A comparison of literature models for the oxidation of normal heptane

David A. Sheen* and Wing Tsang

Chemical Sciences Division
National Institute of Standards and Technology
100 Bureau Drive, Mail Stop 8320
Gaithersburg, MD 20899

*Corresponding Author
david.sheen@nist.gov
301 975 2603

Keywords: Chemical model development; heptane; kinetics; uncertainty analysis
A comparison of literature models for the oxidation of normal heptane

David A. Sheen and Wing Tsang

Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

The development of detailed chemical kinetic models has proceeded unabated since the pioneering work of Dixon-Lewis and coworkers forty-five years ago. In that time, computational power has increased ten million-fold, and yet, we do not have a consensus on a complete description for the pyrolysis and oxidation of fuels as simple as hydrogen. This paper presents a comparison of three detailed models and one lumped, semi-empirical model, all from literature, for the oxidation of normal heptane, a fuel of practical interest because of its use in gasoline surrogates. Specifically, the ignition delay times and species concentration histories predicted by the models are compared. We find that most of the models give predictions that agree with each other within the propagated uncertainty from the rate constant estimates, and also show “satisfactory agreement” with experimental measurements. Differences among the models can be attributed to peculiarities in how the models treat the initial decomposition of the fuel. The rate coefficients for these reactions do not agree within the uncertainty assigned for them, however, which means that the models are fundamentally, quantitatively different. The model’s predictions agree with each other and with experiment, however. The predictive ability of the models is the only way we can fairly compare them, and by that measure all of the models are equally good. Given the predictive capability of the semi-empirical model, we suggest that future combustion research should concentrate on developing a model that treats only the key, rate-limiting processes in a rigorous manner, rather than continuing the current trend of attempting to describe all possible elementary reactions exactly.

1 Introduction

Computational physics relies on having a detailed understanding of the fundamental processes occurring in the system under consideration. For instance, simulation of a reacting flow requires understanding macro-scale convection, turbulent transport, diffusive transport, and chemical reaction processes. Of these, it is the chemical reaction mechanism that seems to be the most elusive. There are currently five [1-5] extant reaction models for the oxidation of H₂, with no clear way of distinguishing between them, and, apparently, no closure to the problem of simulating reacting flows immediately in sight. Furthermore, in the case of normal heptane oxidation, a fuel of practical interest, the National Institute of Standards and Technology (NIST) Chemical Kinetics Model Database [6] contains three readily-accessible detailed models [7-9], each of which uses different estimates of the rate constants. If we view the chemical reactions as being a fundamental part of the physics of reacting flows, then it is a poor commentary on the state of knowledge that there should be so many competing representations of what actually happens at the molecular level.

Such history led Schofield, in a recent review [10], to argue that the situation is utterly hopeless, with statements such as “there are always numerous adequate models that can fit any data.” Schofield suggested that there is no way that chemical kinetic modeling can lead to physical insights because all the models have flaws, some of which he addresses in detail. Instead, the focus should be on developing models only for specific engineering applications.
We propose, in contrast, that the situation might not be so dire. Box and Draper famously argued [11] that all models are wrong, but some are useful. A metric of utility for a physical model such as a reaction rate model is whether it reproduces reality, that is, a physical measurement. If a simulation of an experiment using a particular model does not reproduce the measurement, then the model is not useful. As an example, many chemical kinetic models do not include an ionization mechanism, and thus are not consistent with flame ionization observations [10, 12]. One could argue that these models are objectively wrong. However, the failure of the models to reproduce flame ionization may not affect their ability to reproduce fundamental combustion measurements, and therefore not affect their utility for combustion science. Furthermore, even if no experiment has yet been performed that a model cannot reproduce, the possibility that such an experiment will be done will always remain, meaning that no model is ever complete.

Several models may reproduce the same data and therefore be equally useful. Many kinetic models may all treat the chemical mechanism in the same way, that is, the reaction list is the same but the rate parameters are different. A recent paper by Fibich, Gavious, and Solan [13] showed that, if a model’s parameters show variability on scales of some amount \( d \), then the model’s outputs will show variability \( d^2 \) due to cancellation of errors. We should therefore not be surprised when different models give similar results.

