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Development of an Experimental Database and Chemical Kinetic Models for Surrogate Gasoline Fuels

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ABSTRACT

The development of surrogate mixtures that represent gasoline combustion behavior is reviewed. Combustion chemistry behavioral targets that a surrogate should accurately reproduce, particularly for emulating homogeneous charge compression ignition (HCCI) operation, are carefully identified. Both short and long term research needs to support development of more robust surrogate fuel compositions are described. Candidate component species are identified and the status of present chemical kinetic models for these components and their interactions are discussed. Recommendations are made for the initial components to be included in gasoline surrogates for near term development. Components that can be added to refine predictions and to include additional behavioral targets are identified as well. Thermodynamic, thermochemical and transport properties that require further investigation are discussed.

INTRODUCTION

Gasoline is a complex mixture of hundreds of hydrocarbons. While the majority of research engine tests utilize full-boiling range fuels, often it is desirable to limit the chemical and/or physical complexity of the fuel to generate insight and understanding into the underlying fundamental processes. In general, the term surrogate gasoline denotes a simpler representation of a fully-blended fuel. The simplest surrogate fuels consist of single components, e.g., the use of iso-octane as a gasoline surrogate. Binary blends of n-heptane and iso-octane, the primary reference fuels for octane ratings, also find widespread use as convenient surrogates for variable octane number fuel. Ternary and larger surrogates are commonly used to investigate the effects of chemical composition on internal combustion engine (ICE) efficiency and emissions. With a suitable number of components, it is also possible to model a fuel's physical properties (for example, its distillation characteristics). Not surprisingly, a substantial number of surrogate fuel mixtures have been proposed, evaluated in engines and fundamental experiments, and studied numerically.

Computational combustion modeling is an essential, complementary tool to engine experiments. The combination of computational fluid dynamics (CFD) and detailed chemical kinetics provides the opportunity to efficiently optimize ICE performance. Consequently, computational chemistry models are needed to represent the combustion of gasoline in practical devices such as homogeneous charge compression ignition (HCCI) engines and spark ignition (SI) engines. Unfortunately, it is not currently possible to represent the complex chemistry of full blend gasolines in a detailed chemical kinetic model. Not only are the kinetics of all of the components not well determined, but the chemical kinetic interactions among them are not fully understood. Moreover, the large number of components would lead to an unwieldy number of reactions, species, and thermochemical parameters. Even restricting the number of initial fuel species to be considered to less than ten results in a very large dimensional chemical model. In fact the inclusion of complex geometries and transport phenomena required in an engine combustion model and the available computational resources limit the number of species that can be considered within engine combustion codes. While the long-term goal to increase the number of species considered should remain, there are presently practical reasons to represent full blend gasoline chemical kinetics with a small number of pure components.

A team of scientists and engineers from industry, universities and US national laboratories was assembled to draw coherence to surrogate fuel efforts and to develop medium-term and long-term visions for the definition of surrogate fuel compositions for gasoline

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(this paper), diesel [1], and jet fuels [2]. The goals of each effort are to define a small number of appropriate hydrocarbon molecules that can be (a) blended into useful experimental fuels and (b) modeled computationally. Essential components of item (b) are (c) the present availability of laboratory combustion data (e.g., from flow reactors, shock tubes, combustion bombs, opposed flames, rapid compression machines etc.) of sufficient quality to validate the kinetic models, (d) identification of important species to be included and for which additional validation data are needed, and (e) fundamental chemical kinetic, thermochemical, and physical property data that need to be better defined to support the surrogate fuel model development. The short-term vision covering a three to five year time frame should include specific recommendations for surrogate components, composition, and experiments required for the development of chemical kinetic schemes. The long term vision will present possible extensions in targets and surrogate components for more general applicability.

In order to determine the best composition for a surrogate fuel, one needs to specify and understand how the surrogate fuel will be used. Specifically, one needs to decide what quantities need to be predicted accurately when using a surrogate fuel model. These quantities can be termed “targets”. Example targets for surrogate fuels include fuel properties (chemical composition, C/H ratio, density, evaporation characteristics), engine characteristics (combustion phasing, bulk burn duration, emissions), and laboratory data (flow reactor concentration histories, flame speeds, ignition delays, etc.). Targets in engine and laboratory experiments need to be provided over a range of conditions including pressure, temperature and reactant concentrations. The selection of targets will be an important determining factor in the choice of components to be included in a surrogate fuel and the proportions of each. Moreover, it is important to determine whether the surrogate mixture is to emulate all of the possible targets, or whether specific surrogates might be used to emulate specific sub-sets of targets.

The selection of the relevant set of targets for a particular surrogate fuel is intimately tied to the particular application, e.g., SI, compression ignition (CI), HCCI, spark ignition direct injection (SIDI), and in fact, even to what the envelope of operating conditions for each application includes. The HCCI application is an interesting example of the challenges that must be dealt with when attempting to develop appropriate targets for a surrogate fuel. In HCCI combustion, the heat release rates differ significantly depending upon the pressure- and temperature time histories during the compression process. To varying degrees, the fuel components utilized to study HCCI operation, exhibit “negative temperature coefficient” (NTC) behavior. For example, n-butane and n-heptane can exhibit considerable NTC behavior, while toluene exhibits none. Under certain HCCI operating characteristics and with fuels which exhibit NTC behavior, up to 10% of the overall heat release can occur from NTC activity, stimulating autoignition of the remaining charge and a second overall heat release stage. With the same fuels, but at other HCCI operating conditions, no low-temperature energy release is observed [3] and only a single period of heat release occurs. The importance of the low-temperature energy release depends on engine speed, compression ratio, equivalence ratio, intake charge temperature and dilution strategy (internal or external exhaust gas recirculation). While the low temperature energy release of a fuel may be of importance for some HCCI engine configurations, for others there is little effect of low temperature kinetics and single-stage ignition controls the ignition timing.

OVERVIEW OF GASOLINE COMPOSITION

Commercial gasoline is a complex blend of several hundred individual species [4-6], the majority of which is distilled from crude oil. The gasoline boiling range material (~ C_4-C_{10}) is primarily of paraffins, naphthenes (cycloparaffins), and aromatics. This material has a very low octane number. Without additional processing and upgrading, it is a poor fuel for spark ignition engines. Olefins are not naturally present in crude oil but are produced at the refinery and blended into finished gasoline to improve the octane rating. While market gasoline meets stringent regulations regarding volatility, octane number, stability, and a number of other product quality parameters [7], there is a wide variation in composition between market fuels as shown in Fig. 1 [5]. This variability reflects differences not only in the crude source, but in the various refinery processes utilized to blend finished gasoline.

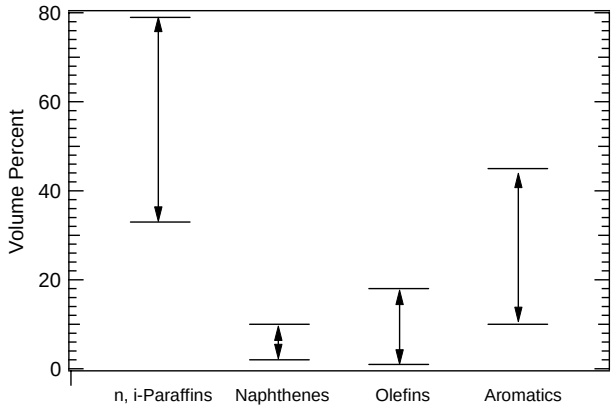

Figure 1: Approximate ranges of paraffins, naphthenes, aromatics, and olefins in commercial U.S. gasoline.

A key decision in the design of surrogate fuels is the choice of individual molecules to include. One approach is to choose a species representative of each hydrocarbon class and to assume that its chemical

kinetic interactions are typical of others of similar chemical structure. An ideal choice would be a species well-represented in commercial fuel for which detailed fundamental data and a kinetic mechanism exist. This premise provided guidance in developing the recommendations presented here.

A more detailed embodiment of this approach would be to define surrogate fuel mixtures of components to achieve the same representative functional group composition as the gasoline of interest. This more detailed methodology has been used by the petrochemical industry to characterize feedstock impacts on product properties derived through chemical processing [8-12]. The structural groups of interest can be readily determined using a number of analytical tools. NMR is particularly useful and has been applied to determine the aromatic, aliphatic, napthenic contents, and details on substituent groups [13] in fuels. This approach holds promise for use in defining surrogate mixtures for real fuels where the surrogate mixtures can be selected to match the relative abundance of the different functional groups in the fuel identified by NMR or other analytical methods. Considerable development of thermochemical and chemical kinetic algorithms remain to be developed to apply this method to yield accompanying chemical kinetic, and thermochemical properties of the resulting surrogate mixtures.

