LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-CONF-724918

An updated comprehensive chemical kinetic model of C8-C20 n-alkanes.

G. Kukkadapu, S. W. Wagnon, M. Mehl, K. Zhang, C. K. Westbrook, W. J. Pitz, M. J. Mcnenly, S. M. Sarathy, A. Rodriguez, O. Herbinet, F. Battin-Leclerc, C. J. Sung

February 22, 2017

10th U. S. National Combustion Meeting
College Park, MD, United States
April 23, 2017 through April 26, 2017

Disclaimer

10th U. S. National Combustion Meeting
Organized by the Eastern States Section of the Combustion Institute
April 23-26, 2017
College Park, Maryland

An updated comprehensive chemical kinetic model of C8-C20 *n*-alkanes.

Goutham Kukkadapu[1], Scott W. Wagnon[1], Marco Mehl[1], Kuiwen Zhang[1], Charles K. Westbrook[1], William J Pitz[1], M. J. Mcnenly[1], S. M. Sarathy[2], Anne Rodriguez[3], Olivier Herbinet[3], Frédérique Battin-Leclerc[3], Chih-Jen Sung[4].

[1]Lawrence Livermore National Laboratory, Livermore, CA 94551, USA.
[2] Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.
[3] Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, 1, rue Grandville, BP 20451, 54001 Nancy Cedex, France.
[4] University of Connecticut, Storrs, CT 06269, USA.

[*]Corresponding Author: kukkadapu1@llnl.gov

Abstract: Large *n*-alkanes are important reference components in the formulation of surrogates for Jet and Diesel fuels. This work focuses on the kinetics of *n*-alkanes larger than *n*-heptane with carbon chain length varying between 8 (*n*-octane) to 20 (*n*-eicosane) through newly acquired experimental data and detailed kinetic modeling. Extending the previous work by Zhang et al. on *n*-heptane, recent literature quantum chemical calculations have been used to generate a new set of consistent reaction rate rules for large alkanes. Based on these rules, the existing LLNL kinetic mechanisms for large n-alkanes has been revised and the model results have been compared to literature data and new stirred reactor experiments including important low temperature oxidation intermediates. The optimized model had generally been found to perform a good job against experimental data from current study and archived shock tube, and jet stirred reactor data in the literature.

Keywords: Diesel surrogates, alkanes, ignition, detailed chemical kinetic model

1. Introduction

Transportation fuels are made up of several hundreds to thousands of hydrocarbons from different hydrocarbon classes. Of the different hydrocarbon classes found in transportation, *n*-alkanes make up to 20% by weight [1] and are widely used surrogate fuels which are used to model transportation fuels. Large *n*-alkanes are important reference components in the formulation of surrogates for jet and diesel fuels [2-6]. The chain length of the *n*-alkanes used for jet fuel surrogates vary from 8-12 [2,3] while the chain length of constituents of diesel surrogates are often in the range of 10-20 [4-6]. The earlier mechanism developed at LLNL describes the kinetics of alkanes with carbon chain length varying between 8 (*n*-octane) to 16 (*n*-hexadecane). Recognizing the recent interest in ignition characteristics of *n*-alkane larger than *n*-hexadecane, we have developed a detailed kinetic model which describes the kinetics of *n*-alkanes with chain lengths up to 20 (*n*-eicosane). In addition to extending the model to span a wider range of *n*-alkane, the model has been updated to include the reaction pathways which were missing in the earlier models and the reaction rules used have also been updated as per recent literature quantum chemical calculations. Furthermore, novel speciation measurements were conducted in

the current work for assessing and refining the updated kinetic model. The subsequent sections of the current article shall briefly describe the experimental and modeling procedures followed by a section which shows the validation of the mechanism.

2. Atmospheric Pressure Jet-Stirred Reactor (JSR)

The experimental work was performed using a spherical fused silica JSR (volume of 85 cm^3) already described in the literature [7]. A mixture of fuel and oxygen diluted in helium entered the reactor through an injection cross located at its center. The homogeneity in composition and temperature of the gas phase is obtained due to the high turbulence created by gaseous jets entering the reactor through four nozzles. The JSR was preceded by a quartz annular preheated zone in which the gaseous temperature was increased up to that of the reactor. The gas mixture residence time inside the annular preheater was very short compared to its residence time inside the reactor. Both the reactor and the preheating zone were heated by Thermocoax resistances rolled up around the reactor. Oxygen and helium were provided by Messer (purities of 99.995 and 99.999%, respectively), *n*-decane was provided by Sigma Aldrich (purity of ≥ 99%). Gas flow rates were controlled by mass flow controllers; Coriolis flow controllers were used for liquid fuels. Measurements were made at isothermal and steady state conditions, at a pressure of 1.05 atm, at a residence time of 2 s, at temperatures ranging from 500 to 1100 K, and for stoichiometric mixtures with an initial fuel mole fraction of 0.0025. Directly connected to the outlet of the reactor, via a heated transfer lines kept at 423 K to limit condensation problems, three chromatographs were equipped with a carbosphere packed column, a PlotQ capillary column and a HP-5 capillary column, respectively, as well as with a TCD (thermal conductivity detector) or an FID (flame ionization detector). A GC-MS operating with electron ionization was used for products identification.

