the individual species is simply its mass fraction in the liquid [46]. This in turn implies that volatility differential has no influence on the relative rates of vaporization. The parameter that controls the behavior is a vaporization Peclet number (Pe), which is the ratio of the droplet  $d^2$ -law vaporization rate constant to the liquid-phase mass diffusivity. Large Pe favors the onion-skin limit, while small Pe favors the distillation limit [47]. In realistic situations the vaporization behavior is a mixed one [45]. Moreover, as a result of convective shear that occurs during the atomization process, the liquid phase within droplets is not quiescent. The resulting internal convective motions within individual droplets significantly modifies their "effective" Pe number.

The above fundamental understanding may also be further modified in diesel applications by two additional factors: namely (a) the increase of the droplet temperature and the attainment of the thermodynamic supercritical state by the droplet; and (b) the fact that the droplet size is excessively small compared to diffusive transport length scales. Both factors could promote the distillation behavior. A number of papers have explored supercritical vaporization as a means to enhance mixing with multi-component fuels, e.g., [48-52], but further work is required to understand the details of supercritical vaporization at engine conditions and the effects on in-cylinder mixture formation. Another issue of key importance is the mechanism of droplet breakup and coalescence in dense sprays, which affects virtually all aspects of diesel combustion, e.g., spray penetration, fuel vapor distribution, ignition, etc.

As far as the development of gas-phase reaction mechanisms is concerned, such an uncertainty perhaps does not matter as long as the mechanisms are sufficiently comprehensive that they can describe fuel mixtures of any composition. On the other hand, care is needed when interpreting experimental results affected by both the vaporization and gas-phase reaction processes.

In summary, the key issue in the vaporization of fuel blends is the sequence in which components of different

volatilities and chemical identities vaporize, through either droplets or ligaments. Current understanding indicates that the mechanism is neither batch-distillation-like, controlled primarily by volatility differentials, nor onion-skin-like, controlled by liquid-phase mass diffusion. A mixed-mode behavior, with the attendant complexity in solution, could be the controlling mechanism. On the other hand, the attainment of super-criticality at a sufficiently early stage in vaporization could imply a completely different vaporization mechanism, although there is little understanding of this phenomenon for multicomponent fuels.

## CHEMICAL KINETIC PROPERTIES

### *Previous Kinetic Development Target Research*

Experimental data from laminar premixed and diffusion flames, flow reactors, shock tubes, and rapid compression machines (RCMs) constitute valuable development targets for surrogate fuel model development and validation. A large number of studies have been reported for molecules relevant to hydrocarbon transportation fuels, including those listed in Table 2. As noted earlier, many of the species listed in Table 2 fall in the gasoline/jet boiling range, reflecting the limited availability of validation data and kinetic models for components relevant for diesel fuel. However, the kinetics significant to the combustion of these smaller components are important to describe the kinetics of intermediates formed in the combustion of diesel species of larger molecular weight. Thus, in the absence of suitable diesel-range molecules, these species may constitute a reasonable basis from which to formulate surrogate fuels to meet various near-term development targets. The discussion that follows includes illustrative examples of the research performed for various fuel components, with particular focus on diesel boiling range molecules.

*n-Paraffins:* The kinetics of *n*-paraffins have been extensively studied, with most efforts concentrating on species smaller than diesel fuel-range molecules. Of particular relevance for surrogate fuel development, the oxidation of *n*-heptane has been studied in numerous experiments that emphasize chemical kinetics and kinetics coupled with laminar convective/molecular diffusive transport. Much of this research has been motivated by the use of *n*-heptane as one of the gasoline primary reference fuels. Reference 53 contains a review of relevant experimental investigations of *n*-heptane useful for surrogate fuel development.

The detailed model development and validation efforts are substantially fewer for larger *n*-paraffins. *n*-Decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane fall within the diesel boiling range and are more suitable diesel surrogate components. Of these, *n*-decane has received the most attention in fundamental experiments

and computational kinetic model development. For example, n-decane oxidation was explored in a jet-stirred reactor at temperatures of 900–1300 K, 0.1 MPa pressure, and equivalence ratios of 0.5–2 [54] to obtain concentration profiles of intermediate species. High-temperature pyrolysis and oxidation data have been acquired at atmospheric pressure in a flow reactor, and shock tube ignition delays have been measured at 1.3–1.5 MPa [55]. Laminar burning velocities and burner-stabilized premixed species profiles are also available and have been used in modeling studies [56]. Vovelle and coworkers have reported measurements from fuel-rich, laminar premixed n-decane flames [57–59]. The authors used extractive sampling to determine species profiles for both stable and radical intermediates and products. At present, all of the above studies concentrate on the high-temperature pyrolysis and oxidative aspects of n-decane oxidation. Few experimental validation data presently exist for low and intermediate temperature characterization and modeling, which are important to diesel applications.

The amount of validation data and the number of experimental modeling efforts for n-paraffins larger than n-decane are sparse, and are mostly an outcome of jet fuel surrogate studies (see Reference 15). Intermediates for n-dodecane oxidation were quantified in a flow reactor at temperatures of 600–800 K, 0.8 MPa pressure, and 0.25 equivalence ratio [60]. As part of a jet fuel surrogate study, n-dodecane was also investigated in a counterflow diffusion flame, with oxygen molar fraction extinction limits and temperature profiles measured [61]. The oxidation of n-hexadecane has been studied in a jet-stirred reactor at 0.1 MPa pressure, temperatures of 1000–1250 K, and equivalence ratios of 0.5, 1, and 1.5 [62]. Few data besides these have been reported.

In part, the shortage of data on diesel-range molecules reflects the difficulty of carrying out experimental measurements with fuels of such low volatility. Typically, experimental studies are limited to those for which very low concentrations (~ less than a thousand ppm) of hydrocarbon are required due to the difficulty of vaporizing these heavy fuels and keeping the original fuel and reaction intermediates from condensing in gas sampling systems. This limitation affects all diesel-range molecules, not just n-paraffins, and constitutes a barrier to surrogate diesel fuel development. Moreover, high-temperature operation leads to the potential of thermal degradation of the fuel, which may be particularly problematic in experimental apparatuses that rely on preheating to vaporize the fuel. Additionally, experimental studies of premixed systems that utilize prevaporization and mixing with oxidizers (air or O<sub>2</sub>) may be problematic with fuels such as long-chain n-paraffins that exhibit low-temperature kinetic activity and autoignition thresholds.