In the following discussion, we examine the principal components present in gasoline that are in each of the hydrocarbon classes. The discussion is meant to be general but is not representative of the entire fuel supply. We defer the discussion of available fundamental data and kinetic mechanisms until later.

The paraffins in gasoline are primarily iso-paraffins. This is due to the greater number of iso-paraffin vs. n-paraffin isomers for a given carbon number, as well as the selective inclusion of iso-paraffins as a means to increase the octane rating. Normal and iso-butanes are typically blended into gasolines due to their favorable octane properties and high volatility (which favors cold-start during the winter). Their concentration depends on whether the gasoline is blended as a summer or winter grade; in the latter, butanes can be present at levels of several percent. The majority of paraffins are in the C_5-C_7 carbon number range. Broadly speaking, the most abundant n- and iso-paraffins include n-butane, n-pentane, iso-pentane, methyl pentanes (iso-hexanes), and iso-octane. It is interesting to note that n-heptane, which is one of the primary reference fuels for which significant experimental and modeling work has been performed, is present at very low concentrations (< 1%) in market fuel because of its low octane. As for iso-octane, the other primary reference fuel, it is also present at relatively low levels in regular gasoline but can be present in much higher percentages (5 – 15% by mole) in premium gasoline.

The naphthenes in gasoline mostly represent "leftover" material from other refinery processes (e.g., conversion to aromatics in reformers [6]). The C_6-C_7 isomers are most prevalent, with the cyclopentane and cyclohexane isomers most common. Methyl substituted (mono and di) isomers predominate, with more numerous methyl and alkyl substitutions less prevalent. The most abundant molecules include methyl cyclopentane, methyl cyclohexane, and cyclohexane.

Olefins follow the same general trend as paraffins, i.e., C_4 species are present at relatively low concentrations, with C_5-C_7 isomers being most prevalent. Branched isomers predominate over linear, again due to the higher number of isomers and the greater octane rating of branched molecules. The most abundant olefins include methyl butenes and methyl pentenes.

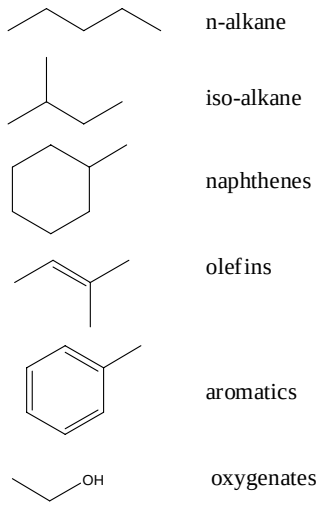

Figure 2: Representative molecular structures of hydrocarbons found in commercial U.S. gasoline.

Unlike the paraffins, naphthenes, and olefins, the peak carbon number for aromatics is skewed to higher carbon numbers. This reflects the fact that there are no stable C_4 and C_5 aromatics, and the concentration of benzene (C_6H_6) is limited to 1% in U.S. gasoline based on carcinogenicity concerns. Toluene (C_7H_8) is the most prevalent aromatic in gasoline. In particular it is added to premium fuels and can reach levels of 35%. C_8 and higher aromatics are also present, with 2- and 3-methyl substituted benzenes most common. Roughly, the isomer distribution for the larger aromatics is well approximated by the ~800-1000 K thermodynamic equilibrium distribution. The most common aromatics include toluene and m-xylene.

Oxygenates are another molecular class that are not naturally present in crude oil (at appreciable levels) but are blended into gasoline at the terminal. Until recently, methyl tert-butyl ether was added to some US gasoline at levels as high as 15%, though it is no longer used.

Ethanol use is becoming increasingly widespread as a blend component.

Molecular structures of representative fuel molecules in commercial gasoline from each chemical class are shown in Fig. 2.

BACKGROUND AND DISCUSSION

APPLICATION AND TARGETS

There are many applications for surrogate fuels for gasoline including SI, HCCI, premixed charge compression ignition (PCCI), and SIDI engines. In order to focus the present work, we chose HCCI engine combustion as the initial application for study, rather than broadening the effort to include general spark ignition engine operation. This will allow for the definition of a surrogate and the development of detailed and reduced chemical schemes in a short-term time frame. A plan for a more generally applicable surrogate will include more components and the targets have to be drawn from additional combustion processes such as flame propagation, flame extinction, and soot formation. But even a surrogate for HCCI will require consideration of traditional SI combustion at high load operation as discussed below.

An important target for HCCI is the phasing in the engine cycle of the point when 50% of the fuel is burned. Simple zero dimensional engine models (such as Ricardo WAVE) show that the work output from an engine is most sensitive to the phasing of the 50% mass fraction burned. The work output is not sensitive to the total burn duration. As long as the phasing of the 50% burn is the same, the net work from the engine will be essentially the same for a 10 crank angle degree (CAD) burn duration (representative of HCCI combustion) or a 50 CAD burn duration (typical of SI engine operation). Thus, for an HCCI engine predicting the 50% burn phasing so that work output and engine efficiency can be maximized is more important than matching the total burn duration.

While predicting the 50% burn phasing is an important target for engine modeling, it is also one of the more difficult targets to achieve because of problems with correctly modeling the heat transfer from the cylinder during compression. In addition, there appear to be effects of mixing and mixture stratification on the CA50 phasing. Work by Dec and Sjöberg [14] shows that predicting the phasing of the 10% mass fraction burned location in an HCCI engine is easier than predicting the 50% burn location by use of the current chemical kinetic mechanisms and a simple engine model. A reasonable speculation for this difference is that the 10% burn point is controlled by an “adiabatic core” of gas in the combustion chamber that tends to ignite first, while the 50% burn point is affected more by initial stochastic inhomogeneities in gas composition and temperature within the combustion chamber and their effects over longer integrated reaction time scales. This highlights the need for further development in modeling the fluid mechanics and mixing in HCCI engines in order to predict HCCI engine performance.

It should be kept in mind that HCCI is only one operating mode of an engine. Since HCCI combustion is controlled primarily by chemical kinetics, the combustion rate is very fast and high levels of dilution need to be used in order to moderate the combustion rate. To achieve high load operation, it is not possible to attain the required dilution levels without supercharging the engine, and the combustion mode must transition into traditional spark ignition combustion. Considering applications where the engine must operate at full load using flame propagation means that the compression ratio for gasoline operation using conventional valve timings is limited to 12:1. If late intake valve closing is used (Miller cycle), the compression ratio may be increased to the 14:1 range. For many applications, an “HCCI” engine will inherently be a multi-mode combustion engine, and HCCI combustion is only one part of the operating strategy with which engine developers and calibrators must contend.

The required exhaust dilution levels can be achieved with either internal or external exhaust gas dilution. Means to obtain internal exhaust dilution are a) exhaust rebreathing, where the exhaust valves are re-opened during the intake process, or b) exhaust recompression where the exhaust valves are closed early in order to trap the residuals within the cylinder. Discussions with original equipment manufacturers (OEMs) indicate that exhaust recompression is the preferred operating mode for HCCI combustion. In order to make the surrogate fuels research relevant to the current HCCI engine development efforts, one target application for automotive applications should be recompression HCCI.

In recompression HCCI, the internal residual levels in an engine vary from a low of 30% at the highest loads (400-450 kPa NMEP (Net Mean Effective Pressure)) to up to 70% at the lowest loads (100 kPa NMEP). There is a significant amount of recycled fuel in the cylinder during the recompression stroke that can react during the recompression. This energy release during recompression increases the temperature and may produce intermediate species that promote ignition during the main compression. Urushihara et al. [15] have shown this recompression energy release can be enhanced by injecting a small amount of fuel directly into the cylinder near top dead center of the recompression. More importantly, the injection timing and the mass of fuel injected during the recompression phase can be used as an active means to control the combustion phasing on the main compression event. Thus, the ability to predict this energy release will be important for developing models that can predict HCCI combustion phasing. Thus, matching the total amount of energy

release during the recompression will most likely be a useful target for the modeling efforts.