Additionally, some models might treat certain processes differently. Some models, such as the highly-detailed model of Sarathy, et al. [7], attempt to describe every elementary step that is believed to occur. Others for expedience may lump several elementary reactions into a single “semi-global” step, such as the semi-empirical model of Held, Marchese and Dryer [14]. Such models are not “chemically rigorous,” but on the other hand there may not be, and might not ever be, enough experimental information to constrain the rate constants of some of the elementary steps that have been lumped. Empirically, the lumping may make therefore make little difference.

Furthermore, when we say “reproduce,” we must be extremely careful what we mean. In a strict sense, two estimates can only be said to agree when the range of values admitted by their uncertainties overlap. Consider two measurements \( \eta_1 \) and \( \eta_2 \), with uncertainties \( \sigma_1 \) and \( \sigma_2 \). The measurements agree if the intervals \( [\eta_1 - \sigma_1, \eta_1 + \sigma_1] \) and \( [\eta_2 - \sigma_2, \eta_2 + \sigma_2] \) overlap. Such an analysis requires a rigorous estimate of the uncertainties, both in the experimental measurements and simulation predictions. Detailed chemical kinetic modeling of high-temperature systems is a much older field [15-23] than uncertainty quantification in such systems [24], and to this day kinetic model development has been known to proceed with no direct comparison of experimental uncertainty with simulation uncertainty [25]. Consequently, a model exhibits “good agreement” with experimental measurements under the conditions chosen by the developers, but when applied to a different condition might exhibit “poor agreement,” which is often the motivation for a new model. Without uncertainty analysis, it is impossible to know whether the poor agreement is due simply to uncertainty in the rate parameters, meaning the model could be tuned against this new condition, or if the poor agreement is caused by a fatal flaw that justifies the new model.

This paper presents an estimate of the uncertainty in a set of simulations as predicted by the Jet Surrogate Fuel Model, version 2.0 (JetSurF) large alkane oxidation model [8]. The model is
then compared with a set of shock tube measurements of normal heptane \((n\text{-}C_7H_{16})\) oxidation, both ignition delay times [26] and in-situ species concentration histories [27]. Other heptane oxidation models [7, 9, 14] are also compared with the same experimental measurements, as well as with JetSurF. Because of the uncertainty in the rate constant estimates, there is some uncertainty in the simulation predictions, which has already been calculated for JetSurF [28]. We will therefore be able to make conclusive statements about fundamental differences in the predictive abilities of the model, and will show that most of the models agree with each other, both in their predictions and in the underlying physical behavior.

2 Methodology

The shock tube ignition experiments consist of OH and H\textsubscript{2}O concentration histories [27], CH\textsubscript{3} concentration histories [29], and ignition delay times [26] in shock-tube ignition of \(n\text{-}C_7H_{16}/O_2/Ar\) mixtures, presented in Table 1. Kinetic models for the oxidation of \(n\text{-}C_7H_{16}\) are taken from Sarathy, et al. [7] at Lawrence Livermore National Laboratory (LLNL, and henceforth the LLNL model), Babushok and Tsang [9] (the NIST model), and JetSurF [8]. In addition, the semi-empirical model of Held, Marchese and Dryer (the Princeton model) [14] is included for comparison with the detailed models. Ignition simulations are performed using a kinetic integrator based around the DVODE solver [30] using chemical rates provided by Sandia CHEMKIN-II [31]. Uncertainty quantification of the JetSurF simulation predictions was conducted [28] using sensitivity screening to identify 75 active rate parameters. The active parameters were then varied randomly within their uncertainty bounds to obtain 1000 random models. These random models were paired with 1000 random initial temperatures (ignition delay times) or 1000 random times (concentration histories) to obtain a sample of the model prediction uncertainty space.