*Iso-Paraffins:* iso-octane is a gasoline primary reference fuel and by virtue of this has been widely studied (see

[53] and references therein). However, experimental studies of larger iso-paraffins are extremely limited. CO production during HMN oxidation has been studied in a pressurized flow reactor at temperatures of 600–800 K, 0.8 MPa pressure, and 0.70 equivalence ratio [63]. A follow-up study quantified the intermediates produced by iso-hexadecane in that same facility at a leaner equivalence ratio of 0.3 and mixed with n-dodecane to increase the radical pool [60]. Few data have been reported for these diesel-range iso-paraffins over other ranges of conditions, and essentially no data exist for other diesel-range iso-paraffins. This limitation in part reflects the small number of specific iso-paraffin isomers in the diesel distillation range that are available commercially at high purity. This is particularly relevant to experimental apparatuses such as engines that require large quantities of fuel. Specialized, expensive custom synthesis of the components may be required. Similar considerations also apply to diesel-range cyclo-paraffins and aromatics.

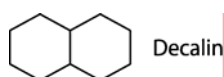
*Cyclo-paraffins:* Virtually no experimental data have been reported for cyclo-paraffins in the diesel boiling range, and even in the gasoline range, only a few data sets are available [53]. Data for alkyl cyclo-paraffins are restricted to experiments in which alkyl cyclohexanes (methylcyclohexane, 1,1-dimethyl-cyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethyl-cyclohexane, 1,4-dimethylcyclohexane, ethylcyclohexane, vinylcyclohexane, ethylidenecyclohexane, and ethynyl-cyclohexane) were added to stabilized co-flow burner flames of methane and air [64]. Measurements of intermediate species identified the aromatic intermediate species produced by alkyl cyclo-paraffin oxidation. Comparing the benzene production from the different cyclo-paraffins and several paraffin and olefin isomers that were also studied revealed that cyclo-paraffins may have a proportionately greater effect than non-cyclic paraffins on soot production because of oxidation routes directly yielding aromatic species as intermediates. This finding is consistent with experimental engine data from conventional diesel combustion experiments showing that cyclo-paraffins have an effect on soot formation that is intermediate between the effects of n-/iso-paraffins and aromatics [65].

*Aromatics:* There are scant data reported for diesel-range aromatics. It is clear, however, that reactions of the phenyl and benzyl radicals will play important roles in the oxidation of these higher molecular weight species [66]. For example, the oxidation of side chains on single-ring aromatics typically occurs first, followed by further oxidation of the remaining ring. Similarly, single-ring aromatic species are formed during the combustion of nonaromatic species and constitute soot precursors [67]. Consequently, a detailed understanding of diesel-range aromatics kinetics will require a detailed understanding of gasoline-range aromatics reactions.

Extant experimental data for gasoline range aromatics are discussed in [53]. The laminar burning velocities and Markstein lengths of several C<sub>7</sub>-C<sub>9</sub> aromatics have been reported at 450 K and 0.3 MPa [68]. The comparative autoignition behavior of numerous alkylbenzenes at high pressure and low temperatures has been investigated in a rapid compression machine [69]. The data show that while toluene, m-xylene, p-xylene and 1,3,5-trimethylbenzene ignite only at temperatures greater than 900 K and pressures greater than 1.6 MPa, ethylbenzene, o-xylene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, n-propylbenzene, 2-ethyltoluene, and n-butylbenzene ignite at much lower temperatures and pressures. The number of alkylated sites, their relative ring locations, and their chain length all affect the relative importance of low- and high-temperature kinetics on autoignition. Methylated aromatics with two or more short alkyl chains ignite at lower temperatures if alkyl substitution is present in an ortho configuration. Alkyl substitutions with groups longer than C<sub>3</sub> also result in low temperature activity.

A follow-up study measured autoignition delays and identified intermediates from the oxidation of o-xylene, o-ethyltoluene, and n-butylbenzene at 600–900 K, equivalence ratio of 1, and 1.4–1.9 MPa pressures [70]. Identification of intermediates showed that in the low and intermediate temperature regimes, the long alkyl chain of n-butylbenzene undergoes oxygen addition and isomerization much as n-paraffins of similar chain length do. Additionally, the oxidation of n-propylbenzene was studied in a jet-stirred reactor at 0.1 MPa pressure, temperatures of 900–1250 K, and equivalence ratios of 0.5–1.5 [71]. Other than these studies, few data are present in the literature on longer chain alkylated benzenes with molecular weights in the diesel fuel range.

**Fuel Blends:** Numerous studies of binary and ternary blends of n-heptane, iso-octane, and toluene have been reported and are discussed in References 53 and 72. Dagaut conducted jet-stirred reactor studies of binary blends of n-decane with either n-propylbenzene or n-propylcyclohexane, as well as ternary blends of these three components [54]. Their studies, carried out over the intermediate temperature range (900–1300 K), atmospheric pressure, and equivalence ratio range of 0.5–2.0, indicated that the ternary mixture reproduced best the species profiles of kerosene. The oxidation of single and binary blends of n-dodecane, methylcyclohexane, decahydronaphthalene (decalin), iso-cetane, and 1-methylnaphthalene has been investigated in the low temperature regime (600–800 K) and at elevated pressures (0.8–1.2 MPa) in a pressurized flow reactor [73,63,74]. Experimental results include CO/CO<sub>2</sub> reactivity mapping and, in the last two references, detailed profiles of intermediate species.



Additionally, ternary blends of n-hexadecane, decalin, and 1-methylnaphthalene have been used to study ignition quality and the effects of cetane improver additives in fundamental ignition bomb [75], and high-pressure flow reactor [76] experiments over a temperature range from 500–900 K at a pressure near 1.25 MPa and a fixed reaction time of 1.8 s. In addition, ignition delays and chemiluminescence during the autoignition process have been measured in shock tube studies for the previously discussed IDEA fuel for several pressures, temperatures, and equivalence ratios [77].

### Previous Kinetic Modeling Work

This section briefly overviews mechanism development work reported for surrogate diesel fuel components. Due to the shortage of diesel-range molecules for which detailed models have been developed, and the hierarchical nature of mechanism development, the predictive capability of gasoline-range molecules is also briefly assessed as appropriate. Recently reported modeling work is emphasized, while earlier references can be found in the cited papers. Reference 78 can be consulted for a recent comprehensive review of mechanism development for a wide range of hydrocarbons.

**n-Paraffins:** A large number of kinetic models have been developed for n-heptane [13,14,79-81]. As discussed by Pitz et al. [53], the kinetics for n-heptane are among the best described of large-carbon-number species, though several combustion parameters are still not well described by existing models, in particular for HCCI combustion with blends.

