2011 7th US National Combustion Meeting -
Organized by the Eastern States Section of the Combustion Institute -
and Hosted by the Georgia Institute of Technology, Atlanta, GA -
March 20-23, 2011 -

A Reduced Mechanism for Biodiesel Surrogates with Low - Temperature Chemistry -

Zhaoyu Luo[a1], Max Plomer[a], Tianfeng Lu[a], -
Sibendu Som[b], and Douglas E. Longman[b] -

[a]*Department of Mechanical Engineering,*
University of Connecticut, Storrs, CT 06269-3139

[b]*Transportation Technology Research and Development Center,*
Argonne National Laboratory, Argonne, IL 60439

Biodiesel is a promising alternative fuel for compression ignition engines. It is a renewable energy source that can be used in these engines without significant alteration in the design. The detailed chemical kinetics of biodiesel is however highly complex. In the present study, a skeletal mechanism with 123 species and 394 reactions for a tri-component biodiesel surrogate, which consists of methyl decanoate, methyl 9-decenoate and n-heptane, was developed for reduced computational cost in engine simulations. The reduction was based on an improved directed relation graph (DRG) method that is particularly suitable for mechanisms with many isomers, followed by isomer lumping and DRG-aided sensitivity analysis (DRGASA). Error cancelation was employed in obtaining the compact skeletal mechanism with DRGASA. The reduction was performed for pressures from 1 to 100atm and equivalence ratios from 0.5 to 2 for both extinction and ignition applications. The initial temperature for ignition was from 700 to1800K. As such the skeletal mechanism is applicable for both low and high temperature ignition simulations. Compared with the detailed mechanism that consists of 3329 species and 10806 reactions, the skeletal mechanism features a dramatic reduction in size while still retaining good accuracy and comprehensiveness. Additional validation is also performed against liquid length and flame lift-off length data available from Sandia National Laboratories under compression-ignition (CI) engine conditions.

1. Introduction

Biodiesel is a promising alternative fuel that can be produced from renewable sources, such as vegetable oil, animal fat, and waste cooking oil. It can be used in existing diesel engines with reduced pollutant emission without significant changes to their design [1]. Biodiesel primarily consists of fatty acid methyl esters (FAME), which feature long carbon chains with certain level of unsaturation. The chemical kinetics of biodiesel combustion is highly complex due to its large molecular size. It is time consuming to perform numerical simulations with detailed mechanisms for biodiesel, which consist of large number of species and reactions [2-4], particularly when the negative temperature coefficient (NTC) range is involved. Mechanism reduction is therefore required before such large mechanisms can be employed in practical engine simulations.

[1] Corresponding author, email: luozy@engr.uconn.edu

Mechanism reduction has been extensively studied over the last few decades [5]. A major reduction method is skeletal reduction, which eliminates unimportant species and reactions from detailed mechanisms. Unimportant species can be identified with such methods as sensitivity analysis [6-7], principle component analysis [8-9], Jacobian analysis[10-12], detailed reduction [13], directed relation graph (DRG) based methods [14-18] such as DRG-aided sensitivity analysis (DRGASA) [19-20]. Further reduction with other methods can be applied on mechanisms obtained through skeletal reduction, e.g. using lumping [21-25], in particular isomer lumping for large hydrocarbons [26-27], time scale analysis, such as quasi steady state approximation (QSSA) [28-32] and partial equilibrium approximation [33-34], computational singular perturbation (CSP) [35-37], intrinsic low-dimensional manifold (ILDM) [38-40], pre-image curve (PIC) [41-42], and tabulation [43-45].

Despite the large number of methods available for mechanism reduction, research on mechanism reduction for biodiesel is rather limited, particularly when low temperature chemistry is involved. This is primarily because the sheer sizes of the biodiesel mechanisms, which render the reduction itself difficult. In previous works, a reduced mechanism with low-temperature chemistry was obtained for methyl butanoate [46], the chain length of which is nevertheless short compared with that of real biodiesel. Skeletal mechanisms for methyl decanoate (MD) were developed for high temperature applications using DRG-based methods [47-48]. These skeletal mechanisms consist of approximately 120 species, but they are not suitable for studies involving low temperature ignition in engines. A comprehensive and accurate skeletal mechanism for MD with low-T chemistry was derived using DRG for 1-D flame analysis [49]. However, the mechanism consists of more than 600 species and is not suitable for practical engine simulations.

In the present study, an integrated method that combines skeletal reduction and isomer lumping will be employed to obtain a skeletal mechanism for biodiesel combustion with low temperature chemistry. The method of DRGASA was extended to take advantage of error cancelations during species elimination, targeting at obtaining a compact skeletal mechanism that can be employed in multi-dimensional engine simulations.