The detailed kinetic models come from several sources. The heptane chemistry from the LLNL model was taken from the LLNL gasoline surrogate model [32], which was based on the small-hydrocarbon chemistry from Curran and co-workers [33-40]. JetSurF used the small-hydrocarbon chemistry from GRI 1.2 [41], Wang and co-workers [42, 43], and Tsang [44-48], with updated hydrogen chemistry from Davis, et al. [1]; the chemistry of large radical decomposition was taken from recent studies by Tsang and coworkers [49, 50]. The NIST chemistry presented new calculations for \(n\text{-}C_7H_{16}\) decomposition; smaller alkene chemistry was taken from Sumathi, et al. [51], while the small-hydrocarbon chemistry was taken from Wang and co-workers [42, 43], Marinov, et al. [52], and Curran, et al. [39], who in turn used the estimates of Tsang [44-48]. Likewise, the Princeton model derived its chemistry from similar sources. These models therefore represent a sampling of the chemistry from a relatively few sources, and so should be expected to give similar predictions. The models can also be ranked in order of their level of detail. The LLNL model is intended to be comprehensive. JetSurF omits low-temperature chemistry. The NIST model omits the chemistry of large radicals, assuming that \(C_7H_3\) fragments immediately into alkenes, 1-\(C_3H_7\), \(C_2H_5\), and \(CH_3\) radicals. The Princeton model abstracts further by omitting 1-\(C_3H_7\) chemistry.

All of the models express the rate constant \(k_i\) for the \(i\)\(^{th}\) reaction \(R_i\) in the same way. For reactions with no pressure dependence, the modified Arrhenius expression is used. As a function
of temperature $T$, the rate constant $k_i = A_i T^{b_i} \exp\left(\frac{E_i}{T}\right)$, with Arrhenius prefactor $A_i$, temperature exponent $b_i$ and activation temperature $E_i$. Pressure-dependent reactions have a low-pressure and high-pressure limit and use Lindemann or Troe expressions to interpolate between these limits. In order to narrow in on the important processes of the model, the logarithmic sensitivity coefficients were calculated using the formula,

$$\eta_i = \frac{\eta_i}{\eta_r}$$

where $S_{r,i}$ is the sensitivity of the $r^{th}$ model prediction $\eta_r$ to $A_i$.

3 Results and Discussion

3.1 Comparison of models’ performance

Our comparisons of the models’ predictions begin with ignition delay times at equivalence ratio $\phi = 0.5$ in Fig. 1. The uncertainty in the simulation prediction covers approximately a factor of 5. For comparison, the spread among the detailed models is 5% at low $T_5$, increasing to 20% at high $T_5$. Similarly, the detailed models all pass through the scatter of experimental measurements [26], suggesting that any of the detailed models would be suitable for simulating ignition under these conditions. The semi-empirical Princeton model predicts ignition delay times within the scatter of the detailed model predictions at high $T_5$, gradually increasing outside the scatter of the detailed models as $T_5$ is reduced below 1500 K. Such a result would suggest that there is something mechanistically wrong with the semi-empirical model, a possibility that will be discussed later. However, the semi-empirical model’s predictions still lie within the JetSurF uncertainty, and it exhibits “good agreement for an untuned model,” a phrase that is all too common in combustion kinetic modeling.

As the $O_2$ fraction is decreased, however, the situation begins to change. Ignition delay times for $\phi = 1$ and $\phi = 2$ are shown in Fig. 2. Similar to the lean case, the detailed model predictions span about 20%, much less than the JetSurF uncertainty. For $\phi = 1$, the predictions of the semi-empirical model start to deviate from the detailed models below 1500 K, reaching almost a factor of 3 greater at low $T_5$, so whatever mechanistic differences exist between the semi-empirical model and the detailed models must be in the low-temperature chemistry. The semi-empirical model still agrees with the JetSurF uncertainty, however. For $\phi = 2$, the deviations of the semi-empirical model from the detailed models occurs a higher $T_5$ (1600 K), and begins to leave the JetSurF uncertainty band at around 1500 K. It should be noted that, for this condition, the detailed models differ by nearly a factor of 2 from the experimental measurements at 1700 K; an optimization study [28] had some difficulty reconciling these high-$T_5$ experiments with those at lower equivalence ratios.