3. Chemical Kinetic model development

The updated model developed herein is based on the earlier LLNL *n*-alkane models [8,9] and is built hierarchically on the *n*-heptane mechanism of Zhang *et al.* [10] which includes the kinetics of C5-C7 *n*-alkanes and the base chemistry (C0-C4) from AramcoMech 2.0 [11]. The updates to the model can be classified into three major categories which are re-evaluating the thermochemistry of the intermediate species, modifying the reaction rate rules and addition of the new reaction channels which shall be discussed in detail in following sections.

3.1 Thermochemistry of intermediate species

Bugler *et al.* [12] recently demonstrated the effect of the thermochemistry of intermediates on the global performance of the kinetic model and suggested the need for re-evaluating the thermochemistry used in our earlier kinetic models. Based on the finding of Bugler *et al.* [12], the thermodynamic properties of the intermediate species herein were re-evaluated using group additivity method i*n*-conjunction with the latest group values from Burke *et al.* [13].

3.2 Reaction rate rules

The kinetics of alkanes have been studied for many years both experimentally and computationally. The progress in computing power have aided in conducting *ab-initio* quantum chemical calculations to further understand the chemical kinetic pathways and the associated rate parameters. In the current study the reaction rate parameters of several important reaction classes

have been taken directly from high level quantum chemical calculations. Detailed information of the rates used in the mechanism can be found in Zhang et *al* [10].

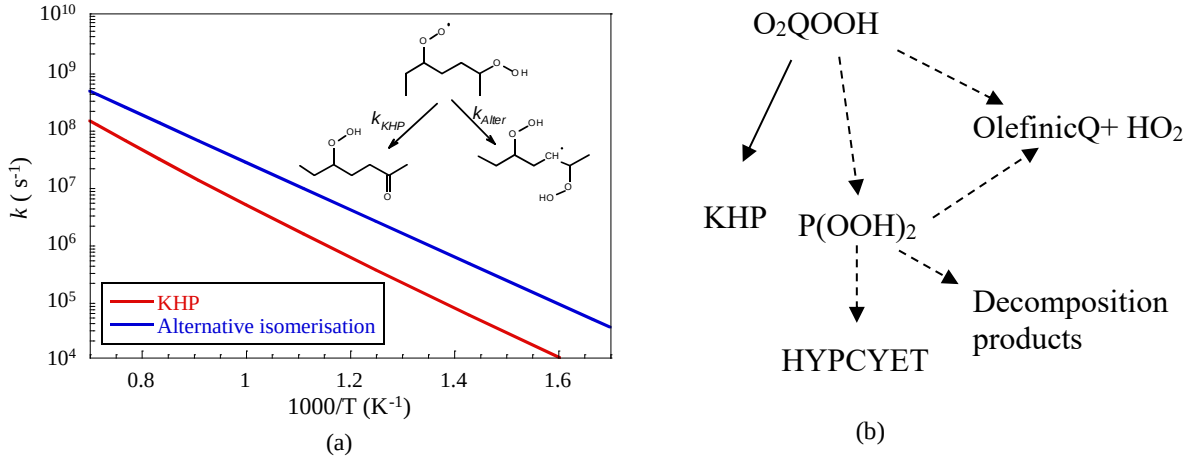


Figure 1: (a) Plot comparing the rates of H migration reactions possible in O2QOOH species of *n*-heptane (b) Plot showing summary of possible reaction channels of O2QOOH. Broken arrows indicate pathways which were not included in the earlier model.