Another target for chemical kinetic models is the prediction of experimentally measured K-factors [16] that describe a fuel's autoignition propensity in a specific engine and operating condition. A K-factor is expressed in terms of "octane index" (OI), RON and the fuel sensitivity (S),

OI = RON – KS

where S = RON – MON and K is the K-factor. The engine's OI, or octane requirement, depends on operating conditions. For example, during the MON test, the unburned gas is at a higher temperature at a given point in the piston compression than in the RON test (since the MON intake air temperature is ~ 100 K higher). The different T-P-time-history gives rise to different autoignition kinetics. In a typical spark ignition engine, the autoignition (knock) behavior is of interest at a specific point (high load, low speed). With an HCCI engine, however, ignitability over a wide range of conditions must be modeled. These conditions encompass widely different T-P-time histories, over which the autoignition behavior can be related to first order by a linear combination of RON and MON. Since the K-factor is specific for a given engine and operating condition, the use of the K-factor as a modeling target requires data from an engine that can be modeled accurately.

Kalghatgi has successfully extended the application of the K factor to HCCI engine operation [16]. In many applications, an “HCCI” engine will still rely on SI combustion at higher loads and the gasoline fuel must maintain all the good anti-knock qualities that it possesses. The fact that HCCI engine performance can be correlated with RON and MON through the use of the K factor suggests that traditional octane ratings remain useful for evaluating gasoline combustion under HCCI conditions.

SURROGATE COMPOSITION

Fuel components considered by three teams of scientists and engineers for fuel surrogates for gasoline, diesel and jet fuels are given in Table 1. The candidate gasoline components are shown under the column heading “Gasoline” under “Relevance to Practical Systems”. Each component has been labeled A, B, C, D, or F which denotes the relative importance assigned by the team for inclusion as a surrogate component. For example, n-decane, n-dodecane, n-tetradecane and n-cetane have all been assigned an F under the “Gasoline” column, to indicate that they have no relevance for this fuel. These components are included in the table because of their relevance for the “Diesel” and “Jet” fuel columns. In the next two columns of the table, a qualitative consensus of the team as to knowledge of the chemical kinetic mechanism of surrogate fuel components is noted under “Understanding of Mechanism”. For example, n-heptane and iso-octane, have been assigned an “A” indicating that detailed mechanisms exist for these components and have been validated. This should not be interpreted to mean that every facet of the kinetic mechanism is understood. Toluene has been assigned a “C” for “low and intermediate temperature” indicating that major features of the present mechanistic understanding remain to be determined. Similarly, the table provides a qualitative consensus on the available thermodynamic and transport property data. The table also includes columns of relevant references for both mechanism development and experimental validation data.

There was a consensus that three of the components in any gasoline surrogate should be n-heptane, iso-octane and toluene. n-Heptane and Iso-octane were chosen since they are the primary reference fuel components and toluene is typically the most abundant aromatic in gasoline. Other candidates that could be considered and for which kinetic mechanisms exist are 1-pentene [17], diisobutylene [18], cyclohexane [19, 20], and methyl cyclohexane [21]. Ethanol [22-24] is an additional component that is important to include based upon present and continuing uses as a petroleum fuel additive and fuel extender.

PREVIOUS EXPERIMENTAL WORK

In this section, we discuss the experimental work that has been performed on the oxidation of fuel components identified in the previous section as being important for gasoline surrogates. For a much more complete review of experimental work on the oxidation of hydrocarbons, see the recent review by Simmie [25].

Experimental research on the primary reference fuels iso-octane and n-heptane has been ongoing for several decades. Seminal papers on detailed kinetic models such as those on iso-octane [26] and n-heptane [27] provide broad overviews of earlier experimental research.

More recently, the focus has been on lower temperatures, higher pressures, and speciation of intermediate and radical species. For example, iso-octane was oxidized in a jet-stirred-flow reactor over the temperature range 550 – 750 K, at 7 atm pressure and 400 ms residence time [28]. Intermediate species were identified and quantified, and high yields of cyclic ethers and conjugate alkenes were produced by iso-octyl radicals formed at the tertiary site of the parent fuel molecule. Iso-octane was oxidized in a shock tube at temperatures of 855 – 1269 K, pressures of 14 – 59 atm, and equivalence ratios of 0.5 and 1 [29]. Ignition delay times were measured. Furthermore, the autoignition of iso-octane was studied in a rapid compression facility to determine the effects of HCCI conditions on ignition

Table 1: Fuel Surrogate Components									
Fuels	Relevance to Practical Systems			Understanding of Mechanism		Property Information		Selected References	
	Gasoline	Diesel	Jet	Low & Intermediate Temperatures	High Temperatures	Thermo-physical	Transport (thermal conduct-ivity and transport)	Mechanism	Experimental
Straight-chain Alkanes									
n-Heptane	A	B	B	A	A	A	A-	[27, 30-35]	[28, 34-51]
n-Decane	F	B	A	B	A-	A	A	[52-58]	[54, 55, 58, 59]
n-Dodecane	F	B	A	B	B	A	A	[60-62]	[61, 63-65]
n-Tetradecane	F	B	A	B	B	B+	B		[66]
n-Cetane (n-hexadecane)	F	A	B	C	C	B+	B	[67-69]	[68]
Branched-chain Alkanes									
iso-Octane (2,2,4-trimethyl-pentane)	A	C	B	A-	A	B+	B	[26, 30, 34, 35]	[28, 29, 34, 35, 38, 41-47, 70-73]
iso-Cetane (2,2,4,4,6,8,8-heptamethyl-nonane)	F	A	B	C	C	B-	C+	[61]	[61, 63-65]
iso-Dodecane (2-methyl-undecane)	F	C	A	D	D	D	D		
Cycloalkanes									
Methylcyclo-hexane	C	C	B	C	C	B+	B	[21, 74]	[41, 61, 63-65, 74-76]
Ethyl/propyl/butyl-cyclohexane	C	B	A	D	D	B	C		[76]
Decalin	F	B	B	D	D	B	B-		[61]
Alkenes									
1-Pentene	B	F	C	B	B	B+	C	[17]	[51, 77]
Di-isobutylene	B	F	C	D	B	B	D	[18]	[18]
Single-ring Aromatics									
Toluene	A	A	C	C	C	A	B+	[35, 78-84]	[35, 38, 41, 43, 46, 51, 75, 78, 79, 83, 85, 86]
Ethyl/propyl/butylbenzene	C	B	A	C	C	B	B	[87]	[85, 87-90]
Xylene	B	B	C+	C	B	B	B	[91]	[85, 89]
n-decyl-benzene	F	A	C	D	D	D	D		
Multi-ring Aromatics									
Tetralin	C	C	C+	D	C	B+	B-		
1-Methyl-naphthalene	C	C	B	C	C	B	C	[92, 93]	[61, 63-65]
Oxygenates									
Ethanol	B	B	F	D	A	A	B+	[22-24, 94, 95]	[23, 50, 94]
Dimethyl ether	F	F	F	A	A	B+	B	[96-98]	[96-101]

Legend					
	A	B	C	D	F
Relevance to Practical Systems	Very important	Important	Possible surrogate, but not crucial		No relevance
Understand-ing of Mechanism	Detailed mechanism(s) that has been 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	EOS 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	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

delay times [70]. Experiments were conducted at equivalence ratios of 0.25-1.0, pressures of 5.12-5.23 atm, temperatures of 943-1027 K, and oxygen mole fractions of 9-21 %. An equation defining ignition delay time as a function of pressure, equivalence ratio, oxygen mole fraction, and temperature matched the experimental data well. Equivalence ratio had a great effect on ignition delay time, and it was suggested that ignition delay times were increased at leaner conditions because of the decreased production of carbonyl-hydroperoxide species, which lead to chain branching at these temperatures. To explore the effects of exhaust gas components on HCCI combustion, experiments with CO_2 and H_2O were also run. CO_2 mole fractions of 0.5, 2.0, and 3.0% were added, and no chemical effect on the ignition delay time was observed. The addition of 3% mole fraction H_2O reduced the ignition delay time. Other species typically present in systems with high levels of internal EGR (e.g., unburned hydrocarbons, partial oxidation products, etc.) were not included in the study. In a follow-up study, OH radicals were quantified during iso-octane oxidation in the facility at 945 – 1020 K temperatures, 8.5 – 15 atm pressures, and 0.25 – 0.35 equivalence ratios [71]. OH concentration is a key feature in HCCI conditions because it is the main radical that consumes the fuel and is an indication of the reactivity of the mixture. Figure 3 shows the experimental OH mole fraction compared to four models. OH concentration increases sharply at ignition, and then decreases until reaching a plateau. Sjöberg and Dec [14] studied iso-octane behavior in an HCCI engine. They examined the effect of equivalence ratio and intake temperature on combustion phasing in the engine.