The ignition delay is representative of the overall reactivity of a mixture; if the predicted ignition delays of two models agree with each other, it does not necessarily mean that the detailed processes that led to ignition are the same. The motivation behind the species concentration measurements [27] was to observe the details of the ignition process in order to get a better understanding than ignition delay by itself could provide. We compare the model
predicted concentration histories at 1500 K in Fig. 3. JetSurF and the LLNL model agree closely with each other and with the experimental measurements, and both agree with the JetSurF uncertainty. Although the Princeton model predicts a faster ignition and more OH production than either JetSurF or the LLNL model, it still agrees with the JetSurF uncertainty. The NIST model, however, predicts OH and H₂O concentration far outside the JetSurF uncertainty for short times (< 100 μs); the ignition delay time is also longer than the other models, although it is still within the JetSurF uncertainty. Likewise, we compare the predicted concentration histories at 1365 K in Fig. 4; as in Fig. 3, the ignition delays predicted by all the models agree with the JetSurF uncertainty. Likewise, the early-time OH and H₂O concentrations agree with JetSurF, except for the NIST model which predicts as much as a factor of 30 less.

It is worth noting that none of the models presented here were tuned against these particular experimental measurements; indeed, two of the models predate the experimental studies and so it would be impossible. Both JetSurF [8] and the NIST model [9] contain influences from the GRI-Mech [41, 53] series of optimization studies, and the LLNL model [7] has likewise been tuned against experimental measurements. However, the data considered in all of these studies were for small hydrocarbons, and it is still an open question whether a model tuned against only small hydrocarbon data could be extrapolated to more complex fuels.

### 3.2 Origin of differences among detailed models

To begin exploring why the model predictions are different despite the models’ similar origins, we calculate the sensitivity coefficients of the OH concentration at various times to the reaction rate constants of JetSurF; they are shown in Fig. 5. At times comparable to the ignition delay time, the OH concentration is sensitive almost exclusively to the small hydrocarbon chemistry, and most sensitive by far to the rate constant for H + O₂ ↔ OH + O (R1) (S₁ ≈ 2). The reactions with the next highest sensitivity are C₃H₆ + H ↔ a-C₂H₅ + H₂ (R2) and CH₃ + H ↔ CH₄ (R3), which in turn compete with a-C₃H₅ ↔ a-C₂H₄ + H (R4). In essence, the most efficient thing that an H atom can do is to attack on O₂ molecule through chain branching; all other reactions are terminal and serve only to further delay the ignition. By the time the mixture begins to ignite, the fuel has mostly disintegrated into a soup of smaller species whose main kinetic effect is to soak up H atoms and prevent them from reaching their desired targets. Hence, the behavior of all the models at long times is determined by the small-hydrocarbon chemistry, which is similar for all models; once the soup is saturated, the H atoms will have nothing left to attack except O₂ molecules.

The situation is different at times much less than the ignition delay time. At these short times, the strongest sensitivities of the OH concentration, other than to R1, are to H abstraction reactions from the fuel by H and OH, and C-C bond fission, either of the 2-3 bond to form 1-C₅H₁₁ and C₂H₅ or the 3-4 bond to form 1-C₄H₉ and 1-C₃H₇ radicals, that is,

\[
\text{n-C}_7\text{H}_{16} \leftrightarrow 1\text{-C}_5\text{H}_{11} + \text{C}_2\text{H}_5 \quad (\text{R5-a})
\]
\[
\text{n-C}_7\text{H}_{16} \leftrightarrow 1\text{-C}_4\text{H}_9 + 1\text{-C}_3\text{H}_7 \quad (\text{R5-b})
\]

The 1-C₄H₉ radical will quickly form C₂H₅ via β-scission, and the C₂H₅ radicals will decompose to form H and C₂H₄, hence the large sensitivity of these rate constants.
H abstraction reactions all slow the overall reaction, and each typically by about the same amount \((S_i \approx 0.05-0.1)\). These reactions produce \(C_7H_{15}\) radicals, which will then fragment as follows:

\[
\begin{align*}
1-C_7H_{15} & \rightarrow 1-C_5H_{11} + C_2H_4 \rightarrow 1-C_3H_7 + 2C_2H_4 & \text{(R6-a)} \\
2-C_7H_{15} & \rightarrow 1-C_4H_9 + C_3H_6 \rightarrow C_3H_6 + C_2H_4 & \text{(R6-b)} \\
3-C_7H_{15} & \rightarrow 1-C_4H_8 + 1-C_3H_7 & \text{(R6-c)} \\
3-C_7H_{15} & \rightarrow 1-C_6H_{12} + CH_3 & \text{(R6-d)} \\
4-C_7H_{15} & \rightarrow 1-C_5H_{10} + C_2H_5 & \text{(R6-e)}
\end{align*}
\]