Lindstedt and Maurice reported an n-decane mechanism that satisfactorily reproduces several species profiles from the n-decane flame experiments of Vovelle and coworkers [82]. Zeppieri et al. [83] and Bikas and Peters [84] have developed n-decane mechanisms based on experimental measurements on shock-tube ignition, flow reactor, and jet-stirred reactor experiments. A unified detailed kinetic model for high molecular weight paraffins, including n-decane, has also been developed for temperatures of 600–1200 K and at pressures of 0.1–5 MPa [85]. An n-decane mechanism for the IDEA fuel was developed by Pitsch and Peters [86]. The high-temperature model for n-decane oxidation developed by Zeppieri et al. [83] has been further revised and compared against a much wider set of experimental parameters, including high-temperature pyrolysis and oxidation data at atmospheric pressure in a flow reactor, and shock tube ignition delay at 1.3–1.5 MPa. More recently, Zhao et al. [56] made additional model/experimental comparisons to laminar burning rate measurements in a jet-wall stagnation flame configuration, burner-stabilized species profiles, and stirred reactor data. Although fundamental experimental data in premixed and diffusion flame configurations are

available, no model comparisons using n-decane exist, and additional model development work is required for this molecule.

A model for n-hexadecane oxidation has been developed by Ristori et al. [62] based on their jet-stirred reactor data. Concentration profiles of intermediate species (though not the parent molecule) compared well with a detailed kinetic model consisting of 242 species and 1801 reactions. Results showed that at lower temperatures ( $\leq 1000$  K) and lean conditions, n-hexadecane reacts by H-atom abstraction via O and OH radicals, while at higher temperatures ( $\geq 1200$  K) and stoichiometric and rich conditions, thermal decomposition dominates. Fournet et al. [87] used the automatic mechanism generation code EXGAS to develop a high-temperature mechanism with 265 species and 1787 reactions. Good agreement was achieved through comparison of the Ristori et al. [62] jet stirred reactor data, though as with the model of Ristori et al., the n-hexadecane profile was not reproduced well. Recently, Chaos et al. [88] have extended the modeling techniques of Zeppieri et al. [83] for high-temperature oxidation, comparing with these data as well as pyrolysis experiments and high-temperature atmospheric pressure flow reactor data on n-heptane/n-hexadecane mixtures.

*iso-Paraffins:* iso-octane, like the other gasoline primary reference fuel n-heptane, has been the subject of a significant amount of mechanism development activities [89-91]. Conversely, little mechanism development has been reported for diesel-range iso-paraffins. A lumped model for HMN has been developed that reproduces the CO production in a flow reactor at temperatures between 600–800 K [63], but additional experimental and modeling work is required.

*Cyclo-paraffins:* As with iso-paraffins, no mechanisms have been reported for diesel-range cyclo-paraffins, and few exist for gasoline-range cyclo-paraffins. The high-temperature oxidation of methylcyclohexane has been modeled by Orme et al. [92] through comparison to their shock tube data and the flow reactor data from Zeppieri et al. [93]. As discussed by Pitz et al. [53], the general trends of the data are reproduced by this model, though several discrepancies have been identified that indicate that further development is necessary. Mechanism development and model validation efforts are also underway to encompass the low temperature aspects of the oxidation. These studies are critical to understanding the competition between direct abstraction and ring rupture that will also be important for modeling diesel-range cyclo-paraffins.

*Aromatics:* Toluene is the aromatic species that has received the most modeling attention. Dagaut et al. have developed a detailed kinetic model for toluene oxidation consisting of 120 species and 920 reactions [94] that reproduces their jet-stirred reactor data well. Skokov et

al. found that this and other toluene mechanisms fail to reproduce experimental flow reactor measurements at 1.25 MPa and 960 K [95]. The mechanisms are all too slow and do not produce the appropriate hot ignition reactivity profiles. Furthermore Skokov et al. show that the phenyl and benzyl production of radicals is insufficient in terms of their subsequent reaction channels [95]. Additionally, Zhao et al. [96] describe a toluene model and n-heptane/iso-octane/toluene model that reproduce the original high-pressure ignition-delay data [95] as well as shock-tube ignition-delay data from Gauthier et al. [97]. Sivaramakrishnan et al. [98] developed a mechanism to model their high-pressure toluene shock tube data that showed good agreement with their experimental results of intermediate species concentrations, particularly at stoichiometric conditions. The aforementioned Dagaut model [94] underpredicted the consumption of toluene at the Sivaramakrishnan conditions. Additionally, the Dagaut model predicts the ignition delay times and OH concentration profiles from Vasudevan et al. [99] well at very dilute conditions but not as well at higher fuel concentrations. With the exception of the toluene model developed by Zhao *et al.* [96], all other models predict significantly slower rates of oxidation of pure toluene at lower temperatures ( $\sim 920$  K, 1.25 MPa) [96]. All models show no low temperature, negative-temperature-coefficient activity for toluene, which is consistent with experimental observations.

Few mechanisms have been developed for aromatics larger than  $C_8$ . A detailed kinetic model with 124 species and 985 reactions has been developed for n-propylbenzene and compared to jet-stirred reactor data acquired at 0.1 MPa pressure, temperatures of 900–1250 K, and equivalence ratios of 0.5–1.5 [71]. Intermediate species were quantified and were in fairly good agreement with the model. Furthermore, a detailed kinetic model for n-butylbenzene has been developed with 197 species and 1149 reactions [100]. The model took the n-butane mechanism from the n-heptane model of Curran et al. [13] and replaced a hydrogen atom with an unreactive aromatic ring. The model was compared to experimental data of n-butylbenzene oxidized in a rapid compression machine at temperatures of 640–840 K, 1.4–1.8 MPa pressures, and equivalence ratio of 1. The model predicted the ignition delay times fairly well. Pitsch et al. [101] developed a mechanism for 1-methylnaphthalene and combined it with the reduced mechanism for n-decane in a modeling study of the IDEA fuel.

*NO<sub>x</sub> and Soot:* NO<sub>x</sub> emissions in engine simulations are typically modeled with a variation of the extended Zeldovich (thermal) mechanism, as this dominates at high temperatures ( $\sim 2400$  K). However, several other pathways may contribute appreciably to NO<sub>x</sub> formation. These include prompt, N<sub>2</sub>O, NNH, and fuel-nitrogen pathways [102,103]. Of these, the fuel-nitrogen pathway should be a negligible source of diesel PCCI NO<sub>x</sub> since fuel nitrogen levels are low in market fuels and should

be zero in surrogates derived from pure components. If the market fuel includes 2-ethylhexyl nitrate (2-EHN) as a cetane improver, the associated kinetics can be incorporated into the surrogate mechanism via reactions outlined by Stein et al. [76]. It is clear, however, that the kinetics of 2-EHN + fuel reactions that promote autoignition require further study.