With regard to recent experimental work on n-heptane, work includes n-heptane oxidation in a shock tube at 720 – 1100 K temperatures, 50 atm pressure, and 0.1 – 0.4 equivalence ratios [36]. Furthermore, detailed speciation of intermediates was analyzed on partially premixed n-heptane/air counterflow flames [37]. n-Heptane was studied in a shock tube with synthetic exhaust gas recirculation (EGR) loadings of 0, 20, and 30% [38]. Experiments were conducted at temperatures of 850-1280 K, equivalence ratios of 0.5, 1.0, and 2.0, and pressures of 15-25 and 45-60 atm. Increasing EGR loading increased the ignition delay time. n-Heptane was studied among nine heptane isomers in a rapid compression facility at temperatures of 640-960 K, pressures of 10, 15, and 20 atm, and stoichiometric conditions [39]. These temperatures captured the NTC region for all the fuels studied. Ignition delay times were measured and burn rates were calculated. In an investigation of partial HCCI combustion, n-heptane, gasoline with a RON of 98, and diesel fuel were studied in a diesel engine with compression ratio of 19, engine speed of 1200 rpm, intake air temperatures of 293-393 K, and EGR rates of 0-40% based on volumetric flow rate [40]. The study focused on measuring NO_x emissions as a function of the premixed ratio, defined as the ratio of energy of premixed fuel to total energy. At premixed ratios of 0-0.4, NO_x emissions decreased as the premixed ratio increased for n-heptane, but at premixed ratios of 0.4-0.8, NO_x emissions increased as the premixed ratio increased, due to the advanced ignition of the fuel and elevated combustion temperature.

As a potential surrogate component for gasoline as well as for diesel and jet fuels, toluene is of considerable interest. Fortunately, the combustion chemistry of toluene is an area that has been receiving increasing attention recently. The low temperature and hot ignition characteristics of toluene at 12.5 atm were compared with those of n-heptane, iso-octane, PRF 87 and 93 mixtures, benzene, and PRF 87+20.6% toluene mixtures in flow reactor reactivity experiments [102] (PRFxx indicates xx % iso-octane in an iso-octane/n-heptane mixture). Toluene was oxidized in a jet-stirred reactor at 1000 – 1375 K temperatures, 1 atm pressure, and 0.5 – 1.5 equivalence ratios [79] OH radicals were quantified from the oxidation of toluene in a shock tube at 1400 – 2000 K temperatures, 1.5 – 5.0 atm pressures, and 0.5 – 1.875 equivalence ratios [86]. A study of toluene oxidation in a shock tube included experiments at temperatures of 1200-1500 K, pressures of 25-610 atm, and equivalence ratios of 1 and 5 [83]. From the experiment run at stoichiometric conditions, stable intermediates that were identified included benzene, acetylene, ethylene, CO, and CO_2. In the fuel-rich

conditions, large amounts of diacetylene were also observed in addition to the other species.

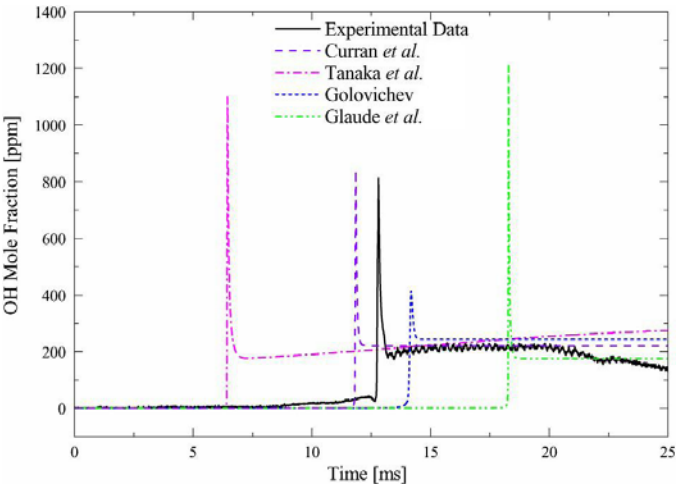

Figure. 3: Hydroxyl radical mole fraction from iso-octane oxidized in a rapid compression facility (solid line) and four models (dashed lines) at 14.27 atm pressure, 971 K temperature, 0.35 equivalence ratio, and 16.6% O_2 mole fraction. Reprinted from [71], copyright (2006), with permission from Elsevier.

Neat runs of n-heptane, iso-octane, cyclohexane, methylcyclohexane, 1-heptene, 2-heptene, 3-heptene, cyclohexene, 1,3-cyclohexadiene, and toluene were run in a rapid compression machine to explore HCCI combustion [41]. The compression ratio was fixed at 16, the initial pressure was 1 atm, the initial temperature was 318 K, and the equivalence ratio was 0.4. n-Heptane, iso-octane, cyclohexane, methylcyclohexane, 1-heptene, and 2-heptene showed two-stage ignition, while 3-heptene, cyclohexene, and 1,3-cyclohexadiene showed single-stage ignition and toluene showed no ignition. In addition, experiments were conducted with the additives 2-ethyl-hexyl-nitrate and di-tertiary-butyl-peroxide, and with PRF blends with and without toluene. The ignition delay in two-stage HCCI combustion was found to greatly depend on the energy release during the first stage of ignition, which depends on the equivalence ratio and octane number. Thus, for HCCI combustion, it was confirmed that the ignition delay and burn rate can be controlled by varying the fuel mixture. No attempt was made in these studies to emulate the C/H ratios typical of gasoline.

PRF, TOLHEP, and TRF blends, as well as other fuel mixtures, have been studied in a number of experiments. Mixtures of n-heptane and iso-octane were studied in a shock tube at 700 – 1200 K temperatures and 40 atm pressure [42]. Increasing the concentration of n-heptane reduced the ignition delay time. PRF blends were also studied in a shock tube at 690 – 1220 K temperatures and 40 atm pressure and a pressurized flow reactor at 550 – 880 K temperatures and 12.5 atm pressure [34, 102, 103]. Intermediates were separated with gas chromatography (GC) and analyzed with Fourier transform infrared spectroscopy (FTIR) and flame ionization detection (FID). Detailed kinetic models allowed the two fuels to interact only through small radicals such as OH, HO_2, O, H, and CH_3. The models predicted major intermediate species, such as alkenes, with good agreement.

PRF blends have also been studied in an HCCI engine with high compression ratio of 18:1 [14]. The phasing of the 10 % and 50 % burn was measured as a function of equivalence ratio and inlet temperature. The behavior of PRF60 and PRF80 was compared to that of iso-octane and gasoline. The two-stage behavior of PRF mixtures was contrasted to single-stage behavior of iso-octane [104]. They show that two-stage behavior of the fuel is an advantage for HCCI operation. A surrogate of 63 % iso-octane / 20 % toluene / 17 % n-heptane and gasoline were studied in a shock tube with synthetic EGR (CO_2, H_2O, O_2, and N_2) loadings of 0, 20, and 30 % [38]. The surrogate successfully matched the ignition delay time of the gasoline.

Mixtures of n-heptane/toluene, iso-octane/toluene, iso-octane/1-hexene, 1-hexene/toluene, and iso-octane/1-hexene/toluene were oxidized in a rapid compression machine at 600 – 900 K temperatures, with ignition delay times measured and intermediates identified [43]. In these mixtures, only co-oxidation reactions, referring to chemical interactions between the reaction paths of each fuel, were only deemed important in the iso-octane/toluene mixture, where active radicals such as the hydroxyl radical reacted with toluene to form stable radicals such as the benzyl radical, thus reducing the pool of radicals. Additional studies detailed the intermediates produced from a mixture of 82 % iso-octane / 18 % 1-hexene at 630 – 840 K temperatures, 8 – 14 atm pressures, and stoichiometric equivalence ratio [72]. Co-oxidation reactions involving radicals were considered, but were concluded to be negligible.