The alkenes and \(CH_3\) radicals form the soup of \(H\)-soaking smaller species that is important at longer times, as mentioned earlier, while the ethyl radicals will generate more \(H\) atoms.

The \(OH\) concentration, and thereby the reactivity of the mixture, has slightly different sensitivities to the different pathways of \(C_7H_{15}\) radical formation. H abstraction by \(OH\) obviously reduces the \(OH\) concentration, and the resulting radical will fragment into alkenes which are efficient radical sinks. H abstraction by \(H\), likewise, consumes an \(H\) atom which would otherwise attack \(O_2\) through chain branching. Because the \(C_2H_5\) from R6-e produces an \(H\) atom almost immediately, the production of \(4-C_7H_{15}\) by \(OH\) has one-half the effect of the other \(H\) abstractions by \(OH\). Similarly, the quenching effect of producing \(4-C_7H_{15}\) through \(H\)-abstraction by \(H\) is almost completely offset by regenerating the \(H\). Conversely, producing \(3\)-heptyl can produce an \(H\)-soaking \(CH_3\) radical immediately.

Since the fuel chemistry determines the behavior of the system at the beginning of ignition, we can examine what precisely is different about the various models. The obvious culprit would be the \(H\) abstraction reactions, the rates for which are presented in Fig. 6. JetSurF and the Princeton model both use an empirical rule where the rate constants for \(H\) abstraction from the fuel are the same as those from propane. The LLNL model uses the same rule, although with a rate for \(H\) abstraction from propane that may be too fast [Sarathy, 2012, personal communication]; this causes the rate for the formation of \(4-C_7H_{15}\), to be much faster than in the other models. The NIST model, on the other hand, does not use the empirical rule. As a result, the rates to produce \(1\)- and \(2\)-\(C_7H_{15}\) are an order of magnitude slower and the rate to produce \(3\)-\(C_7H_{15}\) is an order of magnitude faster than the other models. Alternatively, the \(C-C\) bond fission reactions could cause the difference, and the rates of these reactions are presented in Fig. 7. The rate expression used for R5-b in JetSurF yields a rate an order of magnitude faster than the NIST model and a factor of 5 faster than the LLNL model. These quickly produce \(C_2H_5\) radicals, which almost immediately produce \(H\) atoms. The rate of R5-a in the LLNL model, however, is about 50% faster than in JetSurF at 1365 K. Both models’ rates are still almost an order of magnitude faster than the NIST model. It should be noted that the uncertainty in the rate expressions estimated in JetSurF was about a factor of 3 [28], which is much less than the scatter in the rate constant estimates shown here.

Since the \(C-C\) bond-fission reactions and \(H\)-abstraction reactions differ among these models by a similar amount, they should affect the predicted \(OH\) concentrations by similar amounts. We show the effect of different choices of the \(C-C\) bond fission and \(H\) abstraction reactions in Figs. 8 and 9. In Fig. 8, the LLNL model is altered incrementally by changing its chemistry to more
closely match the NIST model; likewise, in Fig. 9 the same is done with JetSurF. At 1500 K, if the H-abstraction chemistry in the LLNL model is exchanged for that of the NIST model, the early time OH mole fraction is suppressed by a factor of 2, which is small compared to the model uncertainty shown in Figs. 3 and 4. At 1365 K, the early-time OH mole fraction is suppressed by a factor of 3, which is significant compared to the model uncertainty but still much more than the NIST model. Ignition delay is not affected. Replacing the LLNL H-abstraction chemistry has the effect of altering the branching ratio between 3- and 4-C$_7$H$_{15}$, without changing the total consumption rate; once the fuel is consumed, the ignition process is controlled entirely by the small-hydrocarbon chemistry and the altered C$_7$H$_{15}$ chemistry is no longer relevant. Conversely, if the C-C bond fission reactions are replaced by those of NIST, the early-time OH mole fraction is suppressed by a factor of 2 at 1500 K and a factor of 4 at 1365 K, and the ignition delay increases by about 20% at 1365 K and 35% at 1500 K. Replacing both mechanisms with the rate expressions from the NIST model gives a reasonable agreement with the NIST model predictions.