2. Methodologies

The detailed mechanism in the present reduction was developed by Lawrence Livermore National Laboratory (LLNL) [3]. The mechanism is for surrogate mixtures of MD, methyl 9-decenoate (MD9D) and n-heptane, and consists of 3299 species and 10806 elementary reactions. The tri-component surrogate mixture allows the flexibility in matching the fuel's physical properties and important combustion properties such as ignition delays and flame lift-off distance in engine simulations by fine tuning the fuel composition. The reduction of the detailed mechanism was performed based on a large set of reaction states sampled within the parameter space of pressure from 1atm to 100atm, equivalence ratio from 0.5 to 2.0, initial temperature from 700K to 1800K for auto-ignition, and inlet temperature of 300K for extinction in perfectly stirred reactors (PSR). Jet stirred reactors (JSR) with diluted mixtures and intermediate temperatures were also included in the sampling. The fuel mixture consists of 25% MD, 25% MD9D and 50% n-heptane by volume. Note that the NTC region that is important for engine ignition was covered in the reduction.

A DRG method that was improved for robust reduction of mechanisms with large numbers of isomers [48] was employed as the first step in the present reduction. The improved DRG method is highly efficient and has been implemented for parallel computation. It takes only minutes to

process the tens of thousands sampled reaction states using a small PC cluster. H radical was selected as the starting species in the DRG reduction since it is important for hydrocarbon oxidation under almost any condition. By allowing the worst-case reduction error of approximately 30%, a skeletal mechanism with 664 species and 2672 reactions was obtained with DRG. It is noted that this skeletal mechanism is comparable in size to that of pure MD in [49] and substantially larger than that for high temperature combustion of the tri-component surrogate mixtures in [48].

The 664-species mechanism was then reduced with isomer lumping. In contrast to the large extent of reduction achieved in the high-T skeletal mechanism in [48], it was found that only a small number of isomers can be lumped in the present mechanism covering the low-T chemistry. This implies that the isomer concentrations are less strongly correlated at lower temperatures. As a result, only a slightly smaller skeletal mechanism with 641 species and 2670 elementary reactions was obtained after isomer lumping. As a last measure to obtain a substantially small skeletal mechanism, it becomes a challenge to further reduce the mechanism by a factor of 5 in size using DRGASA, since in most previous works only reduction extents by factors of 2~3 had been achieved with DRGASA.

In DRGASA, the reduction error induced by eliminating a species was first estimated by the errors computed with DRG, such that the errors can be sorted in ascending order for sequential sensitivity analysis for species elimination. Since species with DRG-computed errors larger than, say, 50% are frequently important species and may cause difficulties in convergence, and subsequently long computation time, in the global sensitivity analysis if they are eliminated, these species were excluded in the sensitivity analysis in previous studies with DRGASA. However, since the final size of the mechanism, rather than the reduction cost, is the primary concern in the present work, every species is included in the global sensitivity analysis in the following reduction to ensure that the resulting mechanism is minimal in size. In such cases, DRGASA mostly reduces to the brute-force sensitivity analysis.

Furthermore, in previous reduction with DRGASA, if the elimination of an individual species induces significant error, say larger than 10%, the species will be retained in the skeletal mechanism. It was found in the present work that only mechanisms with more than 150 species can be obtained with this conservative approach. To achieve a large extent of reduction, error cancellation was utilized in minimizing the mechanism size in the present work. Specifically, in the ordered sequence of species to be tested by sensitivity analysis, if the individual eliminations of two species result in opposite errors, new sensitivity analysis will be performed by eliminating the pair of species together. The species pair will be eliminated if the error of the skeletal mechanism is smaller than the error tolerance. This process is repeated until no individual species or species pairs can be further eliminated based on a given error tolerance. By specifying a worst-case relative error of 40% in the revised DRGASA, a skeletal mechanism with 123 species and 394 elementary reactions was eventually obtained. It is noted that DRGASA with error cancellation is quite time-consuming. In the present study, it was performed in parallel with 200 CPU cores and took around two weeks to obtain the final mechanism.

3. Results and discussion

The 123-species skeletal mechanism was validated against the detailed mechanism in homogenous applications. Figure 1 shows the calculated ignition delay time of auto-ignition and the temperature profiles in PSR of biodiesel-air at various pressures and equivalence ratios. It is seen that the skeletal mechanism closely agrees with the detailed mechanism for both ignition

and extinction including the NTC range for auto-ignition. It is noted that similar errors were seen for ignition delays for other equivalence ratios between 0.5 and 2.