To the extent that diesel PCCI combustion is “flameless,” the contributions of the prompt and NNH pathways might be expected to play a minimal role, as they typically require high atom concentrations typical of flames. However, calculations by Dean and Bozzelli [103] indicate that the NNH pathway can be much more important than Zeldovich near 1800 K, *i.e.*, a temperature commensurate with diesel PCCI, though the NNH mechanism appears to be most important in diffusion flames where NNH may form on the fuel-rich side and react with O inside the flame sheet [102]. Similarly, the N<sub>2</sub>O channel is important at high pressure and intermediate temperature [102] and has been suggested to be as important as the thermal channel in PCCI combustion, in particular at high pressure [104]. Further work is required to identify the important pathways relevant for diesel PCCI operation and to refine the rate coefficients for the relevant pathways.

Historically, soot production has been modeled by phenomenological empirical models. While good agreement has been demonstrated with these models [105-108], their predictive capability is limited outside the range over which they were developed. Elementary models have received increasing attention over the past two decades [109]. The chemical reactions and physical processes responsible for soot precursor and soot formation are extremely complicated, and involve gas-phase reactions, nucleation, agglomeration, oxidation, and surface growth [110]. As such, detailed models may be too complex to incorporate into CFD calculations. Additionally, model inaccuracies will likely continue to require calibration of empirical parameters by experimental observations. Nevertheless, further efforts focused on developing elementary soot models are required for predictive models, and this is an area where considerable work needs to be devoted.

## COMPUTATIONAL CONSIDERATIONS

It is clear that the computational effort involved in incorporating detailed mechanisms in combustion simulations is overwhelmingly demanding under most situations. This problem will be exacerbated with the large mechanisms required for diesel-range fuels and mixtures, in particular if detailed soot kinetics are incorporated. This section addresses mechanism reduction and engine simulation considerations to facilitate the development of surrogates for premixed diesel combustion.

## Reduced Kinetic Mechanism Development

Reduced kinetic models developed for use in CFD calculations should be derived from validated detailed kinetic mechanisms, and should be constructed based on firm chemical and mathematical principles to ensure that the descriptive ability of the mechanism is not compromised. The large computation time required to resolve the chemistry in reacting flows is due mostly to two factors, namely the typically large number of species and reactions, and the computational stiffness due to the wide range of timescales present in chemically reacting systems in comparison to convective and diffusive timescales. Mechanism reduction can therefore be conducted in two steps. The first, skeletal reduction, involves eliminating “unimportant” species and reactions. The term “unimportant” refers to those species and reactions that do not significantly affect the prediction of the “targets” of interest. The second step is based on time-scale analysis and is discussed in more detail below.

Various methods have been developed for skeletal reduction. Prominent among them is the approach adopted in the development of GRI-Mech [111]. The reduction involves performing a series of zero-dimensional computations over the range of initial target conditions representing those for which original and minimized mechanisms should behave similarly. For each such computation, individual reaction rates are analyzed at each integration time step, and an elementary reaction is retained in the reduced scheme only if certain criteria are satisfied. This procedure provides a clear, robust, and physically sensible means for identifying and removing unimportant reactions from large reaction schemes.

The utility and validity of this strategy have been demonstrated for systems including n-heptane [112], iso-octane, n-heptane/iso-octane mixtures, and real gasolines [113], and a ternary mixture model for n-heptane, iso-octane, and toluene [72]. Genetic algorithm methodologies for mechanism reduction and optimization against kinetic targets have also been described [114]. A particularly notable recent development is the application of directed relation graph (DRG) theory to minimize mechanisms, to similar high degrees of accuracy but in very short computational times [115-118] (See Figure 3). By use of DRG, an n-heptane mechanism consisting of 561 species has been reduced to a skeletal mechanism consisting of 188 species [117].

Of great importance for the development of future reduced chemical mechanisms are recent efforts in automatic mechanism reduction. Several methods have been proposed, for instance by Lovas et al. [119] and Lu and Law [115]. These methods will greatly simplify the reduction work of the anticipated large chemical mechanisms for diesel surrogates and provide the

flexibility that is required to generate application-specific reduced mechanisms. It is important to note, however, that minimization by use of any of the present techniques, including the automatic reduction techniques cited above, yields skeletal mechanisms of very similar size (constrained by the accuracy of replication in comparison to target predictions with the original mechanism).

Time-scale analysis is capable of further reducing the size of the skeletal mechanism. It is based on the observations that fast reaction entities, such as quasi-steady species (QSS) and partial equilibrium reactions, frequently exist and as such can be exploited to remove short time scales as well as the number of variables in the governing equations. The major approaches are intrinsic low-dimensional manifold (ILDM) [120] and computational singular perturbation (CSP) [121-123]. Both methods perform eigenvalue decomposition for the Jacobian matrix, and assume that the reaction rate component vanishes along the direction of the base vectors associated with large negative eigenvalues. CSP, in addition, considers the time dependence of the Jacobian matrix, which can be extremely useful in analyzing controlling parameters in mechanism behavior [124]. Overall, the use of time-scale analysis techniques reduces the computational time requirements by approximately a factor of two.

A major benefit of the methods described above is that they can be automated and the corresponding accuracy quantified. However, these methods typically produce minimized mechanisms that nevertheless remain difficult to incorporate into most CFD simulations, and in particular, if the goal is to parametrically investigate design variations and parameters.

As a result, further dimensionally reduced mechanisms, even ones that encompass smaller envelopes of target predictions remain of interest. "Hand reduction," *i.e.*, non-automated reduction achieved by reaction substitution or modification by individual researchers can be invoked to further reduce the mechanism dimensionality. Along these lines, a detailed mechanism for the auto-ignition and heat release of n-heptane has been reported [125,126] that consists of 185 reactions and 43 species. A reduced 18-step mechanism has been provided [126]. The larger mechanism shows good results compared with experimental auto-ignition delay times and species concentrations profiles from laboratory experiments.