3.3 Addition of new reaction paths

One of the important reaction classes in the low temperature oxidation of alkanes is the isomerization of peroxyalkylhydroperoxide (O_2QOOH). The O_2QOOH radicals in the earlier models were assumed to be consumed by internal isomerization reaction via an H-abstraction from the carbon attached to the hydroperoxy group (OOH) leading to formation of ketohydroperoxides (KHP). The isomerization reaction leading to formation of KHP were treated similar to the isomerization of alkylperoxy radicals and the activation energy for the internal H-abstraction was reduced by 3Kcalmol^{-1}. The activation energy for the KHP was lowered based on the assumption that the presence of OOH group would make it easier to abstract the H atom. Sharma *et al.*[14] in their study on isomerization of QOOH and O_2QOOH radicals found the reduction in the activation energy for H migration to be dependent on the size of the transition state (TS) and consequently some of the reaction channels of O_2QOOH radicals are missing in the kinetic models which is illustrated by Figure 1a. Figure 1a shows the comparison of rates of internal isomerization reactions of O_2QOOH radicals leading to formation of KHP and dialkylhydroperoxy radicals ($P(OOH)_2$) through 7 member and 6 member TS respectively. From, Figure 1a it is clear that formation of $P(OOH)_2$ might be more important than formation of KHP. Recently, Bugler *et al.* [12] have investigated the effect of the alternative reaction pathways of pathways of O_2QOOH on oxidation of *n*-pentane and found the alternative reactions of O_2QOOH to have a discernible effect on the oxidation of *n*-pentane. It is to be noted that as the chain length increases the available sites for alternative isomerizations also increases and the effect of alternative isomerizations could be higher in larger alkanes. To study the effect of the reaction pathways which were not considered in our earlier model, we included all the possible reaction channels for O_2QOOH as shown in Figure 1b. The added channels are concerted elimination of O_2QOOH radicals leading to formation of olefinichydoperoxides (olefinicQ) and alternative isomerization reactions leading to formation of $P(OOH)_2$ radicals. The $P(OOH)_2$ radicals are modelled to be consumed by reactions similar to those of QOOH radicals leading to formation of hydroperoxy cyclic ethers (HYPCYET), olefinicQ (via β-elimination) and decomposition reactions. As the new reaction channels added to the model are similar to the reactions of RO_2

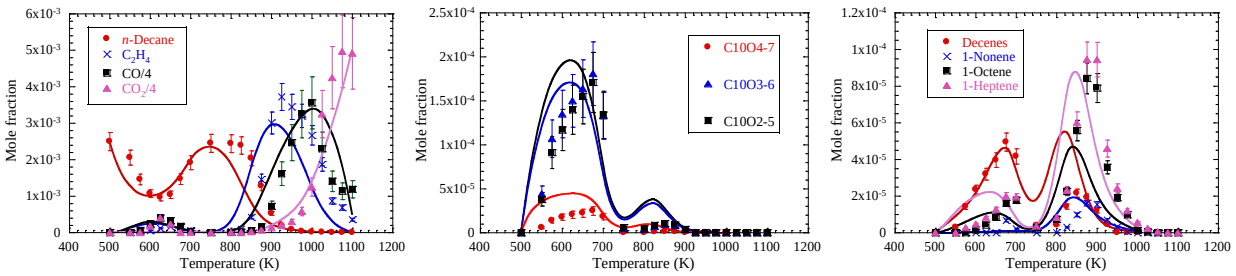
and QOOH radicals, the rates of the analogous reactions of RO_2 and QOOH radicals have been used.

4. Validation of the kinetic model.

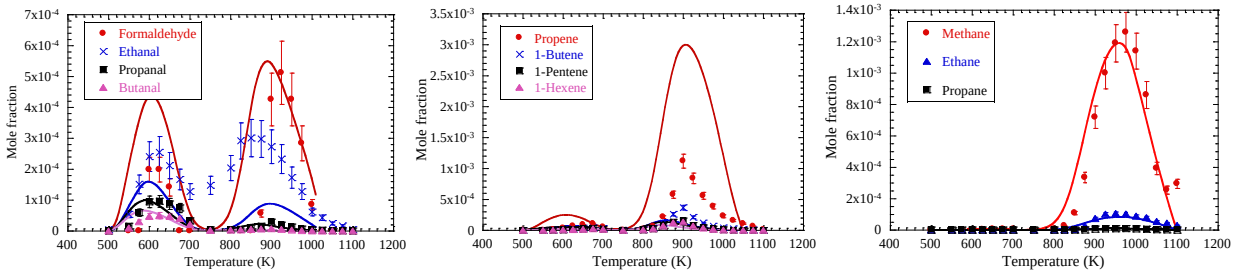
The kinetic model has been validated against a wide range of pyrolysis and oxidation data obtained from jet stirred reactors, shock tubes and also against laminar flame speed measurements of which only a few validations are shown in the current work. All the simulations were conducted using Chemkin-Pro package [15].