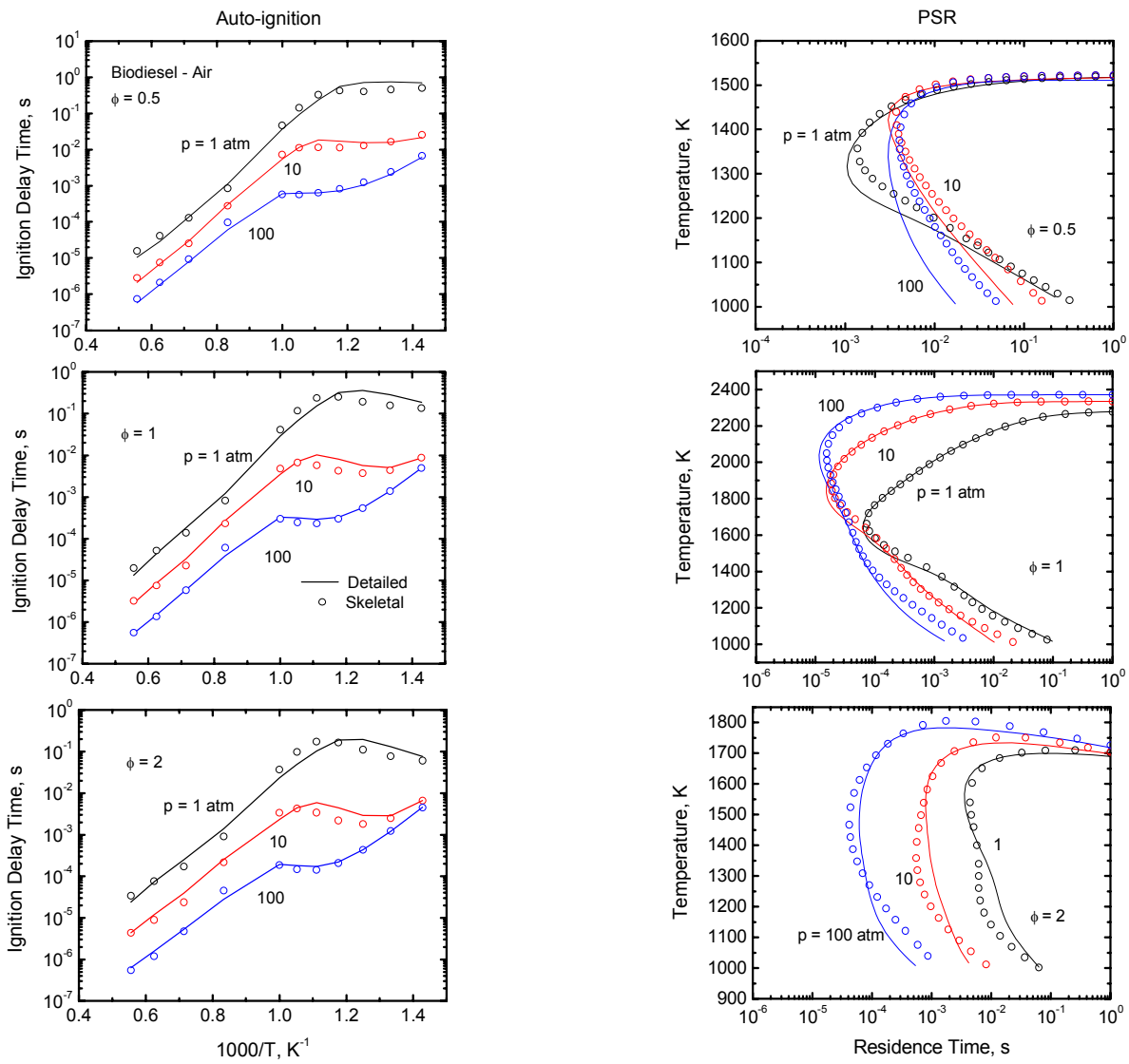

Figure 1: Comparison of the 123-species skeletal mechanism with the detailed mechanism for biodiesel-air, a) ignition delays, and b) extinction temperature profiles in PSR.

Figure 2 shows the validation of the skeletal mechanism in JSR. The calculated concentrations of selected major species as a function of temperature in JSR for lean and rich mixtures of biodiesel-O_2 diluted with N_2. Moderate errors close to that specified in the reduction were observed in the species concentration profiles. However there is no guarantee that minor species concentrations can be accurately predicted by the skeletal mechanism considering that the reduction with DRGASA was targeted only at the global parameters and major species concentrations.