Combustion characteristics including ignition timing, burn duration, and emissions of carbon monoxide, unburned hydrocarbons, and nitric oxides were investigated for the oxidation of n-heptane, iso-octane, and blends of PRF25, PRF50, PRF75, and PRF90 in a four-cylinder direct injection diesel engine modified for HCCI combustion with a compression ratio of 18.5 [44]. The heat release during the first stage of combustion depended strongly on the n-heptane concentration. A critical equivalence ratio was determined where NO_x emission increased greatly due to increasing temperature. Furthermore, the effects of EGR rates, temperature, and engine speed on carbon monoxide and unburned hydrocarbons emissions were studied [45].

The autoignition of fuel mixtures was investigated in a single-cylinder engine under HCCI conditions to determine the importance of including co-oxidation

reactions in chemical kinetic models [46]. Mixtures of 94 % iso-octane / 6 % n-heptane, 84 % iso-octane / 16 % n-heptane, 25 % n-heptane / 75 % toluene, and 35 % n-heptane / 65 % toluene by volume were oxidized in the engine at a compression ratio of 16.7, engine speeds of 900 and 1200 rpm, intake air temperatures of 313 and 393 K, intake pressures of 1 and 2 atm, and equivalence ratios of 0.18, 0.25, 0.29, and 0.33. Autoignition was determined by the pressure rise in the engine, and the authors suggested that none of the existing toluene mechanisms combined with the n-heptane and iso-octane mechanisms of Curran could reproduce experimental measurements. The inclusion of co-oxidation reactions of large radical species of toluene and paraffins were shown to be required to improve the agreement of model predictions and experiments Figure 4 shows the PRF0, PRF80, and PRF100 experiments of [42] with an updated n-heptane model of [27] and the iso-octane model of [26], compared with the models each incorporated with the co-oxidation reactions of [46]. The PRF80 model with the additional co-oxidation reactions improved the prediction. However, some of the rate constants of the co-oxidation reactions were increased compared to literature values. For example, the rate constants of the reaction type fuel + HO_2 => fuel radical + H_2O_2 were 30– 50 times greater than the recommended values of Scott and Walker at 753 K [82].

However, none of the toluene mechanisms used in the above study predict sufficient radical production in pure oxidation at high pressures and temperatures around 920 K [105, 106]. The oxidation rate of toluene at these conditions is far more rapid than predicted. Revision and re-validation of the toluene oxidation kinetics against new data re-confirm the work of Klotz [107] which clearly showed experimentally that the interactions of large radicals is not substantial in the oxidation of toluene/alkane mixtures [35]. The ternary PRF plus toluene model developed in this work reproduces new high pressure data on binary and ternary mixtures of PRF components and toluene in a high pressure flow reactor, as well as the recent single component, binary and ternary mixture shock tube ignition delay experiments of Vasudevan, Gauthier, Davidson and Hanson [29, 38, 86]. Model predictions also compare favorably with laminar burning rate data for all of these conditions [35].

Experimental investigations on the alkene and cycloalkane surrogate components in Table 1 are scarce. The oxidation of 1-pentene and 1-,2-,3-hexenes has been studied at low temperatures in a rapid compression machine [77, 108, 109]. The oxidation of diisobutylene has been studied in a shock tube [18]. A potential cycloalkane intermediate is methylcyclohexane (MCH). The oxidation of MCH has been studied in a shock tube at temperatures of 1200-2100 K, equivalence ratios of 0.5, 1.0, and 2.0, and pressures of 1.0, 2.0, and 4.0 atm [74]. The low temperature oxidation (680 - 980K) of methylcyclohexane has been studied in a rapid compression machine at stoichiometric conditions at 10, 15, and 20 atm [18, 21]. Experimental ignition delay times were measured. A mechanism for the low temperature oxidation of MCH was developed based on the high temperature mechanism of Orme et al. [74]. The ignition delay times calculated by the model compared fairly well with the measured times. In addition, cyclohexane was oxidized in a jet-stirred reactor at 750 – 1000 K temperatures, 1 MPa pressure, and equivalence ratios of 0.5, 1.0, and 1.5, with intermediates identified and quantified by GC/MS [110]. Cyclohexane has also been studied in a rapid compression machine at temperatures of 600 – 900 K and pressures of 0.7 – 1.4 MPa at a stoichiometric equivalence ratio [111]. Autoignition delay times were measured, and intermediate species were identified and quantified with GC/MS.

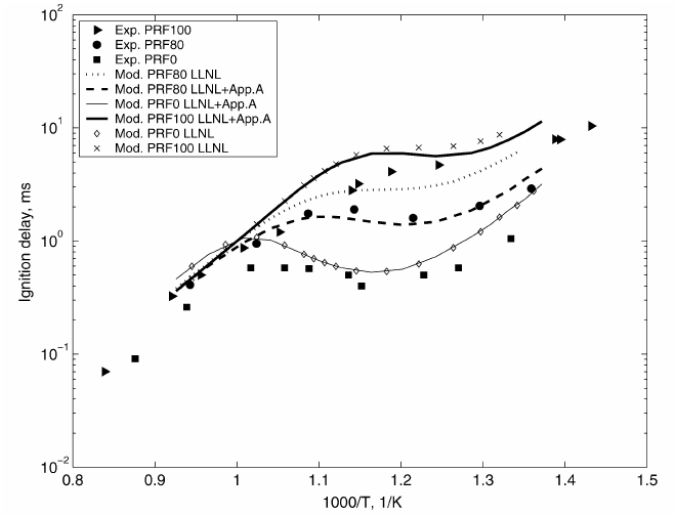

Figure 4: PRF blends oxidized in a shock tube at 40 atm pressure and stoichiometric equivalence ratio, showing experiments, models, and models with co-oxidation reactions (labeled: "+ App. A"). Reprinted from [46], copyright (2005), with permission from Elsevier.

Oxygenates may also be added to gasoline surrogates in the future. Blends of ethanol and diethyl ether were explored in a single-cylinder engine under HCCI conditions to investigate a blend that would spread the combustion event and reduce the autoignition temperature relative to that of ethanol [112]. Experiments were conducted with a compression ratio of 16.25, equivalence ratios of 0.3 and 0.4, and an intake boost pressure of 1.7 atm. The combustion of ethanol and diethyl ether was monitored; the latter proceeded toward complete combustion more rapidly, but not as much as anticipated. Furthermore, bioethanol was studied in a single cylinder SI engine under HCCI conditions at an engine speed of 1500 rpm [113]. Trapping of internal residual gas and heating of intake at high compression ratio were studied as options for HCCI.

EXPERIMENTAL DATA NEEDS

While work on iso-octane, n-heptane, and toluene, individually, in flow reactors and shock tubes is expansive, and the studies of mixtures in HCCI engines are also broad, there is a gap between the fundamental studies of neat fuels and the engine studies of fuel mixtures. That is, investigations of mixtures oxidized in fundamental experimental setups and analyzed thoroughly with detailed intermediate speciation are still rare. Further studies on other pure components mixtures such as those in the pressurized flow reactor studies of 1-pentene/n-heptane/iso-octane/toluene [51] are important to expanding the validation data and model development for more complex surrogate mixtures.

The performance of proposed surrogate fuels must be initially tested in zero or one-dimensional systems, as a failure to reproduce data in those configurations would be a clear indication that the surrogate is not performing well. Zero-dimensional experiments obtained in flow reactors, shock tubes and rapid compression facilities will be essential for assessing the performance of the surrogate in the absence of fluid mechanics. Existing and new stirred reactor data may supplement these approaches. One-dimensional experiments, which are ideally obtained in stagnation flow flames, would provide additional validation when the synergistic effects of fluid mechanics and molecular transport are present. HCCI experimental data demonstrate that ignition is not necessarily homogeneous, given that hot spots can favor ignition locally but result in reaction zones that can potentially extinguish. While laminar flame speeds have been traditionally used to test the high-temperature flame response, there is now concrete evidence, achieved both experimentally and computationally, that flame extinction may be controlled by notably different processes, even though it is also a high-temperature phenomenon. In other words, while a surrogate and the real fuel may have very similar laminar flame speeds, their extinction responses can differ significantly. Both flame propagation and extinction results are valuable validation tools. Also, assessing ignitability of surrogates when their mixtures with air are in contact with hot surfaces relative to that of the real fuels will be important. While atmospheric pressure, 300 K unburned gas temperature, and stoichiometric fuel-air dilution are good starting conditions for one-dimensional flames, clearly engine-like conditions, i.e. conditions of elevated pressure, temperature, and dilution, must be considered as well.