4.1 JSR validations

JSR experiments were conducted to obtain the concentration profiles of several intermediates produced during oxidation of *n*-decane. The experiments were conducted with stochiometric *n*-decane/O_2/N_2 mixtures with an initial fuel concentration of 0.0025 at a pressure of 1.06 bar and residence time of 2 sec. The intermediates measured include the C_{10} olefins, C_{10} tetrahydrofurans and several smaller species. Figure 2 shows the comparison of the experimental and simulated concentration profiles of the intermediate species. The experiments show that *n*-decane exhibits a negative temperature coefficient (NTC) response at temperatures between 600-800 K which is accurately captured by the current kinetic model. In addition the concentrations of fuel predicted by the model match very closely with the experiments for temperatures in the NTC regime. But for conditions other than in the NTC, the model predicts a higher fuel conversion. The parent fuel conversion at low temperatures (T<600 K) was found to be very sensitive to the rates of decomposition of ketohydroperoxides (KHP) which in the current study were taken from the recent work Goldsmith et al. [16]. Reducing the rate of decomposition of KHP helps in reducing the % fuel conversion at low temperatures (T<600 K), but doing so was found to adversely affect the simulated ignition delays which shall be presented in due course and hence were left unchanged. Figure 2b shows the concentration profiles of C10 olefins and substituted THF's which are produced from of RO_2 and QOOH radicals respectively. Accurate prediction of the concentration of these molecules is necessary to ensure that the model accurately captures relative flux between the chain terminating, chain propagating and chain branching reactions relevant to low temperature chemistry. The current kinetic model is found to capture the measured concentrations of these intermediates and predictions by the model closely match with the experimental values thus providing confidence in the reaction rates used for the two important reactions [Fig. 2(b,c)]. The kinetic model is also observed to predict the measured concentrations of several important intermediates such as carbon monoxide, carbon dioxide, ethylene, methane, ethane, propane, and C3-C9 olefins reasonably well. Among aldehydes, the predicted concentrations of ethanal shows significant differences compared to measurements while most of the other aldehydes match closely with the experiments.

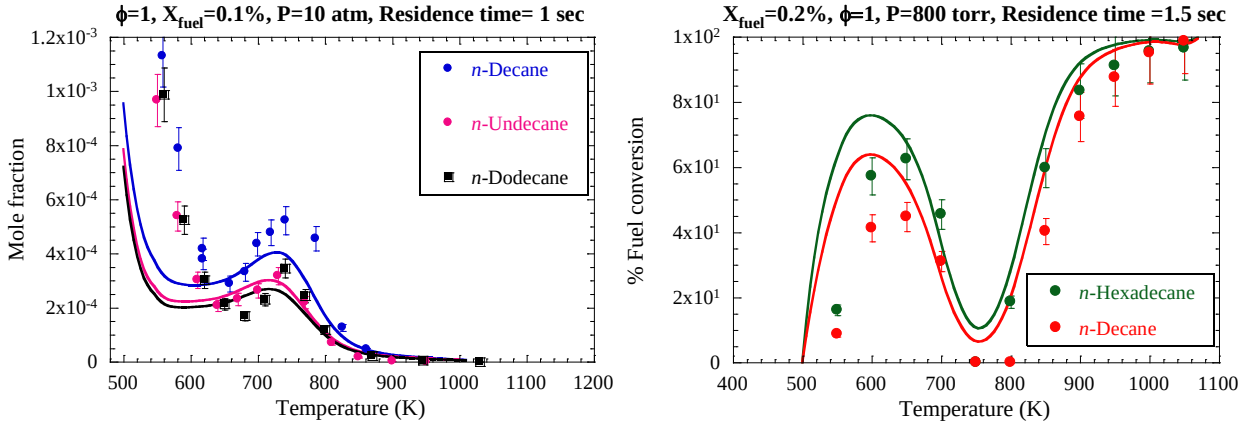


(a) (b) (c)



(d) (e) (f)

Figure 2: Comparison of concentration profiles of intermediate species from CNRS JSR experiments and simulations.



(a) (b)

Figure 3: Comparison of concentration profiles of fuels obtained from JSR experiments and simulations. Symbols correspond to experimental data taken from [17,19], lines correspond to profiles predicted by the current mechanism.

The current kinetic model as mentioned earlier has been developed hierarchically using a consistent set of reaction classes and rate rules. JSR simulations were conducted to ensure that the kinetic model could predict reactivity trends observed in experiments. For this exercise, the kinetic model was validated against JSR data from Dagaut and co-workers [17,18] who studied the oxidation of *n*-decane, *n*-undecane and *n*-dodecane in a JSR. The experimental data used for validations were conducted with diluted stochiometric mixtures fuel/O_2/N_2 with initial fuel concentrations of 0.1% at a pressure of 10 atm and at a fixed residence time of 1 sec. The comparison of the experimental and simulated concentrations of the three parent fuels are shown in Figure 3a. The experiments show that as chain length increases, the mole fraction of the fuel after a 1sec residence time generally reduces which is qualitatively well captured by the model. The model also predicts the fuel concentrations to good agreement for temperatures in NTC and intermediate temperatures (T>820 K), but the % fuel conversions at lower temperatures (T<600 K) is over predicted by the model. The reason for this differences at low temperatures has been discussed earlier.

In the final set of JSR validations, the model performance was compared against the data of Biet *et al.* [19] who studied the oxidation of 76/24 (% molar) binary blend of *n*-decane/*n*-hexadecane blends in a JSR. This exercise aids to validate the model against binary mixtures and also check the performance of the *n*-hexadecane submodel. To better understand the reactivity trends, the % fuel conversion profiles are compared in Figure 3b. The experiments show that in

the binary blend investigated, *n*-C16 is clearly more reactive than *n*-C10 for temperatures below 900 K and for temperatures greater 900 K both the alkanes exhibit similar reactivity. These reactivity trends are accurately captured by the current kinetic model. It can also be seen that the model accurately predicts the drop in reactivity due to NTC response.