Exchanging the H-abstraction chemistry in JetSurF with that of NIST would be expected to have a stronger effect than on the LLNL model, since the total rate of H abstraction is significantly greater in the NIST model than in JetSurF. Indeed, Fig. 9 shows that the early-time OH mole fraction is suppressed by an order of magnitude at 1365 K, and the ignition delay increases by about 10%; this is most of the disagreement between the NIST model and JetSurF. The C-C bond fission chemistry accounts for the remaining disagreement. At 1500 K, the ignition delay increases by 20%, but the early-time OH mole fraction is reduced by only a factor of 3, leaving a large difference between the two models, which is again accounted for by the C-C bond fission chemistry.

3.3 Performance of the semi-empirical model

The remaining concern, then, is the difference between the Princeton model and the detailed models. Being semi-empirical, this model was not intended to describe the chemistry in a detailed manner [14]. Rather, it was meant to represent the chemistry in a manner that was “good enough” for engineering applications but at the same time could be used in reacting flow simulations; that is, it was designed to give an answer. As we have shown, it succeeded admirably in this task. At higher temperatures (>1500 K), the model produces results that are as good as the highly-detailed (and therefore much bigger) LLNL model. As the temperature is reduced, as shown in Fig. 4, the short-time behavior of the model (< 300 µs) still agrees with the detailed models; on such short timescales, the ignition process is controlled by competition between consumption of H atoms by fuel and by oxygen. The problems begin to arise on the longer timescales, caused by the treatment of the C$_7$H$_{15}$ radicals in the Princeton model. These radicals decompose by β-scission immediately into a CH$_3$ or C$_2$H$_5$ radical and C$_2$H$_4$. At low temperatures, the small alkyl radicals such as C$_3$H$_7$ have a significant lifetime, and so the Princeton model inaccurately predicts larger CH$_3$ and C$_2$H$_5$ concentrations than the detailed models; CH$_3$ concentrations for the Princeton and JetSurF models are compared in Fig. 10, and indeed the Princeton model predicts more CH$_3$ radicals. For comparison, the OH and C$_2$H$_4$ concentrations are shown as well. The point of maximum CH$_3$ concentration corresponds to the point where the methyl radical takes over from the fuel as the main sink of H atoms, because the
fuel runs out at approximately this time. At the lower temperature (~1400 K), because of the higher maximum CH$_3$ concentration, R3 proceeds faster and the minimum CH$_3$ concentration (and therefore minimum H) is lower than in JetSurF, which delays the ignition of the C$_2$H$_4$ produced from the fuel pyrolysis. At 1550 K, the Princeton model still predicts a higher CH$_3$ maximum, but the C$_2$H$_4$ ignition is faster due to the higher temperature, which compensates.

3.4 Relevance to model development and reduction

It has been observed previously [28, 53, 54] that combustion processes are usually sensitive to a relatively small number of reactions, compared to the size of the full model. For instance, for the heptane system as observed here and elsewhere [28], the ignition process is controlled primarily by the initial fuel decomposition and by the oxidation of small radicals. Using a multiparameter optimization [28], JetSurF could be brought into agreement with the experimental measurements by changing only a few reaction rates. As such, only these few reaction rates need to be known with much precision; the rates of other reactions are either sufficiently fast that they are not rate-limiting, and their exact rates do not matter, or so slow that they need not be considered. Constraining this number of reaction rates is well within present capabilities.