HCCI engine experiments are needed with which to compare the model results. Based on the conditions of interest in many OEM studies, the engine should use an exhaust recompression dilution strategy and have a compression ratio that is no higher than 12 to 14:1 so that it can still operate in SI combustion mode at higher load conditions. [Note: There may be some applications where HCCI mode only operation is possible, e.g., hybrid vehicles and stationary engines.] The experiments should be performed over the full range of HCCI engine operation and at speeds ranging from 1000 to 4000 rev/min. At least three load points within the available HCCI operating regime will be needed.

Once surrogate mixtures of iso-octane, n-heptane, and toluene are more thoroughly investigated in experimental setups in the next few years, additional components can be added. Additionally at this time, the effects of improved computer speed and the development of reduced mechanisms will make such mixtures easier to model. Possible components include alkenes such as 1-pentene and diisobutylene, cycloalkanes such as cyclohexane and methyl-cyclohexane, and oxygenates such as ethanol.

While not necessarily extensive, significant experimental data are available for the surrogate components listed in Table 1, as well as for blends of these components.

Data, both published and unpublished, are also available from ongoing HCCI programs throughout the world. For the Sandia based effort, the data are taken from an HCCI engine running at high compression ratio to increase efficiency and low equivalence ratios to reduce NOx emissions. The data are available for pure components, some multicomponent mixtures, and gasoline (e.g. [14]). The data are available for 0.1 MPa (1 atm) intake pressures and pressure boosted operation. These data were obtained using traditional valve timings and excess air dilution. As a result, the mixture composition at intake valve closing is very homogeneous and the chemical kinetics model can be validated.

CHEMICAL KINETIC MECHANISMS AND MODEL VALIDATION

Detailed Mechanisms

In this section, we assess detailed chemical kinetic models that have been developed for fuel components that are important for gasoline surrogates. For a much more complete review of detailed chemical kinetic models for the oxidation of hydrocarbons, see the recent review by Simmie [25].

The kinetics for n-heptane and iso-octane are perhaps the most mature of present large-carbon-number species mechanisms [26, 27, 30, 47]. They have been developed over the last 20 years or so by various research groups. However, there are still some issues with n-heptane, iso-octane, and primary reference fuel mechanisms. Dec and Sjöberg found that the LLNL model (Appendix A of [14]) for PRF 80 mixtures had a different behavior with 10% burn phasing as a function of equivalence ratio than the experimental observations

in an HCCI engine. However, the LLNL model for isooctane behaved well compared with experiments [14]. The chemical kinetic models for toluene have been developed over the past 15 years or so [78-81, 83], but significant fundamental mechanistic issues remain unresolved. The rate parameters and reaction rate paths are not understood, particularly at higher pressures, where the above toluene mechanisms show too little branching ability at temperatures around 900-1000 K [105, 106]. This branching deficiency has been addressed in the recent modeling studies on ternary mixtures of n-heptane, iso-octane and toluene by Zhao et al. [35].

Studies to date have shown that toluene does not exhibit any significant low temperature reactivity on time scales important to autoignition in engines, but acts essentially as a radical scavenger [102, 114]. The question as to whether aromatic fragments and large alkyl radicals interact under high pressure oxidative conditions appears to be have been resolved as being unlikely even at pressures higher than 12.5 atm. [35] However, further confirmations at still higher pressures are worthwhile. Under low pressure conditions, no such interactions have been observed in direct studies of the kinetics. Nonetheless, at low temperatures and elevated pressures, separate studies in a flow reactor [51] and a rapid compression machine [43] identified chemical interactions between toluene and paraffins when in mixtures. Experiments in more venues and additional modeling can resolve this issue.

For additional components beyond an initial three-component surrogate of n-heptane, iso-octane and toluene, methylcyclohexane and diisobutylene should be considered. Methylcyclohexane is representative of cycloparaffins in gasoline. However, there are only about 2% cycloparaffins in gasoline. This component will be more important to the diesel surrogate fuel. Recently, mechanisms for methylcyclohexane [21] and cyclohexane [19, 20] have become available. Diisobutylene has been used to represent olefins in gasoline in two experimental studies [115, 116]. A diisobutylene mechanism has been recently developed with some initial validation at high temperature [18]. More validation at high temperature is needed and low temperature mechanistic studies and experimental validation data are needed.

As noted above, the detailed kinetic models for n-heptane, iso-octane, and their mixtures have received the most attention in terms of detailed kinetic model development. For example, Ranzi and co-workers [31, 34, 62], Côme et al. [30] and Curran et al. [26, 27] have all published large, comprehensive detailed kinetic mechanisms for PRF components and mixtures, and these models continue to be further refined as additional experimental and elementary kinetic information appear [e.g., [117, 118]. However, these detailed models are too large to be utilized effectively, even in one-dimensional applications that couple transport and chemistry, such as laminar flame speed calculations. The use of analysis tools, such as sensitivity analysis, is difficult with these large mechanisms. These mechanisms impose large computational requirements on sensitivity codes and computational singular perturbation codes. Use of these analysis tools is very valuable in identifying the rate-controlling reactions in these detailed mechanisms. Thus, it is necessary to reduce these mechanisms for use in multidimensional fluid dynamic models. This mechanism reduction is discussed in the section below.

However, there is an approach called the multizone model that has been very successful in the use of large detailed chemical kinetic models to simulate combustion in HCCI engines [119]. In this approach, CFD calculations are performed for an engine cycle without chemical reactions being considered. Different regions in the chamber are identified by their similar temperature histories and partitioned into a limited number of zones (perhaps 40). This procedure is possible for HCCI simulations because the gases in the chamber are much more homogeneous in composition and temperature than in other types of engine combustion. Calculations with relatively large detailed reaction mechanisms can performed on these limited number of zones with different temperature histories. The zones can be combined based on the mass in each zone and the emissions of hydrocarbons and oxides of nitrogen from the engine can be predicted.

Reduced Mechanisms

Systematically reduced mechanisms have been developed from the detailed PRF mechanism of Curran, Pitz and Westbrook by Pitsch [120] and by Dryer and co-workers [35, 121, 122]. An interesting outcome of the work of Pitsch [120] was that interactions between the fuel components were unimportant and it was possible to develop a reduced mechanism for the mixtures by combining the skeletal mechanisms for the single components. This cannot be a general conclusion for future reduced mechanisms, but can possibly greatly simplify their development. Reduced chemical mechanisms for three-component surrogates also have been developed. The accuracy of the reduced mechanisms is typically very similar to that of the detailed schemes, while the size is drastically reduced. A typical detailed three-component mechanism consists of approximately 4,000 to 10,000 elementary reactions among 1,000 chemical species. The minimized, optimized ternary detailed model of Zhao *et al.* [35] consists of 469 species and 1,221 reactions. The initial detailed kinetic model was reduced using the same minimization methods described in references [121, 122].

Quite accurate skeletal mechanism can have as few as 130 species. Introducing steady state assumptions

reduces the number of species that have to be carried in numerical simulations by an additional factor of about two. Automatic reduction strategies have been developed in the past. However, these are presently not capable of achieving such high reduction rates, and typically lead to mechanisms that are about three times as large [44, 123] as a rigorously reduced, skeletal mechanism.

Several small dimensional models have also appeared in the literature for n-heptane [124-126]. For example, Rente et al. [124], Peters et al. [125], and others have published mechanisms with many fewer dimensions (60 species, 237 reactions; a 56-step "skeletal mechanism" containing 35 species, respectively) that consider two-stage chemistry. These models do not behave well in comparison to the large-dimensional models [121], but can meet ignition delay targets [126]. It is likely that in the near term, models of even smaller dimensional size that more closely match the fidelity of the large dimensional systems will be needed for CFD applications.

Overall, a large body of information presently exists in the literature upon which to base ternary mixture models, involving n-heptane, iso-octane, and toluene. However, even for these systems the coupling of the individual components under engine conditions remains complex with a remaining need for additional fundamental sub-mechanism refinement and additional validation experimental data on mixtures and full blend gasolines under similar experimental conditions. Automatic model generation methodologies have been developed and new methodologies are emerging [52, 127, 128]. They are now developing the ability to generate mechanisms for more complex mixtures. With those inputs, the manual techniques described above for model minimization along with new computationally based methods that are now reaching the general research community (e.g., [123, 129, 130]) lead to constrained minimized detailed models that can be refined and optimized based upon new experimental validation data, as well as fundamental elementary kinetic, and thermochemical information. These techniques will not, however, produce models with small enough dimensions to be utilized effectively in complex CFD calculations. The minimized detailed constructs can provide a rigorous platform for deriving the required smaller dimensional models for any level of specific application. Other methodologies, including computational singular perturbation based methods [131] will be required to achieve the necessary dimensional reductions. However, the robustness of the minimized models from which they are derived will continue to depend on significant and varied sources of validation data and continual re-visitation of the fundamental parameters that are embodied in them.