4.2 Ignition delay validations

The mechanism has been validated against the first stage and total ignition delays of C8-C12 alkanes available in literature covering a wide range of pressures, equivalence ratios and temperatures. The ignition delay simulations were conducted using closed homogenous batch reactor module in Chemki*n*-Pro with the constant volume constraint [15]. The initial conditions for the simulations were maintained identical to experimental conditions when the information was provided and for cases where the scatter in post shock pressures are not available a nominal value of the initial pressure for simulations was used.

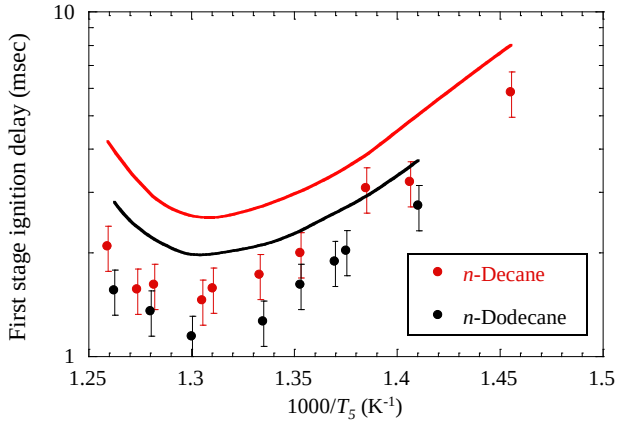
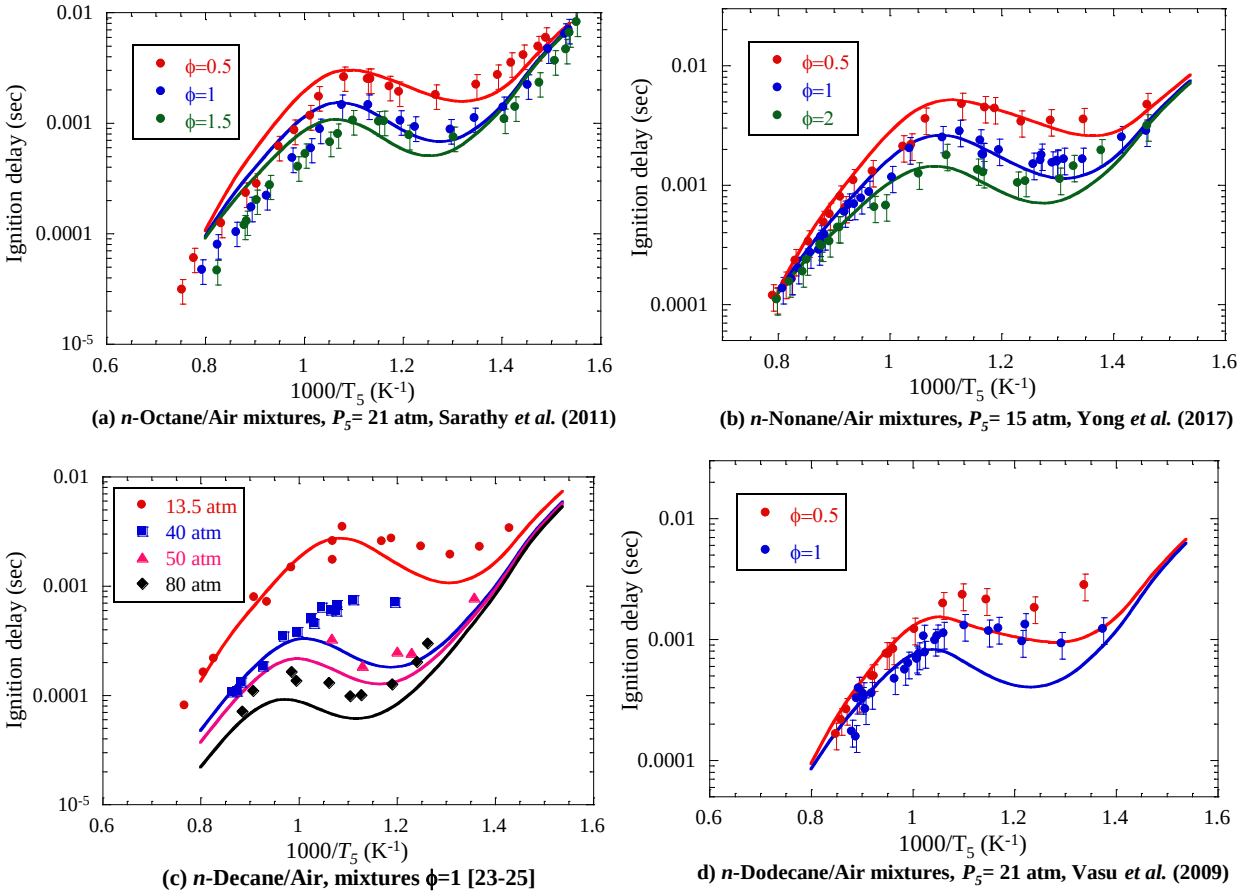


Figure 3: Comparison of experimental and simulated first stage ignition delays. Experimental data taken from Tekawade *et al.* [20].