A reduced n-heptane mechanism with a wider range of application was derived by systematic reduction [127] from an updated and enhanced version of the detailed mechanism by Chevalier et al. [128]. The mechanism describes auto-ignition, the general heat release, soot precursor, and NO<sub>x</sub> formation. This skeletal mechanism includes approximately 100 species and has been

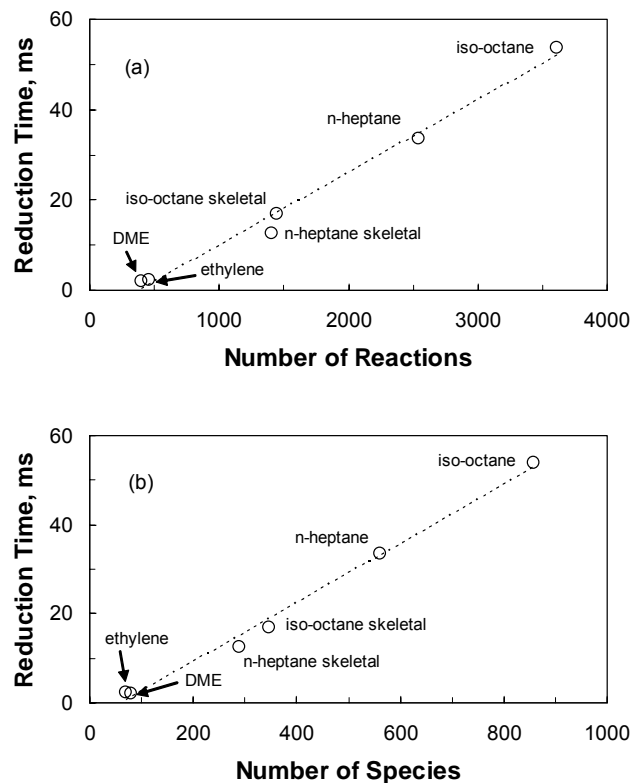


Figure 3. Measured average reduction time of Direct Relation Graph (DRG) for a single reaction state as a linear function of (a) number of reactions, and (b) number of species, of the detailed mechanism.

successfully applied in simulations of a high-pressure combustion chamber and predictions of NO<sub>x</sub> and soot formation in a direct injection diesel engine [129].

To facilitate efficient integration of the detailed chemistry into three-dimensional CFD calculations, a compact n-heptane mechanism was developed by further reducing the existing 42-species mechanism of Golovitchev [14]. In this work [80], the researchers first reduced the mechanism against 24 points representing a range of pressure, temperature, and equivalence ratio. They then optimized the ignition delay with a micro-Genetic Algorithm against the ignition delay calculated from the n-heptane mechanism by Curran et al. [13] over the same P, T, and equivalence ratio range. The resulting mechanism was further modified to improve its accuracy when used in KIVA/CHEMKIN to predict diesel-like conditions. The resulting 29-species/52-reaction mechanism showed savings of 70 % in computational time, while giving good agreement against the engine data taken with number 2 diesel as the fuel.

In summary, several strategies have been identified for deriving skeletal mechanisms with quantifiable accuracy, based on eliminating unimportant species and reactions.



The subsequent use of time-scale analyses based on the concepts of steady-state species and partial equilibrium reactions, or more systematically the computational singular perturbation (CSP), can further reduce the mechanism size and stiffness. The requirement of iteration and possible non-convergence in solving the resulting algebraic equations can be moderated through either tabulation such as In-Situ Adaptive Tabulation (ISAT) or analytical solution [130]. It is, however, important to emphasize that the sizes of these reduced mechanisms could still be fairly large if chemical comprehensiveness is required, and that drastic, ad hoc reductions could lead to falsified chemistry. It is also important to note that accuracy in reduction could be further compromised through error propagation. Dynamic reduction performed locally may be the ultimate solution.

### **Thermodynamic and Computational Fluid Dynamic Engine Simulations**

Clearly, engine combustion simulations do not constitute an optimal test platform to evaluate chemical mechanisms. In addition to the influence of the chemical reaction mechanism, it is important to realize that the degree to which a CFD simulation agrees with measured data is also governed by the ability to describe a whole range of subprocesses including turbulence, heat transfer, spray atomization, break-up, collision, evaporation, and wall impingement. The description of these phenomena, each taken individually, can have an impact on the final result equal to or greater than the choice of reaction mechanism. As a result, the following discussion focuses on the engine modeling considerations appropriate for premixed diesel combustion via early injection, in which the spray has been vaporized and the charge is premixed at the time of ignition. These simulations are better suited for testing chemical mechanisms than simulations of conventional, mixing-controlled diesel combustion, since the impact of the spray and turbulence models can be regarded as relatively small at the start of combustion.

Multizone models are the simplest methods that have been applied to premixed diesel combustion. The simplified fluid dynamics permits relatively large kinetic mechanisms to be included. These models can be divided into different classes: (1) Sequential fluid-mechanic chemical kinetic methods, illustrated in Figure 4 [131-135], (2) coupled CFD – multi-zone chemistry solvers [136,137], and (3) direct integration with detailed chemistry [138,139]. The first two methods essentially decouple the numerical solution of the chemistry from that of the fluid dynamics. The computational domain in the CFD-code is divided into a smaller number of zones, each characterized by e.g. a temperature [131-133,136], a temperature and equivalence ratio [134,135,137] or temperature, equivalence ratio, and EGR rate [139,140].

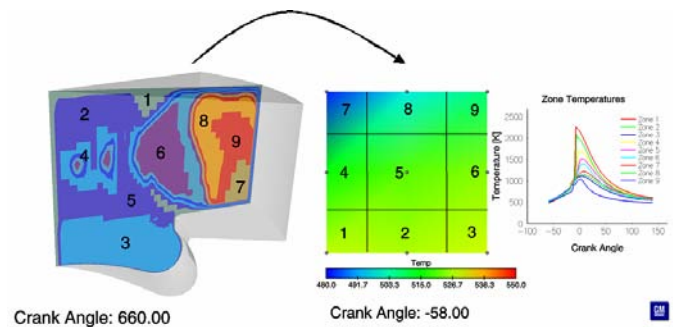


Figure 4. Schematic illustrating 3D sequentially coupled multi-zone approach [135].

Whereas the majority of the referenced multizone models have focused on either natural gas, propane or iso-octane, Hergart et al. [135] applied the sequential multi-zone approach using the IDEA fuel in simulating the combustion process in a mid-range diesel engine. By use of an improved n-decane mechanism, a relatively good match of the low-temperature heat release was achieved. However, as a result of the significantly larger mechanism (118 species, 1000 elementary reactions) the computational times increased markedly. Furthermore, there was some indication that the ability to predict high-temperature combustion suffered as a result of adapting the mechanism to capture the low-temperature heat release.