A related question is whether the full model is even necessary. If only a small number of reactions are rate-limiting, is it possible to construct a model that suitably describes the chemical system without writing every rate? A model that considers a reasonable number of fuel surrogate components will be very large indeed [7], and composing this model is likely to be a tedious and error-prone task. Currently, however, model reduction strategies such as DRG [55] and QSSA [56] rely on having a chemical model written down in its entirety. It is an important question, therefore, whether this model is really necessary. A related question is, if a reduced model can be generated without resorting to a full model, whether the reduction error can be quantified. A full treatment of these questions is beyond the scope of this work, but the results lend some credence to the idea that the answer might be yes. Consider that the Princeton model was called “semi-empirical” by its authors, which essentially means that the model was hand-reduced. As we mentioned earlier, the H abstraction reactions for both the NIST and Princeton models were written by lumping the abstraction and scission reactions into a single step, so that the products of the H abstraction reactions are the scission fragments. Such techniques are becoming common in combustion modeling [57]. It could be argued that this hand-reduction is in fact a crude form of rate-controlled constrained equilibrium (RCCE) [58]. As an example, RCCE has been successfully employed to develop reduced models without needing to write a complete model [59], although in this case a detailed model was available with which to make comparisons. The results of this paper and of the RCCE modeling suggest that model development would be well-served by adopting a lumped-chemistry approach.

4 Conclusions

A set of chemical models for the combustion of normal heptane was collected from the literature and compared, both with each other and with a set of literature experiments for heptane shock tube ignition. The models selected included several detailed models [7-9] and one semi-
empirical, lumped model [14]. It was found that the predictions of the models almost all agreed with each other within the estimated uncertainty, and the detailed models were all able to predict shock-tube ignition delay times to within 20% of each other and to within the estimated uncertainty of the experiments. The semi-empirical model predicted longer ignition delay times than the other models below 1500 K because it does not properly treat propane and propyl chemistry, which have significant lifetimes below this temperature; the predictions still agree with the model uncertainty, however. Likewise, the detailed model published by Babushok and Tsang [9] underestimated the formation of small radicals at early times in the shock tube ignition. Early-time behavior of the ignition process is controlled by competition between initiation reactions to form small radicals and the attack of the small radicals on the fuel, and the detailed models examined here all make different choices for what those rate constants should be.

The measurements which we use to compare the models are generally considered to be the most fundamental that a combustion model would have to reproduce. Because the model predictions generally agree with each other, then, the models are the same to our ability to distinguish them. We can conclude that any detailed kinetic model, so long as it makes reasonable choices for the chemical rate expressions, will make predictions that agree with any other detailed kinetic model. Furthermore, because of the performance of the semi-empirical model [14], we can conclude that the detailed models can be aggressively reduced and lumped while still capturing enough of the chemical details to make quantitative predictions.
References

# Tables

Table 1. List of experimental conditions used for model comparison

<table>
<thead>
<tr>
<th>Series</th>
<th>Data type/conditions&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH, CO₂, H₂O, C₂H₄ time histories [27]</td>
</tr>
<tr>
<td></td>
<td>i) 300 ppm nC₇H₁₆ / 3300 ppm O₂ / Ar&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>( T_5 = 1494 ) K, ( p_5 = 2.15 ) atm</td>
</tr>
<tr>
<td></td>
<td>ii) 300 ppm nC₇H₁₆ / 3300 ppm O₂ / Ar&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>( T_5 = 1365 ) K, ( p_5 = 2.35 ) atm</td>
</tr>
<tr>
<td>2</td>
<td>CH₃ time histories [29]</td>
</tr>
<tr>
<td></td>
<td>500 ppm nC₇H₁₆ / 5500 ppm O₂ / Ar</td>
</tr>
<tr>
<td></td>
<td>i) ( T_5 = 1395 ) K, ( p_5 = 1.72 ) atm</td>
</tr>
<tr>
<td></td>
<td>ii) ( T_5 = 1545 ) K, ( p_5 = 1.61 ) atm</td>
</tr>
<tr>
<td>3</td>
<td>Ignition delay</td>
</tr>
<tr>
<td></td>
<td>i) 0.4% nC₇H₁₆ / 2.2 % O₂ / Ar</td>
</tr>
<tr>
<td></td>
<td>( T_5 = 1499\text{-}1700 ) K, ( p_5 = 1 ) atm [26]</td>
</tr>
<tr>
<td></td>
<td>ii) 0.4% nC₇H₁₆ / 4.4 % O₂ / Ar</td>
</tr>
<tr>
<td></td>
<td>( T_5 = 1429\text{-}1486 ) K, ( p_5 = 1 ) atm [26]</td>
</tr>
<tr>
<td></td>
<td>iii) 0.4% nC₇H₁₆ / 8.8 % O₂ / Ar</td>
</tr>
<tr>
<td></td>
<td>( T_5 = 1300\text{-}1499 ) K, ( p_5 = 1 ) atm [26]</td>
</tr>
</tbody>
</table>
Figures