First set of ignition delays comparison shown are the first stage ignition delays of diluted (X_{O2}=5%) stochiometric fuel/O_2/Ar mixtures of *n*-decane and *n*-dodecane conducted at a nominal pressure of 10 atm by Tekawade *et al.*[20] The experiments of Tekawade *et al.*[20] show that the first stage ignition delays decrease with increase in chain length and the first stage ignition delays exhibits a local minima around 770 K, these two characteristics of first stage ignition delay are well captured by the model but the current model is found to be less reactive experiments with difference in ignition delays generally less than a factor of two.

The second set of ignition delays of alkanes shown are the total ignition delays of different C8-C12 alkanes obtained from shock tube experiments. Several interesting are observed in the comparison of the experimental and simulated ignition delays. From Figure 4a-4d, it can be observed that the kinetic model does a very good job in estimating the ignition delays of different *n*-alkanes for temperatures in the low temperature regime (LTR). The ignition delays for the temperatures in LTR were found to be very sensitive to KHP decomposition; however, decreasing the rate of decomposition of KHP to improve the JSR predictions affected the ignition delay comparisons shown in Figure 4. For this reason the further refinements to model to improve the JSR simulation were not sought.

For temperatures in NTC regime, it can be observed that the current kinetic model ignition delay predictions from the kinetic model match closely with the ignition delays of *n*-octane and *n*-nonane obtained from experiments, but a similar level of agreement is not observed while comparing the ignition delays of *n*-decane and *n*-dodecane with the differences of about a factor of two for some data points in the NTC. At higher temperatures, specifically in the intermediate temperature range, the kinetic model is found to predict the ignition delays of *n*-nonane, *n*-decane and *n*-dodecane to agree well with the experimental values while some differences were observed between the experimental and simulated ignition delays of *n*-octane values. The ignition delays in the intermediate temperatures were found to sensitive to the hydrogen (H) abstraction by hydroperoxyl radicals (HO_2). The rate parameters for this reaction class used in the current model was taken from the Aguilera-Iparraguirre *et al.* [21] which is close to the mean of the different values in literature. The uncertainty in the reaction rate from literature values is around a factor of five. The A-factor for H abstractions was increased conservatively by a factor of 1.5 from the recommendation of Aguilera-Iparraguirre *et al.* [21] to improve the agreement against majority of data sets.



(a) *n*-Octane/Air mixtures, P_5= 21 atm, Sarathy *et al.* (2011)

(b) *n*-Nonane/Air mixtures, P_5= 15 atm, Yong *et al.* (2017)

(c) *n*-Decane/Air, mixtures ϕ=1 [23-25]

d) *n*-Dodecane/Air mixtures, P_5= 21 atm, Vasu *et al.* (2009)

Figure 4: Comparison of the experimental and simulated total ignition delays of different *n*-alkane/air mixtures.

The reason for the observed difference in the quality of the predictions could be partly due to the inconsistencies in the experimental data available in literature and partly due to the deficiencies in the kinetic model literature as demonstrated by Figure 5. From Fig. 5 it can be inferred that the experiments demonstrate that the ignition delays are less sensitive to carbon

chain length while the ignition delays computed using the kinetic model suggest a stronger sensitivity to chain length. Another interesting observation from Fig. 5a is that the experimental ignition delays from literature show that *n*-decane is marginally less reactive than *n*-nonane which is in contradiction with the simulated trends and also is unexpected. The trend observed in Fig.5a is thought be unexpected as the ignition delays are expected to be either insensitive to chain length or expected to decrease with increase in chain length which is reflected by the cetane number ratings [27]. The comparisons shown in Fig. 5 demonstrate the need for more high-quality benchmark experimental data.