The 123-species skeletal mechanism was further compared in predicting the experimental measurements of the oxidation of rapeseed oil methyl ester (RME) in JSR to investigate its

extensibility. RME is a complex mixture of C14–C22 esters with highly saturated carbon chain and its experimental study was first reported by Dagaut *et al* [50]. In the present study, the same fuel mixture as that in the reduction process, i.e. 25% MD, 25% MD9D and 50% n-heptane in mole fraction, is used in the simulation. Figure 3 compares the calculated species profiles for the biodiesel surrogate mixture using the skeletal mechanism to the experimental results at various equivalence ratios in JSR with nitrogen dilution. It is seen in fig.3 that the simulation results agree well with the measured datasets at most of the displayed conditions, while large discrepancies between the calculations and measurements can be observed at some cases, such as the CO_2 profile at fuel-lean condition.

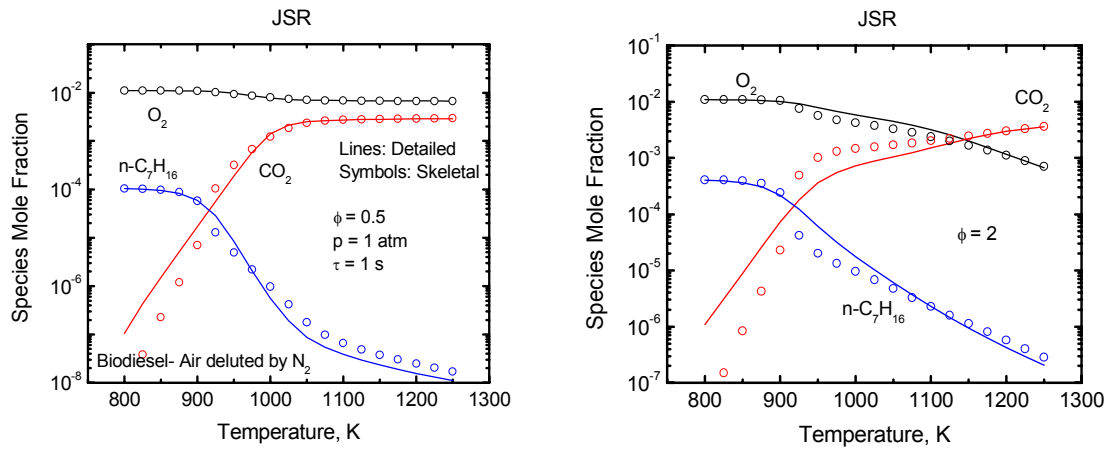

Figure 2: Calculated species profiles in JSR as a function of temperature for the biodiesel oxidation in diluted air (99% N_2 in mole) under atmospheric pressure with fixed residence time of 1s, calculated with the detailed and the 123-species skeletal mechanisms, respectively, for a) equivalence ratio $\phi = 0.5$, and b) $\phi = 2.0$.

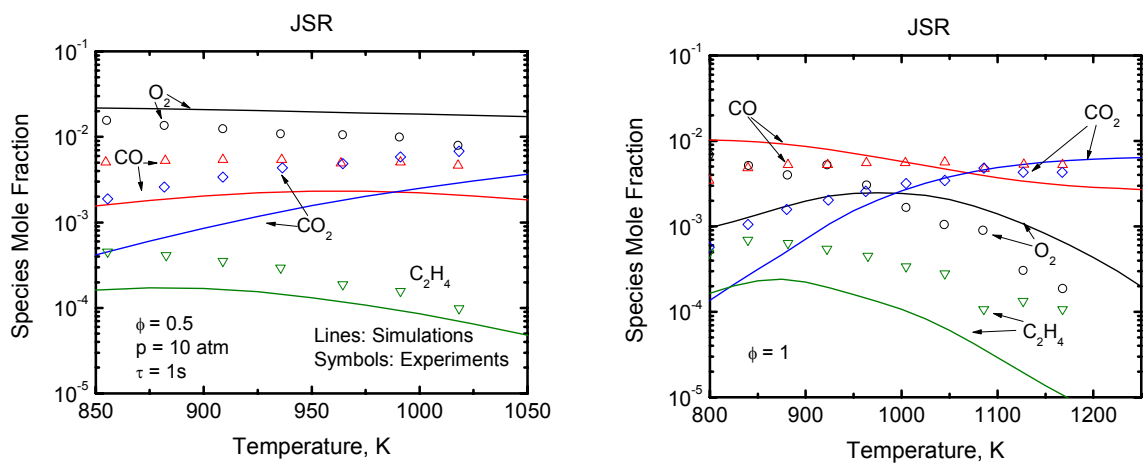

Figure 3: Species concentration in JSR as a function of temperature for RME at pressure of 10 atm and residence time of 1s. Symbols: experimental data[50], lines: values calculated with the 123-species skeletal mechanism.