Direct integration with detailed chemistry involves the use of detailed kinetics to solve the chemistry of each computational cell in the CFD domain. In the approach presented by Singh et al. [141] for modeling the combustion in a DI diesel engine operating in five different modes, each computational cell is treated as a perfectly stirred reactor for which the detailed chemistry is solved by a separate solver (CHEMKIN). A skeletal mechanism of n-heptane featuring 30 species and 65 elementary reactions was used to represent diesel. Since the physical properties of n-heptane, such as density and volatility, are very different from those of actual diesel fuel, a higher hydrocarbon (n-tetradecane) was used in modeling injection, break-up, collision, and evaporation. Relatively good agreement was obtained in capturing the heat release and NO<sub>x</sub> emissions of low-temperature combustion, but the soot model was unable to reproduce measured data.

All the multi-zone models discussed above rely on the assumption that variations in the relevant quantities (temperature, equivalence ratio, and possibly EGR rate) are negligible within each zone. This assumption is likely to be valid when port injection strategies and very early direct-injection cases are simulated. However, in the presence of significant stratification, it is important to account for variances in the parameters provided to the chemistry solver. In order to address the issue of stratification, statistical approaches are required. Zhang et al. [142] used a joint PDF of 40 chemical species and



mixture enthalpy to model HCCI combustion in a gasoline engine. Their results demonstrate the importance of accounting for turbulence-chemistry interactions with increasing stratification. Other examples of approaches involving the use of a PDF combined with detailed chemistry have been presented [127,129,143,19].

The assumption that fluctuations in the relevant quantities within each zone are negligibly small is a strong function of the size of the zones. Hence, caution needs to be exercised in choosing the number of zones. In cases of significant stratification, the previously described direct integration approach with detailed chemistry [141] has merit and has been shown to work well. This approach could be viewed as an extreme kind of multi-zone approach, where each computation cell represents a separate zone. Transport between zones is handled in the CFD code following the operator splitting technique.

In situations where one simply cannot neglect the turbulent fluctuations of temperature and species mass fractions within a zone, even if this is chosen to be the computation cell, the previously mentioned PDF method [142] provides a good alternative. Unfortunately, the method becomes rather computationally expensive as the number of species in the reaction mechanism increases.

Another approach involving a PDF, but using a conserved scalar coordinate transformation to reduce the computational cost, is the Representative Interactive Flamelet (RIF) model described by Peters [144]. The concept relies on the assumption that chemical time scales are much smaller than the turbulent ones and the thickness of the reaction zone is much thinner than the smallest turbulent length scale as represented by the Kolmogorov length. Unfortunately, these assumptions are typically not valid for premixed, low-temperature diesel combustion. However, recently Cook et al. [145] presented an enthalpy-based flamelet model that was found capable of predicting HCCI combustion in a rapid compression machine.

Overall, it may be stated that the commonly used approaches to modeling turbulent reacting flows have the capability of accommodating very detailed chemistry. To date, most applications to diesel low temperature combustion have featured either n-heptane or a two-component model fuel as a diesel surrogate. In order to predict primarily soot emissions and CO with a higher degree of accuracy, a more detailed diesel surrogate fuel will be required.

## PROPOSED RESEARCH PLAN

The preceding sections have outlined the current state of fuel surrogate development relevant to diesel

combustion. In this section, we outline a methodology and proposed research plan to develop the necessary database and kinetic mechanisms to develop diesel surrogates. As discussed earlier, we restrict our attention to premixed (but not necessarily homogeneous) diesel combustion targets to minimize complications due to interactions with the spray and the corresponding impact on the local fuel/air/EGR mixture.

### Surrogate Component Selection

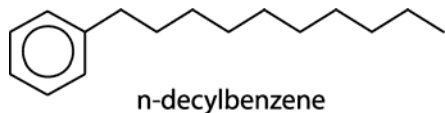
In general, a surrogate fuel should be blended with the smallest number of components that provides the desired agreement with chosen targets. For application targets requiring a description of fuel kinetics, a critical consideration is the level of kinetic understanding for the individual surrogate molecules. Another important consideration is the level of computational complexity that can be accommodated. Even with advances in mechanism reduction and computational efficiencies, there is a strong incentive for minimizing the number of surrogate components. Based on these considerations and the desire for making rapid progress and developing highly accurate surrogate fuel models, a two-tier plan is suggested for the kinetic-related targets:

Tier 1: Given that there will be a non-negligibly large lead time before the required kinetic database and kinetic models for diesel-range surrogate components will be developed, it is appropriate to consider surrogate compositions that can be utilized in the nearer term. It is reasonable to choose surrogate components in the gasoline or jet fuel boiling range for which data are available and mechanisms exist. We recommend that these near-term surrogates be comprised of n-decane, iso-octane, methylcyclohexane, and/or toluene (see Table 3). This recommendation is based on the availability of kinetic models and data for all these components, which, though incomplete, constitute a reasonable starting point for further development.

Near-Term	Longer-Term
n-decane	n-hexadecane
iso-octane	heptamethylnonane
methylcyclohexane	n-decylbenzene
toluene	1-methylnaphthalene

Tier 2: Because of the large amount of work required to develop the database and mechanistic understanding of diesel-range molecules, it is sensible even in Tier 2 to focus the efforts of the community on a small number of candidates. We recommend that in the longer term, surrogates be comprised of n-hexadecane, heptamethylnonane, n-decylbenzene, and 1-methylnaphthalene. While few studies suitable for surrogate development have been reported with these species, they provide the opportunity to blend surrogates with

wide variations in ignitability (CN) and composition, which will be required to match emission targets. Specifically, n-hexadecane and HMN are diesel primary reference fuels, and provide the ability to vary CN over a wide range. n-Decylbenzene provides the ability to adjust the aromaticity of the surrogate fuel, which alters the ignitability and emissions behavior. While it is clear from examination of the entries for n-decylbenzene in Table 2 that virtually no kinetic or property data exists for this component, this same limitation applies to all alkyl aromatic molecules in the  $\sim C_{16}$  range. The choice of an n-alkyl aromatic is motivated by the use of n-propylbenzene (also an unbranched alkyl aromatic) as a jet fuel surrogate component [15,16], though initial tests will be required to establish n-decylbenzene's suitability as a surrogate diesel fuel component. 1-Methylnaphthalene will likely find the greatest utility as a component added in small concentrations to help meet soot formation targets. While kinetic mechanisms for these components are at very early stages of development, they can be readily built upon those of smaller molecules for which accurate mechanisms exist.



An additional, key attribute of these components is their availability at high purity commercially. Although it would be desirable to include a cycloparaffin in the longer term species list in Table 3, there are no  $C_{14}$ - $C_{16}$  range, single-ring alkyl cycloparaffins known to the authors to be available commercially at high purity. Under circumstances where a diesel-range ( $\sim C_{10}$ ) cycloparaffin is desired, either butylcyclohexane or decalin may be suitable.