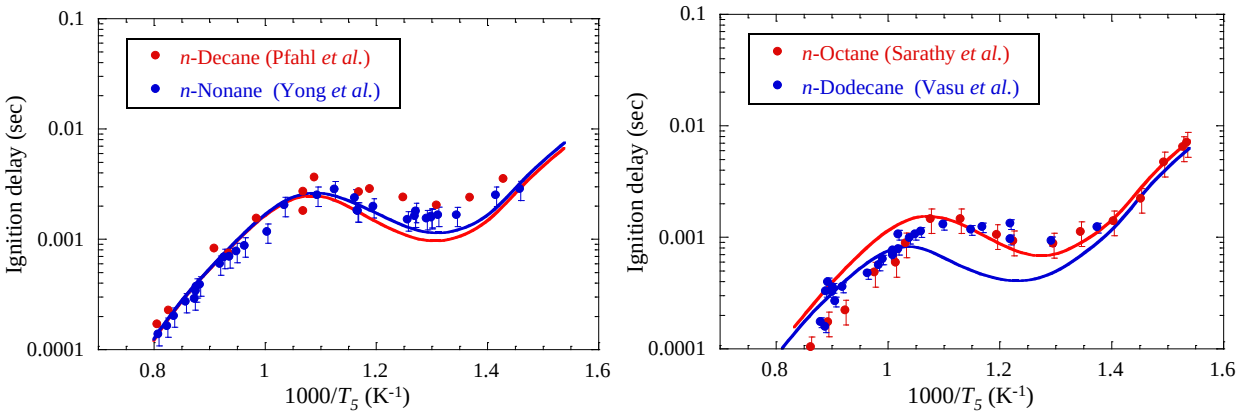


Figure 5: Comparison of ignition delays of different alkanes at identical test conditions for stoichiometric fuels/air mixtures. Plot (a) Ignition delays of *n*-decane [23] and *n*-nonane [22] at 15 atm (b) Ignition delays of *n*-octane [9] and *n*-dodecane [26] at 21 atm.

5. Conclusion

An experimental and kinetic modeling study has been performed to study the kinetics of *n*-alkanes. The experiments have been conducted to obtain novel speciation measurements in a jet stirred reactor. The kinetic model has been extended the to cover range of carbon chain lengths of interest for jet and diesel fuel surrogates. Additionally, the kinetic model incorporates new reaction rates taken from high level quantum chemical calculations and also includes the reaction classes which were missing in the old models. The updated rate rules in the mechanism achieved good performance against the novel speciation measurements. Also, the refined kinetic model was found to perform well against various shock tube ignition-delay data sets available in literature.

Acknowledgements:

The work at LLNL is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Office (program managers Gurpreet Singh and Leo Breton) and performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. C. J. Sung would like to thank the support from National Science Foundation under Grant No. CBET-1402231. The work at KAUST was supported by Saudi Aramco under the FUELCOM program and by the King Abdullah University of Science and Technology (KAUST) with competitive research funding given to the Clean Combustion Research Center (CCRC). The work At LRGP was supported by COST Action CM1404.

References:

1. R. Gieleciak, C. Fairbridge, Detailed hydrocarbon analysis of FACE diesels using comprehensive two-dimensional gas chromatography.

http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/FACE/GCxGC%20analysis%20of%20FACE%20fuels%20-RG%20v4%200%20Nov2013.pdf.