Further validation of the 123-species biodiesel surrogate mechanism is performed in a constant volume combustion chamber under compression igntion engine conditions[51-53]. The experimental conditions are reported in Table 1[54]. Fuel spray and combustion simulations were performed using the Eulerian-Lagrangian approach in the computational fluid dynamics (CFD) software CONVERGE [55-57]. It incorporates state-of-the-art models for spray injection, atomization and breakup, turbulence, droplet collision, and coalescence. The gas-phase flow field is described using the Favre-Averaged Navier-Stokes equations in conjunction with the RNG k-ε turbulence model, which includes source terms for the effects of dispersed phase on gas-phase turbulence. These equations are solved using a finite volume solver. The details of these models can be found in previous publications[58-59].

Parameter	Quantity
Injection System	Bosch Common Rail
Nozzle Description	Single-hole, mini-sac
Duration of Injection [ms]	7.5
Orifice Diameter [μm]	90
Injection Pressure [Bar]	1400
Fill Gas Composition (mole-fraction)	N_2=0.7515, O_2=0.15, CO_2=0.0622, H_2O=0.0363
Chamber Density [kg/m^3]	22.8
Chamber Temperature [K]	1000
Fuel Density [kg/m^3]	877
Fuel Injection Temperature [K]	436

Table 1: Test conditions for combustion experiments at Sandia National Laboratories[54].

Figure 4 presents measured [54] and computed OH profiles under conditions presented in Table 1. Due to the axisymmetric nature of the spray and combustion processes, images are presented on a cut-plane through the center of the fuel jet. The flame lift-off location is shown by red dashed line and the average equivalence ratio at flame lift-off location is also shown. The spray axis is demarcated using a white dashed line. The field of view is 75 mm x 25 mm in the axial and radial directions respectively. It is seen that the lift-off length is over predicted by about 25% under these conditions. However, the average equivalence ratio at lift-off length is fairly well captured in the simulations. The measured ignition delay is 0.396 ms, while the simulated value is about 0.5 ms, again showing a 25% over-prediction. The width and length of the flame is also well captured by the simulation. The liquid length and spray penetration matched well (not shown here) with the experimental data, thereby showing the model's capability to predict the mixing process. Hence, the over-prediction of flame lift-off length and ignition delay could be due to the uncertainities in the detailed mechanism or the reduction error in the skeletal mechanism.

. -

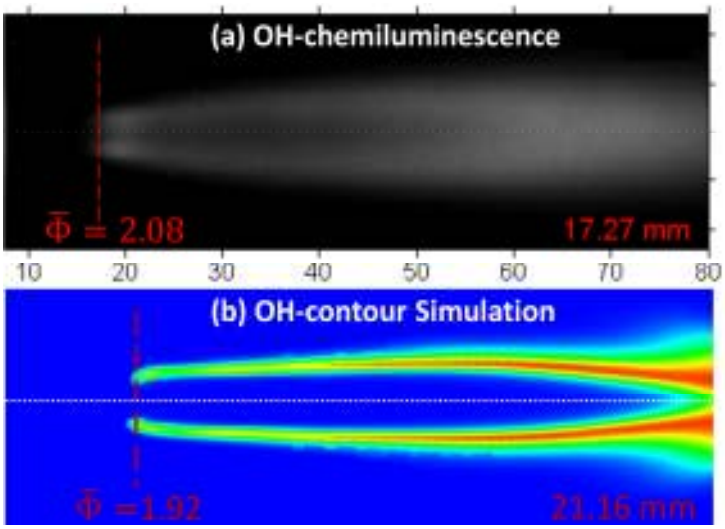

Figure 4: Validation of flame lift-off length against the OH-chemiluminescence data from [54]. The average equivalence ratio at flame lift-off location is also indicated.