In summary, the development of reduced chemical mechanisms is a must for the application of multi-component surrogate fuels in numerical simulations. As pointed out earlier, at present, parts of the reduction can be done automatically, but manual reduction still leads to much higher reduction levels. An additional complication is that there will not be one reduced mechanism for one surrogate. Different mixtures of different components will emerge as the optimal surrogate for specific applications. The reduction should then have the flexibility to lead to different size mechanisms of appropriate accuracy. Ideally, the level of reduction should adjust during a simulation. It is therefore essential, to provide not only more efficient automatic reduction procedures, but also an automatic framework for composing combined mechanisms from different components, validation of the resulting mechanism with real fuel data, generation of reduced mechanisms for specified targets and accuracy, and finally testing of the reduced mechanism for performance and accuracy.

THERMOPHYSICAL PROPERTIES

The thermophysical properties of the real fuel and the surrogate govern the hydrodynamic equations associated with flow, thermal transport, and species diffusion. The distillation curve is usually an input in engine modeling studies, but the subtleties of droplet evaporation also depend on properties. As the models of the combustion process become more sophisticated, the importance of matching a comprehensive set of thermophysical properties between the surrogate and a real gasoline increases. In the absence of reliable property parameters in the codes, it is difficult to assess the basis for any disagreement or agreement between model and experiment: it then becomes impossible to have confidence in any predictive extension of the model. Although the initial targets established by the team are not very sensitive to the physical properties of the surrogate, it is important to set short and long term goals in the properties area so that properties information on surrogate and real fuels is available for later targets related to directed injected fuel sprays for example. In addition to the distillation curve, properties such as the surface tension and viscosity over a large range of temperatures and with pressures to more than 10 MPa are of primary significance. The common thermodynamic properties—density, heat capacities, compressibilities, sonic velocity, etc.—and other transport properties, such as thermal conductivity and diffusion parameters are also of interest. Representing such thermophysical properties of a complex mixture such as gasoline with a few-component surrogate is a major challenge.

Generally, CFD and computational combustion modeling require consistent property information to maintain fidelity between the model and the system to be simulated. Comparisons of models require an agreed upon set of properties, and studies of variations in fuels, and the significance of additives, such as oxygenates and lubricity agents, generally require studies of mixture

properties. System simulations, including more than the combustion process, will require a broader suite of property information. There is a need from more accurate equations of state from vapors and liquids. Often ideal gas assumptions are made for the vapor and the liquid is assumed to be incompressible. Studies have shown that such approximations within CFD code can lead to problems [132], and it is clear that these are only rough approximations for the vapor under the high pressures encountered and in the liquid, for the range of temperatures being considered. To illustrate this point, we note that for pure n-heptane at 500 K and 10 MPa, the density differs by more than a factor of two from its ideal gas value.

There is an extensive literature which compiles property information and which suggests procedures for estimating thermophysical properties when validated data are not available. The monograph by Poling *et al.* is a standard source for prediction and estimation techniques [133]. Computer databases and calculational software, such as the NIST REFPROP program [134] and the AIChE DIPPR software [135] provide some information on fuel components and their properties.

An initial step in studying the properties of a surrogate mixture is an analysis of data available for each potential constituent. We summarize the property information available for each species (or class) listed in Table 1. The quality codes (A through F) represent a rough summary of our current knowledge base. For instance, for species with a thermodynamic code of "A," there is a reference-quality equation of state (EOS) available in the literature. In general densities calculated from such an equation are known to better than 0.3 % over an extensive range of temperatures and pressures. For some of these systems, uncertainties are closer to 0.03 %. These equations also allow consistent calculations of all thermodynamic properties, including vaporization, and heat capacities. For the transport property column in Table 1, we have not made a clear distinction between information for viscosity and that for thermal conductivity, the two properties considered. The qualified symbol (B+) indicates that one or the other of the properties is better known than class B. We have not summarized the information available for surface tension or diffusion coefficients, although these are also important in the current context.

Next, we discuss some of the specific thermodynamic property references for key components of a gasoline surrogate. For heptane, the equation of state available from Span and Wagner [136] provides densities and vapor pressures with uncertainties to about 0.2 %; all other fluid thermodynamic properties can be calculated from the same EOS, and details are provided in the cited reference. The general equations of state for these fluids are generally written as an algebraic expression for the Helmholtz energy as a function of temperature and density. These equations accurately describe the transition from the ideal gas state to the dense gas, and consistently describe the full phase space—liquid, gas, and supercritical fluid—over an extensive range of temperatures and pressures. Such an equation for toluene is available in a paper by Lemmon and Span [137]. Liquid phase densities from this EOS are good to about 0.05 % for a large range of conditions and vapor densities have a reported uncertainty of 0.2 %. An equation for n-octane is available in the Span and Wagner reference (above), but no similar EOS for isooctane can be recommended at this point. However, there are substantial property data available in the literature for this compound, and multiple ways of constructing and evaluating equations of state for isooctane.

Mixture property models generally require some information about the binary interactions in the system. For a few of the binary pairs in the table, such data are available, although the situation has not been thoroughly examined for this paper. For most of the systems, information on the binary pairs is not available; for some of these, predictive models may be adequate. Sufficiently accurate quantum calculations are not currently feasible for most of the binary pairs under consideration.

Distillation curves for complex mixtures provide the basic phase information needed for characterizing the fuel. These curves generally provide the volume fraction of distillate for a given temperature. Thermophysical property models often rely on more complete phase behavior information. An advanced distillation apparatus and approach [138] can provide compositions in addition to volume fraction of the distillate, and provide more direct determinations of the fuel's vapor-liquid equilibrium (VLE) behavior.

A full description of the thermodynamic and transport property surfaces of the surrogate mixture, including a distillation curve, and comparisons of the surrogate to a real gasoline requires additional study. However, such a long term study may have significant benefit in the industry. Such a model would allow "virtual" study of alternative fuel scenarios, consideration of additives, and optimized system design strategies. The model would be implemented in a computer code that would allow exploration of alternatives, within CFD or other simulation approaches. A full comparison between surrogate properties and gasoline properties may not be a primary consideration in combustion studies, but would have a broad impact.

THERMOPHYSICAL PROPERTY GOALS:

In the shorter term, studies of the properties of selected pure fluid components to be included in surrogate must be completed. In some cases, additional property measurements are required, in particular for the transport properties (viscosity and thermal conductivity);

studies of surface tension and diffusion coefficients will also be required. Research on selected binary pairs should be completed early in the program; we anticipate that these studies will require some property measurements. The systems chosen will be those determined to most efficiently improve the development of equation of state models for the multicomponent mixtures. The distillation curves of standard gasolines, using the advanced distillation protocols, should be measured. These should be compared with distillation curves determined for the surrogate mixtures. An initial model for the thermodynamic properties (an equation of state) and for the transport properties of the surrogate mixture should be developed and implemented in computer code.

In the longer term, systematic comparisons of surrogate properties to gasoline properties must be completed. This will include the distillation curve, and a more complete study of the variability of the distillation curves for commercial gasolines will be necessary. Further property models, incorporating key additives (for gasolines) should be developed. This will undoubtedly require additional measurements. Property models for the surrogates mixed with combustion products and intermediates (may include measurements) should be developed. The final comprehensive property codes should include algorithms for gasolines, surrogates (at arbitrary composition), additives, and combustion products/intermediates—including the relevant mixture models.

RECOMMENDATIONS

APPLICATIONS AND TARGETS

As previously discussed, the short term project objectives are: (1) identify an initial application for which to develop the surrogate fuel, (2) identify appropriate targets for which to match the performance of the surrogate fuel, and 93) identify the composition of the surrogate fuel that mimics the behavior of gasoline within the application. In order to keep the gasoline surrogate work focused, our team recommends choosing HCCI engine combustion as the initial application for study, rather than broadening the focus to include general spark ignition engines as well. Considering that the preferred engine operating strategy from OEM manufacturers is migrating towards the exhaust recompression dilution strategy, the team recommends using this as the initial application for developing the surrogate fuel mechanism.