Figure 1. Ignition delay times behind reflected shock waves (Series 3iii). Large symbols are the experimental measurements from Smith, et al. [26]. Small symbols are the Monte Carlo-sampled uncertainty from JetSurF [8]. Lines are the nominal calculations of the LLNL model (dash-dot, [7]), Princeton model (dotted, [14]), NIST model (long dash, [9]), and JetSurF (short dash, [8]).

Figure 2. Ignition delay times behind reflected shock waves (Series 3ii, left; 3i, right). See Fig. 1 for symbol and line description.
Figure 3. OH and H$_2$O mole fraction histories behind reflected shock waves (Series i). The solid line is the measurement from Davidson, et al. [27]. Other lines are the nominal calculations of the models [7-9, 14] (see Fig. 1). Symbols are the Monte Carlo-sampled uncertainty from JetSurF [8].

Figure 4. OH and H$_2$O mole fraction histories behind reflected shock waves (Series ii). The solid line represents the measurement from Davidson, et al. [27]. Other lines are the nominal calculations of the models [7-9, 14] (see Fig. 1). Symbols are the Monte Carlo-sampled uncertainty from JetSurF [8].
Figure 5. Logarithmic sensitivity coefficients of the OH mole fraction history in Series 1ii to selected reaction rate A factors in the JetSurF model [8].

Figure 6. Bimolecular rate constants with respect to temperature for n-C$_7$H$_{16}$ + H ↔ H$_2$ + x-C$_7$H$_{15}$ published in the models under study. Left, abstraction to form 1- and 2-heptyl; right, abstraction to form 3- and 4-heptyl. Note that the Princeton and NIST models lump the decomposition pathways and abstraction reactions together; the rate constant shown is the total rate of n-C$_7$H$_{16}$ consumption to produce x-heptyl decomposition products.
Figure 7. Unimolecular rate constants for R5-a, \( n\text{-C}_7\text{H}_{16} \leftrightarrow 1\text{-C}_5\text{H}_9 + \text{C}_3\text{H}_5 \) and R5-b, \( n\text{-C}_7\text{H}_{16} \leftrightarrow 1\text{-C}_4\text{H}_9 + 1\text{-C}_3\text{H}_7 \), published in the detailed models (LLNL [7], NIST [9], JetSurF [8]).
Figure 8. OH mole fraction histories (Top, series 1i; bottom, series 1ii). Lines are (a) the nominal LLNL model [7], (b) the LLNL model using the H abstraction reaction rate expressions from the NIST model [9], (c) the LLNL model using the C-C bond fission rate expressions form the NIST model, (d) the LLNL model using the H abstraction and C-C bond fission rate expressions from the NIST model, and (e) the NIST model.
Figure 9. OH mole fraction histories (Top, series 1i; bottom, series 1ii). The solid line is the experimental measurement from Davidson, et al. [27]. Other lines are (a) the nominal JetSurF model [8], (b) JetSurF using the C-C bond fission rate expressions from the NIST model [9], (c) the JetSurF model using the C-C bond fission rate expressions from the NIST model, (d) JetSurF using the H abstraction and C-C bond fission rate expressions from the NIST model, and (e) the NIST model.

Figure 10. OH, CH$_3$, and C$_2$H$_4$ mole fraction histories (Series 2i, left) and CH$_3$ mole fraction histories (Series 2ii, right) from the Princeton model (dotted, [14]), and JetSurF (dashed, [8]).