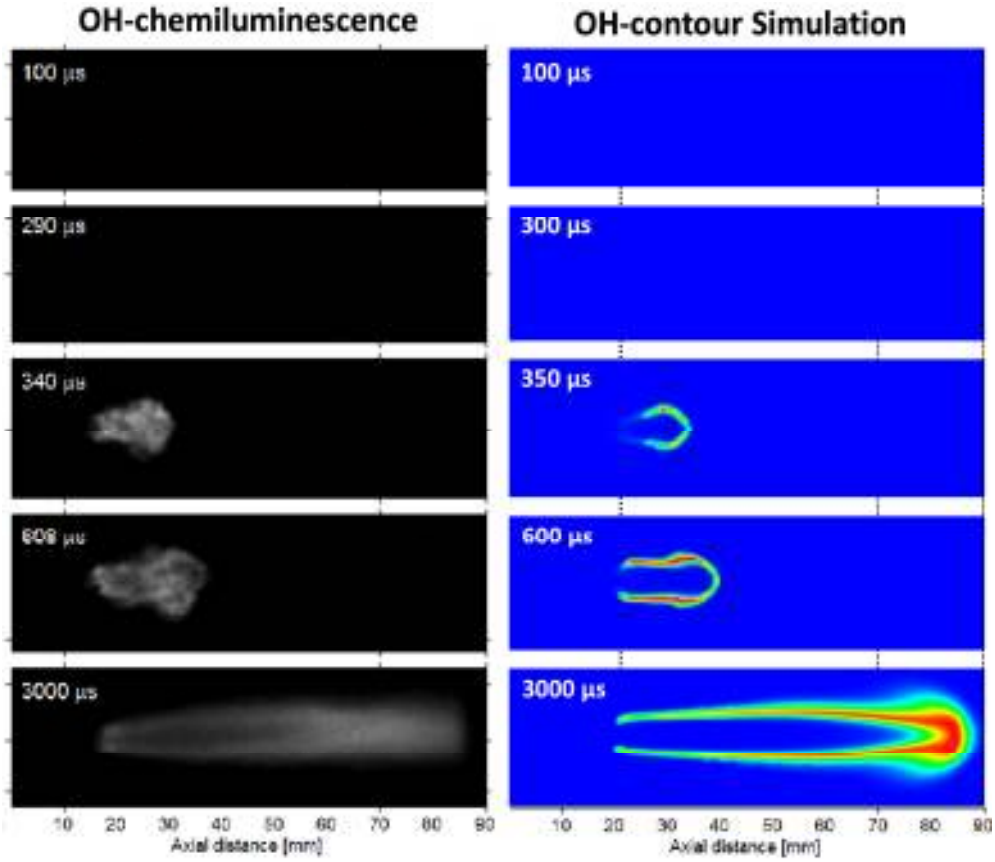

Figure 5: Comparison of OH mole-fraction contours from simulations against the OH-chemiluminescence data from [54], at different instances during the combustion process.

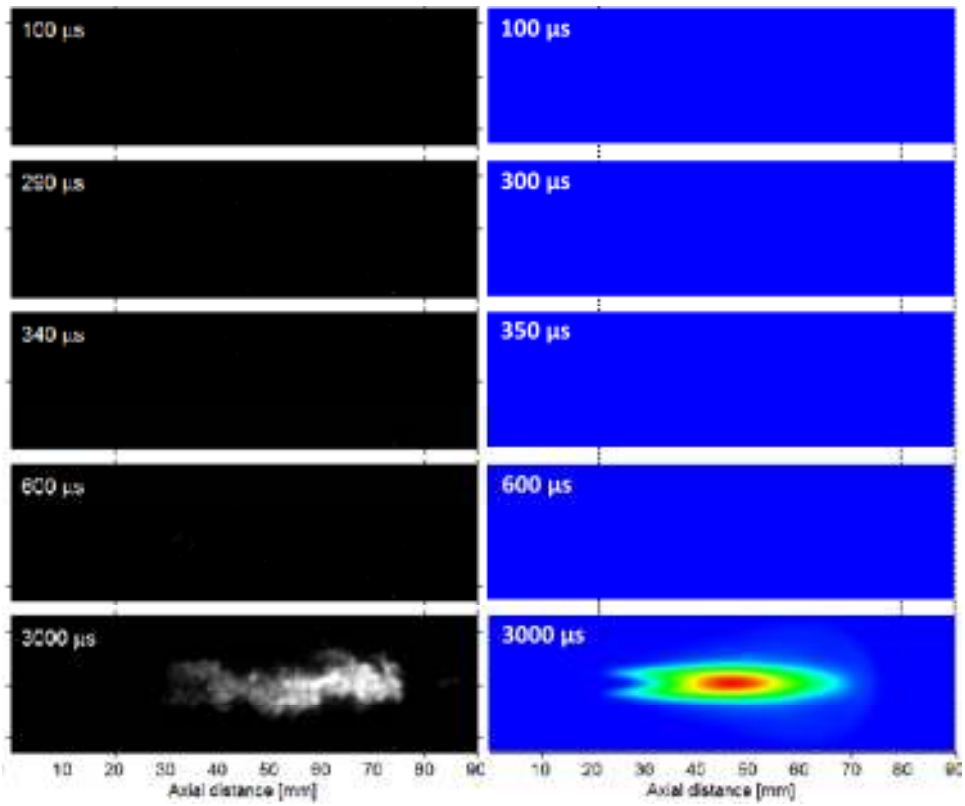

Figure 6: Comparison of soot mole-fraction contours from simulations against the soot data using LII from [54] at different instances during the combustion process.