The targets that the surrogate fuel should be measured against can be broadly classified into a) fuel properties, and b) engine performance characteristics. The initial selection of performance targets are as follows.

Fuel Property Targets:

1. Lower heating value of the surrogate fuel is within +/- 5 % of the reference gasoline. In the engine experiments the fuel flow for the surrogate fuel will be adjusted as required in order to maintain the same chemical energy input to the engine as that from gasoline. Maintaining the heating value of the fuel to be close to that of gasoline will ensure that large changes in fuel flow will not be required for the surrogate fuel experiments.

2. The hydrogen-to-carbon ratio of the surrogate fuel is within the range of 1.6 to 2.0. With this range of H/C ratios the stoichiometric air/fuel ratio will range from 14.2 to 14.78. In the engine experiments the airflow will be adjusted to maintain a fixed air/fuel equivalence ratio. Maintaining this range of H/C ratios will ensure that changes in air flow to the engine are no larger than +/- 5 %.

Engine Performance Targets:

1. Phasing of the 10 % mass fraction burned. Experience with modeling HCCI combustion has shown that this is a good parameter to match since it is not affected as much by heat transfer during compression as the other combustion phasing parameters.

2. Phasing of the 50 % mass fraction burned. This is the most important combustion parameter to match in terms of predicting combustion performance from the engine. Irrespective of the total combustion duration, as long as the phasing for the 50 % burn point (and net energy flow to the engine) of the surrogate fuel matches that of the reference gasoline, the engine performance characteristics will match those of the reference gasoline.

3. Total energy release during recompression. One of the important attributes of recompression HCCI is the ability to control the combustion phasing by injecting small quantities of fuel during the recompression event. While there may be intermediate species produced by partial “reforming” of the fuel during the recompression, the main physical manifestation that can be detected from the cylinder pressure data is the energy release during the recompression event.

Other targets for matching the surrogate fuel?

It should be pointed out that this list should not be considered as totally fixed. As work progresses, the target parameters should be re-evaluated to make sure that work is focused on the appropriate variables for HCCI engine operation.

FUEL SELECTION

As discussed, the initial selection of surrogate fuel components includes: n-heptane, iso-octane, toluene, 1-pentene, diisobutylene, cyclohexane, methylcyclo-

hexane, and ethanol. The next step will be to identify candidate surrogate fuel compositions and perform engine experiments to compare the surrogate fuel performance with the reference gasoline. The initial screening experiments should be performed over a small set of operating points that span the speed and load range of HCCI combustion. Once the surrogate fuel composition has been identified additional experiments should be performed to obtain a complete set of experimental data to use for model comparisons after the reduced chemical kinetic mechanism has been developed.

MODEL DEVELOPMENT

The goals for model development are: (1) obtain fundamental chemical kinetic data on the surrogate fuel on a wide range of experimental apparatuses, (2) develop a detailed chemical kinetic mechanism that can reproduce the observed behavior, (3) reduce the chemical mechanism to a size that is suitable for implementation in engine models, and (4) model the original engine data using the reduced chemical kinetic mechanism. The recommendations for achieving these goals are described below.

ESTABLISH A FUNDAMENTAL, EXPERIMENTAL COMBUSTION DATABASE

It is important that surrogate fuels and the attendant kinetic mechanisms are developed in a comprehensive manner that will render them reliable. To do that, it is essential that an experimental database is established covering a range of the parameter space of relevance that is as wide as possible. Based on what has been learned over the last 20-30 years, it can be stated with a great degree of confidence that to achieve this goal, a well-coordinated experimental effort in homogeneous systems and flames is required. The parameter space is determined by:

1. combustion mode
2. combustion phenomena
3. fuel type
4. relative reactant concentrations
5. reactant dilution
6. pressure
7. time scales determined by engine speed
8. unburned reactant temperature

The combustion mode should include studies at minimum in flow reactors, shock tubes, rapid compression facilities, laminar flames, and stirred reactors over a range of pressures, equivalence ratios, and dilutions. Flow reactors, shock tubes, and rapid compression facilities will provide information regarding species profiles and ignition delays that are essential for surrogate fuel and kinetic mechanism development. Flame systems on the other hand, must be used as a final stage of mechanism validation tool as the kinetics are tested throughout the entire temperature and species concentration ranges of relevance. Additionally, the effect of molecular transport must be assessed. Typically, uncertainties associated with molecular transport are ignored in favor of kinetics, so that the problem becomes manageable. However, state-of-art transport theories, e.g. Chapman-Enskog, assume spherical potentials centered on molecules. Whether or not this is a valid assumption when linear chain molecules, e.g., n-heptane and iso-octane, are considered, is debatable. After all, large-scale simulations of gasoline-powered engines must include models describing molecular transport, and it is possible that uncertainties associated with transport may compromise the fidelity of the simulations as much as errors in chemical kinetics rates would. In flames, both non-premixed and premixed modes must be considered. While the premixed mode will be the prevalent one when fuel and air are mixed before injection, non-premixed behavior will be important when the fuel is directly injected into the chamber.

The phenomena that need to be considered depend on the combustion mode that is considered. Rapid compression facilities provide ignition delay times and species time evolution in the low to intermediate temperature regime. In flow reactors, temperature and species profiles can be obtained in the intermediate temperature regime. Shock tubes provide species time evolution and eventual ignition delay times, typically in the high temperature regime. Spherically expanding or stagnation type flames can be used to determine laminar flame speeds. Stagnation flames can be also used to determine ignition and extinction limits for both non-premixed and premixed combustion modes. The phenomena of flame ignition, propagation, and extinction are sensitive to different kinetics and the extent of their dependence on molecular transport can also vary notably. Stirred reactors provide complementary combustion data in yet another configuration.

The fuels that need to be considered must include a variety of real gasolines, and a range of straight-chain hydrocarbons in the C5-C9 range, as well as aromatics. While single component experiments are essential, studies of fuel mixtures must also be considered in order to assess the possible kinetic couplings between fuels.

The reactant concentration should vary from ultra fuel-lean to ultra fuel-rich conditions, and in all cases the effect of reactant dilution by combustion products must be considered. While changing the equivalence ratio will affect the controlling kinetics, reactant dilution by combustion products will provide information about the influence of carbon dioxide, water, NOx, and partial oxidation products on the overall oxidation process.

Finally, the thermodynamic pressure must change from atmospheric to 1.5 MPa or higher and the unburned reactant temperature from 300 K up to 800 K.

THERMOPHYSICAL PROPERTY NEEDS

In the short term, studies of properties of pure fluids to be included in surrogate may be needed. Also, some property measurements of select binary pairs will probably be required. The development of models for thermodynamic properties and transport properties of surrogates, and implementation in computer code will be needed.

In the long term, a systematic comparison of surrogate properties to gasoline properties will need to be made. Property models for key additives will need to be developed. Some property measurements of key additives may be required.

Property models for surrogates mixed with combustion products and intermediates will need to be developed. Some property measurements of these mixtures may be required. Also, comprehensive property codes for gasolines, surrogates, combustion products, intermediates, and potential additives will need to be developed.

CONCLUSION

We have evaluated the status of available detailed chemical kinetic models, reduced chemical kinetic models and fundamental experimental data for fuel components and fuel mixtures to represent surrogates for gasoline fuels. Recommendations for the needs for the short term and long term in these areas were made. We emphasized the importance of establishing appropriate targets for the surrogate fuels for gasoline. These targets include both application targets and targets based on fundamental, well-characterized laboratory experiments.

For an initial target application, we chose HCCI engines because of much current interest in this area. We recognized that HCCI engines are likely to be dual mode engines operating in SI mode as well, so that surrogate fuels for gasolines will need to meet SI targets as well as HCCI targets.

Initially, we recommend that a three component mixture of n-heptane, iso-octane and toluene be chosen for gasoline surrogates. The ratio of concentrations in the fuel surrogates will need to be changed to represent different gasolines and probably to allow prediction of relevant experimental targets over broad ranges of (a) operating conditions in an HCCI engine and of (b) pressure and temperature conditions in fundamental laboratory experiments.

For further refinement of surrogate fuels for gasoline, other components may need to be added. Diisobutylene and methylcyclohexane are recommended for consideration.

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