2. S. Dooley, S. H. Won, M. Chaos, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, C.-J. Sung, H. Wang, M. A. Oehlschlaeger, R. J. Santoro, T. A. Litzinger. A jet fuel surrogate formulated by real fuel properties, Combust. Flame, 157 (2010), pp. 2333–39.
3. S. Dooley, S. H. Won, J. Heyne, T. I. Farouk, Y. Ju, F. L. Dryer, K. Kumar, X. Hui, C.-J. Sung, H. Wang, M. A. Oehlschlaeger, V. Iyer, S. Iyer, T. a. Litzinger, R. J. Santoro, T. Malewicki, and K. Brezinsky, The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena, Combust. Flame, 159 (2012), pp. 1444–1466.
4. C.J. Mueller, W. J. Cannella, T. Bays, T. J. Bruno, K. DeFabio, H. Dettman, R. Gieleciak, M .L. Huber, C-B Kweon, S. M. McConnell, W. J. Pitz, M. A. Ratcliff, Energy & Fuels, 30(2016), pp. 1445–1461.
5. A. Krishnasamy, R. D. Reitz, W. Willems, and E. Kurtz, Surrogate Diesel Fuel Models for Low Temperature Combustion, SAE 2013-01-1092.
6. J. T. Farrell, N. P. Cernansky, F. L. Dryer, D. G. Friend, C. A. Hergart, C. K. Law, R. M. McDavid, C. J. Mueller, A. K. Patel, and H. Pitsch, Development of an Experimental Database and Kinetic Models for Surrogate Diesel Fuels, SAE International, 2007-01-0201, 2007.
7. Herbinet, O; Dayma, G. Jet-Stirred Reactor. In *Cleaner Combustion*; Batt*i*n-Leclerc, F., Simmie, J. M., Blurock E., Eds.; Springer London, 2013; pp 183–210.
8. C. K. Westbrook, W. J. Pitz, O. Herbinet, H. J. Curran, E. J. Silke, A comprehensive detailed chemical kinetic reaction mechanism for combustion of *n*-alkane hydrocarbons from *n*-octane to *n*-hexadecane, Combust. Flame, 156 (2009), pp. 181–199.
9. S. M. Sarathy, C. K. Westbrook, M. Mehl, W. J. Pitz, C. Togbe, P. Dagaut, h. Wang, M. A. Oehlschlaeger, U. Niemann, K. Seshadri, P. S. Veloo, C. Ji, F. N. Egolfopoulos, T Lu, Comprehensive chemical kinetic modeling of the oxidation of 2-methylalkanes from C7 to C20, Combust. Flame, 158 (2011), pp. 2338–2357.
10. K. Zhang, C.Banyon, J. Bugler, H. J. Curran, A. Rodriguez, O. Herbinet, F. Batt*i*n-Leclerc, C. B'Chir, K. A. Heufer, Combust. Flame, 172 (2016), pp. 116-135.
11. Y. Li, C-W. Zhou, K.P. Somers, K. Zhang, H.J. Curran, The Oxidation of 2-Butene: A High Pressure Ignition Delay, Kinetic Modeling Study and Reactivity Comparison with Isobutene and 1-Butene, Proc. Combust. Inst. 36 (2017), pp. 403-411.
12. J. Bugler, K.P. Somers, E.J. Silke, H.J. Curran, Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes: A Case Study of the Three Pentane Isomers, Journal of Physical Chemistry A 119 (2015) 7510-7527.
13. S.M. Burke, J.M. Simmie, H.J. Curran, Critical Evaluation of Thermochemical Properties of C1–C4 Species: Updated Group-Contributions to Estimate Thermochemical Properties, Journal of Physical and Chemical Reference Data 44 (2015) 013101.
14. S. Sharma, S. Raman, W.H. Green, Intramolecular Hydrogen Migration in Alkylperoxy and Hydroperoxyalkylperoxy Radicals: Accurate Treatment of Hindered Rotors, The Journal of Physical Chemistry A 114 (2010) 5689-5701.
15. Chemki*n*-Pro, Reaction Design, San Diego, 2010.
16. C. F. Goldsmith, M. P. Burke, Y. Georgievskii, S. J. Klippenstein, Effect of no*n*-thermal product energy distribution on ketohydroperoxide decomposition kinetics, PROCI 35 (2015), pp. 283-290
17. P. Dagaut, M. Reuillon, M. Cathonnet, D. Voisin, High pressure oxidation of liquid fuels from low to high temperature. 3 *n*-Decane, Combust. Sci. and Tech. 103 (1994), pp.349-359.
18. A. MZe-Ahmed, K. Hadj-ali, P. Dagaut, G. Dayma, Experimental and modeling study of the oxidation kinetics of *n*-undecane and *n*-dodecane in a jet-stirred reactor, Energy and fuels, 26 (2012), pp. 4253-4268.
19. J. Biet, M. H. Hakka, V. Warth, P. A. Glaude, F. Batt*i*n-Leclerc, Experimental and modeling study of the low temperature oxidation of large alkanes, Energy and fuels, 22 (2008), pp. 2258-2269.

20. A. Tekawade, G. Kosiba, M. A. Oehlschlaeger, Time-resolved carbon monoxide measurements during the low-t-intermediate oxidation of *n*-heptane, *n*-decane and *n*-dodecane, Combust. Flame, 173 (2016), pp. 402-410.
21. J. Aguilera-Iparraguirre, H. J. Curran, W. Klopper, J. M. Simmie, Accurate benchmark calculation of the reaction barrier height for hydrogen abstraction by the hydroperoxyl radical from methane. Implications for C_nH_{2n+2} where n=2-4, J. Phys. Chem A, 112 (2008), pp. 7047-7054.
22. K. Yong, J. He, Q. Zhang, L. Xian, C. Zhang, P. Li, X. Li, Shock tube study of *n*-nonane/air ignition over a wide range of temperatures, Fuel, 188 (2017), pp. 567-574.
23. U. Pfahl, K. Fieweger, G. Adomeit, Self-ignition of diesel-relevant hydrocarbo*n*-air mixtures under engine conditions, 26th International Symposium on Combustion, 1996, pp. 781-789
24. H-P S. Shen, J. Steinberg, J. Vanderover, M. A. Oehlschlaeger, A Shock tube study of the ingition of *n*-heptane, *n*-decane, *n*-dodecane and *n*-tetradecane at elevated pressures, Energy and fuels, 23 (2009), pp. 2482-2489.
25. V. P. Zhukov, V. A. Sechenov, A. Y. Starikovskii, Autoignition of *n*-decane at high pressure, Combust. Flame, 153 (2008), pp. 130-136.
26. S. S. Vasu, D. F. Davidson, Z. Hong, V. Vasudevan, R. K. Hanson, *n*-Dodecane oxidation at high pressures: Measurements of ignition delay times and OH concetration time histories, Proc. Combust. Inst. 32 (2009), pp. 173-180.
27. J. Yanowitz, M. A. Ratcliff, R. L. McCormick, J. D. Taylor, Compendium of experimental cetane number, NREL Report TP-5400-61693, National renewable energy laboratory, Golden, CO, 2014