Figures 5 and 6 present validations of OH and soot contours, respectively, against the chemiluminescence and LII data from Nerva [54], at different time during the combustion event. It is seen in Figs.5 and 6 that the OH and soot contours are well predicted in terms of location and occurrence during the combustion event. It is noted that although the lift-off length in Fig. 4 was over-predicted by 25% using the skeletal mechanism, such a discrepancy is quite encouraging considering that the detailed and the sekeltal mechanisms were not tuned for the experimental conditions. Future studies will involve further improvement of the detailed or reduced mechanisms to better predict ignition and flame lift-off under CI engine conditions.

4. Concluding Remarks

A 123-species skeletal mechanism for biodiesel surrogate (MD, MD9D and n-heptane) including low-temperature chemistry was developed with DRG-based methods. Dramatic extent of reduction was achieved by incorporating error cancellation in the reduction by DRGASA. Validation shows that the small mechanism performs quite well over a wide range of parameters for both ignition and extinction, as such is a good choice for practical engine simulations involving low temperature ignition.

Although reduced mechanisms derived with error cancellation can be problematic in many cases, it is shown to be possible in the present reduction that compact, accurate and comprehensive mechanisms can be obtained with error cancellation, and such mechanisms may

even be extended to predict cases not covered in the reduction. However, thorough validation is required before mechanisms derived with error cancellation being applied in simulations.

Comprehensive validation of the mechanism was performed in homogenous applications such as computation of gas-phase auto-ignition delays and extinction temperatures in PSR. The mechanism was further validated with experimental measurements in the literature for RME in JSR. Extensive validation was also performed in 3-D turbulent spray combustion conditions against the experimental data from Sandia National Laboratories. The mechanism is demonstrated to be very versatile and robust since it performed satisfactorily under almost all the conditions investigated.

Acknowledgements

The work at University of Connecticut was supported by the National Science Foundation under Grant 0904771. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

The submitted manuscript has been created by UChicago Argonne, LLC, operator of Argonne National Laboratory (Argonne). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

The authors thank Dr. Lyle Pickett from Sandia National Laboratories for sharing the flame lift-off data and many insightful discussions.

References

1. - A. Deepak, S. Sinha, and K.A. Agarwal, *Renewable Energy,* 31 (2006), 2356-2369.
2. - Olivier Herbinet, William J. Pitz, and C.K. Westbrook, *Combust. Flame,* 154 (2008), 507-528.
3. - O. Herbinet, W.J. Pitz, and C.K. Westbrook, *Combust. Flame,* 157 (2010), 893-908.
4. - C.K. Westbrook, C.V. Naik, O. Herbinet, W.J. Pitz, M. Mehl, S.M. Sarathy, and H.J. Curran, *Combust. Flame* (2011), *in press*.
5. - T.F. Lu, and C.K. Law, *Prog. Energy Combust. Sci.,* 35 (2009), 192-215.
6. - A.S. Tomlin, M.J. Pilling, T. Turanyi, J.H. Merkin, and J. Brindley, *Combust. Flame,* 91 (1992), 107-130.
7. - T. Turanyi, *J. Math. Chem.,* 5 (1990), 203-248.
8. - S. Vajda, P. Valko, and T. Turanyi, *Int. J. Chem. Kinet.,* 17 (1985), 55-81.
9. - S. Vajda, and T. Turanyi, *J. Phys. Chem.,* 90 (1986), 1664-1670.
10. - T. Turanyi, *New J. Chem.,* 14 (1990), 795-803.
11. - A. Massias, D. Diamantis, E. Mastorakos, and D.A. Goussis, *Combust. Flame,* 117 (1999), 685-708.
12. - M. Valorani, F. Creta, D.A. Goussis, J.C. Lee, and H.N. Najm, *Combust. Flame,* 146 (2006), 29-51.
13. - H. Wang, and M. Frenklach, *Combust. Flame,* 87 (1991), 365-370.
14. - T.F. Lu, and C.K. Law, *Proc. Combust. Inst.,* 30 (2005), 1333-1341.
15. - P. Pepiot-Desjardins, and H. Pitsch, *Combust. Flame,* 154 (2008), 67-81.
16. - L. Liang, J.G. Stevens, and J.T. Farrell, *Proc. Combust. Inst.,* 32 (2009), 527-534.
17. - W. Sun, Z. Chen, X. Gou, and Y. Ju, *Combust. Flame,* 157 (2010), 1298–1307.
18. - K. Niemeyer, C. Sung, and M. Raju, *Combust. Flame,* 157 (2010), 1760-1770.
19. - R. Sankaran, E.R. Hawkes, J.H. Chen, T. Lu, and C.K. Law, *Proc. Combust. Inst.,* 31 (2007), 1291-1298.
20. - X.L. Zheng, T.F. Lu, and C.K. Law, *Proc. Combust. Inst.,* 31 (2007), 367-375.
21. - S.S. Ahmed, F. Mauss, G. Moreac, and T. Zeuch, *Phys. Chem. Chem. Phys.,* 9 (2007), 1107-1126.
22. - G. Li, and H. Rabitz, *Chem. Eng. Sci.,* 44 (1989), 1413-1430.