### **Physical Property Development Targets**

Various surrogate fuel formulations will be blended and tested against the real diesel fuel. As discussed earlier, the development of a suitable diesel PCCI vaporization surrogate may simply require matching the liquid length, density, and T90 [29]. Liquid length experiments in constant volume vessels should be carried out to confirm agreement and requisite refinements if necessary.

*Thermophysical Property Determination:* Accurate thermophysical property models are required that are valid for equilibrium properties, phase behavior (e.g. vapor-liquid equilibrium and distillation characteristics), transport properties, and surface tension over the full ranges of temperature and pressure that might be experienced. Robust equation of state models for few-component surrogate fuels would allow study of variations in composition, behavior of additives, and important comparisons with real fuels. Such models rely on careful study of the component species, and some

measurements on select binary pairs. For some of the proposed components of the surrogate, the experimental database is already adequate, but for others, and for some of the various families of molecules found in current real diesels (and potential commercial fuels), further measurements and evaluations will be necessary.

In particular, the equilibrium properties for n-decane and toluene are well known, and our understanding of these properties for iso-octane, methylcyclohexane, and n-hexadecane may be adequate. Further evaluation of the equilibrium properties of HMN, n-decylbenzene, and 1-methylnaphthalene will be required, although the current experimental data situation may be nearly adequate. Measurements of the density and sound speed over ranges of temperature and pressure for the HMN, n-decylbenzene and 1-methylnaphthalene components would be useful in the longer term. Among the fluids being considered as surrogate components for diesel, standard reference correlations for the viscosity and thermal conductivity are available only for n-decane. Further analysis and measurements for the other components would be beneficial. Measurements of transport properties for n-decylbenzene and 1-methylnaphthalene, in particular, are lacking, and measurements of both viscosity and thermal conductivity of the saturation states and at high pressures should be undertaken.

As the study of diesel surrogates progresses, it will be necessary to (a) study distillation curves of the surrogates and real fuels; (b) conduct transport property measurements and develop models for several of the pure species; (c) conduct densimetry (*i.e.*, PVT studies) and calorimetric experiments on a few of the pure components, as indicated above; and (d) perform some mixture experiments in order to develop and validate the appropriate mixture models. Current information may allow reasonable property estimates, but these are not adequate for rigorous study and understanding.

### **Chemical Kinetic Development Targets**

*Combustion phasing:* One of the major application targets for diesel PCCI is the combustion phasing, *i.e.*, the heat release timing, amount, and duration during compression heating. There are several experimental apparatuses that may be appropriate to evaluate these targets. For example, rapid compression machines and shock tubes have been extensively used to measure the first and second stage heat-release timings and amounts [146,147]. These apparatuses have been routinely operated at 6 MPa pressure [97,98] and capabilities up to 60 MPa have been demonstrated [98]. Experiments at high pressures are particularly crucial as they are most representative of diesel in-cylinder conditions, and high-pressure ignition is poorly predicted by many mechanisms. Ignition delays should be acquired in air and simulated EGR over a wide equivalence ratio range. Additionally, flow reactor experiments have shown that

the CO evolution during low temperature oxidation is a good measure of low temperature oxidation [148,149], and correspondingly, developing a surrogate that has the same CO profile as conventional diesel may be useful. For these targets and the ones that follow, results for individual components must be supplemented with those for binary (and eventually ternary) blends over a range of conditions and varying composition to assist model development and validation.

Spherically expanding and stagnation/opposed jet type flames can also be used to provide laminar burning velocities, Markstein lengths, and extinction limits. While not directly relevant to diesel combustion, these parameters are useful development targets for mechanism validation. Measurements at high pressure (> 1.0 MPa) are desirable yet have been reported only for very light fuels. Stagnation and opposed jet flames can also be used to determine ignition and extinction limits for both non-premixed and premixed combustion modes. Collectively, the flame measurements should be carried out at fuel/air ratios that span the flammability range, at high pressure, and with high levels of simulated EGR.

*Emissions:* Hydrocarbon, CO, and NO<sub>x</sub> emissions represent more challenging targets. Suitable apparatuses include turbulent flow reactors, combustion bombs, shock tubes, and engine-like systems. Rapid compression machines with rapid sampling valves should be employed to provide instantaneous measurements of key intermediates prior to main ignition. Where possible, optical diagnostics should be used to complement the extractive measurements. However, the species amenable to optical detection and the pressure range accessible are presently limited.

Experiments must be conducted at a range of temperatures, from 600 K to 1200 K or greater, thus capturing the low-, intermediate-, and high-temperature regimes of hydrocarbon oxidation, and from atmospheric pressure to higher pressures. While flow reactors and jet-stirred reactors are well suited to this task, they typically have not been designed for pressures greater than approximately 2.5 MPa, and cannot readily investigate low-volatility fuels. Significant efforts need to be devoted to the development of apparatuses and diagnostics (both optical and extractive) for the analysis of diesel-range molecules at higher pressures.

Studies of both premixed and non-premixed flames constitute a rigorous testing ground for reaction mechanisms, in particular when species profile comparisons are made. However, generating stable flames with low-volatility diesel-range fuels will be challenging. Additionally, the effect of molecular transport must be assessed, in particular for fuels of high molecular weight, as flame ignition, propagation, and extinction are sensitive to different kinetics, and the

extent of their dependence on molecular transport can also vary noticeably.

Soot emissions constitute a much more challenging target, reflecting the still incomplete detailed understanding of soot formation (including PAH formation, particle inception, agglomeration, and oxidation). Suitable apparatuses and methods for comparing surrogate and real diesel fuel soot emissions have not been established. Experiments must be conducted at a range of pressures, as soot formation processes are pressure dependent. Reasonable initial venues include flame burners enclosed in high-pressure combustion chambers, where soot volume and temperature are measured by use of the spectral soot emission diagnostic and line-of-sight attenuation technique [150,151]. Additionally, soot formation has been analyzed with laser-induced incandescence and continuous-wave laser extinction techniques from experiments of benzene oxidation conducted in shock tubes [152] and from actual diesel injector sprays at representative engine temperatures and pressures [153].

As this effort proceeds, it will be important to ensure consistency of the experimental data and reaction mechanisms. One method to achieve this results is "Process Informatics" [154]. The primary components of this paradigm include data organization, data analysis and processing, and active participation of the scientific community in the data collection and analysis.

### ***Mechanism Development and Validation***

The mechanism development work required for three of the short-term surrogate species, *i.e.*, toluene, iso-octane, and methylcyclohexane, were discussed by Pitz et al. [53]. For n-decane, the existing high-temperature mechanisms should be validated against the data in the literature and from the experiments outlined above as they become available. The high-temperature mechanism should be augmented with additional pathways, as required. Pathways to describe low temperature oxidation also need to be included and will initially follow the reaction framework outlined for n-heptane. It is anticipated that this scheme should reproduce the majority of the low temperature and negative temperature coefficient behavior of n-decane, though unanticipated complexity may arise due to the increased chain length.

The development of kinetic models for the diesel-range surrogate components listed in Table 3 will proceed via a hierarchical progression of mechanisms built from the smaller molecule models. One strategy is to first develop high-temperature pyrolysis mechanisms, followed by consideration of the interactions of oxygen, with each component being considered individually. Having developed the high-temperature aspects of the models, experiments covering low- and intermediate-temperature kinetic behavior to hot ignition would be needed.

## Engine Experiments and CFD Calculations

Whereas constant-volume combustion vessels, shock tubes, rapid-compression machines, and flow reactors provide excellent fundamental testing platforms, they cannot reproduce all of the relevant characteristics of real engines (e.g., change in combustion-chamber volume with time, geometric details of spray-wall interactions, in-cylinder flow fields, regulated emissions levels, etc.). Hence, experimental results from well characterized, accurately controlled engines will be required for mechanism development and throughout the diesel-surrogate development process. In the near term, this should entail premixed diesel combustion experiments to minimize complications due to sprays and mixing controlled combustion phenomena. Such results are needed to determine the extent to which a proposed mechanism for a surrogate fuel, when used in a suitable CFD code, is capable of quantitative prediction of the important engine performance characteristics (i.e., the desired application targets). Basic application targets to be matched between simulations and experiments include: ignition delay; magnitude and phasing of peak heat release rate during cool-flame and/or high-temperature combustion; and engine-out emissions such as NO<sub>x</sub>, particulate matter, CO, and HC. More detailed data also will be helpful for understanding the underlying causes of (and subsequently eliminating) disagreements between model predictions and experimental observations. Data of this type include in-cylinder fuel/air mixture preparation before ignition, as well as species, flow, and/or temperature fields once combustion has begun.

Subsequently, CFD calculations can be conducted with reduced kinetic models of the surrogate fuel and physical characteristics (boiling range, viscosity, surface tension, etc.) appropriate for the real diesel fuel. The resulting CFD calculations thus will accurately reproduce the fuel/air distribution inside the cylinder, and help to validate both the kinetic and physical models. Massive computational parallelization will be required to reduce the computational times.

## SUMMARY

The goals of the present paper have been to assess the current state of research in diesel surrogate fuels and to outline a research program for the development of the experimental database and modeling tools necessary to adequately emulate the chemical complexity of real diesel fuel. The main points of the present paper are:

- The essential elements required for a detailed diesel surrogate program are presently at a very early stage of development due to the paucity of data and models available for diesel-range surrogate molecules. Thus, in the near term, lower molecular

weight surrogates will provide the most suitable basis for creating surrogate diesel fuels.

- The ultimate goal of surrogate fuels research is to match application targets measured in engines, which for conventional diesel combustion requires accurately reproducing the physical and chemical properties of the real fuel to duplicate mixing- and kinetic-controlled combustion phenomena. This will likely not be feasible with a surrogate of only a few components, and thus matching application targets for conventional diesel combustion constitutes a long-term goal.
- Premixed diesel combustion is proposed as an alternative initial venue from which to choose application targets, and the surrogate fuel development activities outlined in this paper are framed around this application.
- Near- and longer-term research plans are proposed for the development of the experimental database and modeling tools necessary to develop surrogate diesel fuels. In the near term, the recommended surrogate components include n-decane, iso-octane, methylcyclohexane, and toluene. For the longer-term, n-hexadecane, heptamethylnonane, n-decylbenzene, and 1-methylnaphthalene are proposed.
- No attempt has been made at present to define a specific formulation for a surrogate diesel fuel, since the corresponding real diesel fuel properties appropriate for this development effort have not been defined. Consensus from the research community on both the real diesel fuel properties and application targets is required to bring focus to a concerted effort.
- Accurate thermophysical data and property models are available for some of the proposed surrogate components; but for others, and for some of the various families of molecules found in current diesel fuels, further measurements and evaluations will be necessary.
- The sequence with which components of different volatilities and chemical identities are vaporized is a key issue that needs to be clarified in order that the in-cylinder fuel/air/EGR mixture distribution can be modeled. Current understanding indicates that the mechanism is a combination of batch-distillation-like and onion-skin-like. However, the attainment of supercriticality at a sufficiently early stage in vaporization could imply a completely different vaporization mechanism, and further work is required to understand the implications of supercriticality with multicomponent fuels.

- Detailed experimental kinetic measurements of real diesel fuels and surrogate molecules are required in a wide array of experimental devices to match development targets related to ignition and emissions. However, the vast majority of detailed measurements have been carried out on surrogate molecules with molecular weights in the gasoline range. Few data have been reported for diesel-range molecules, reflecting the experimental difficulties of carrying out measurements with low-volatility fuels, in particular at high pressure. These challenges need to be overcome to generate the necessary validation data.
- A detailed mechanistic understanding is required to develop predictive models. For diesel-range molecules, the high-temperature oxidation of n-paraffins is reasonably well understood, though low- and intermediate-temperature oxidation models are significantly less developed. Models for diesel-range iso-paraffins, cyclo-paraffins, and aromatics are in a very early stage of development at best, or non-existent. A significant effort is required to generate the models and validation data for diesel-range surrogates (and mixtures thereof) in these molecular classes.
- Several strategies for deriving reduced mechanisms have been developed based on eliminating unimportant species and reactions. All these techniques yield reduced mechanisms with quantifiable accuracy and a comparable reduction in species/reactions. Further reductions are possible via time-scale analysis and the application of quasi-steady species and partial equilibrium assumptions. However, reduced mechanisms for diesel-range molecules/mixtures generated with these techniques still may be too large for CFD. Alternative analytical methods that yield substantially smaller mechanisms without sacrificing chemical comprehensiveness are required. Dynamic reduction performed locally may be the ultimate solution.
- Commonly used approaches to modeling turbulent reacting flows have the capability of accommodating very detailed chemistry, though the size of the mechanisms that can be accommodated is small. To date, most applications to diesel low-temperature combustion have featured either n-heptane or a two-component model fuel as a diesel surrogate. In order to predict primarily soot emissions and CO with a higher degree of accuracy, a more detailed diesel surrogate fuel will be required.

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