23. - G.Y. Li, and H. Rabitz, *Chem. Eng. Sci.,* 45 (1990), 977-1002.
24. - A.S. Tomlin, G.Y. Li, H. Rabitz, and J. Toth, *J. Chem. Phys.,* 101 (1994), 1188-1201.
25. - E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, and T. Faravelli, *Prog. Energy Combust. Sci.,* 27 (2001), 99-139.
26. - T.F. Lu, and C.K. Law, *Combust. Flame,* 154 (2008), 153-163.
27. - P. Pepiot-Desjardins, and H. Pitsch, *Combust. Theory Model.,* 12 (2008), 1089-1108.
28. - T.F. Lu, and C.K. Law, *J. Phys. Chem. A,* 110 (2006), 13202-13208.
29. - T.F. Lu, *Combust. Flame,* 154 (2008), 761-774.
30. - C.J. Sung, C.K. Law, and J.Y. Chen, *Combust. Flame,* 125 (2001), 906-919.
31. - Z.Y. Ren, and S.B. Pope, *Combust. Flame,* 137 (2004), 251-254.
32. - N. Peters, *Lecture Notes in Physics,* 241 (1985), 90-109.
33. - M. Bodenstein, *Z. Phys. Chem.,* 85 (1913), 329-397.
34. - L.K. Underhill, and D.L. Chapman, *J. Chem. Soc. Trans.,* 103 (1913), 496-508.
35. - S.H. Lam, *Combust. Sci. Technol.,* 89 (1993), 375-404.
36. - S.H. Lam, and D.A. Goussis, *Int. J. Chem. Kinet.,* 26 (1994), 461-486.
37. - S.H. Lam, *Combust. Sci. Technol.,* 179 (2007), 767-786.
38. - U. Maas, and S.B. Pope, *Combust. Flame,* 88 (1992), 239-264.
39. - H. Bongers, J.A. Van Oijen, and L.P.H. De Goey, *Proc. Combust. Inst.,* 29 (2003), 1371-1378.
40. - Z.Y. Ren, and S.B. Pope, *Combust. Flame,* 147 (2006), 243-261.
41. - Z.Y. Ren, and S.B. Pope, *Proc. Combust. Inst.,* 30 (2005), 1293-1300.
42. - Z.Y. Ren, S.B. Pope, A. Vladimirsky, and J.M. Guckenheimer, *J. Chem. Phys.,* 124 (2006).
43. - S.B. Pope, *Combust. Theory Model.,* 1 (1997), 41-63.
44. - J. Lee, H. Najm, S. Lefantzi, J. Ray, M. Frenklach, M. Valorani, and D. Goussis, *Combust. Theory Model.,* 11 (2007), 73-102.
45. - S. Tonse, N. Moriarty, N. Brown, and M. Frenklach, *Israeli Journal of Chemistry,* 39 (1998).
46. - J.L. Brakora, Y. Ra, R.D. Reitz, J. McFarlane, and C.S. Daw, *SAE International Journal of Fuels and Lubricants,* 1 (2009), 675-702.
47. - K. Seshadri, T.F. Lu, O. Herbinet, S.B. Humer, U. Niemann, W.J. Pitz, R. Seiser, and C.K. Law, *Proc. Combust. Inst.,* 32 (2009), 1067-1074.
48. - Z. Luo, T. Lu, M.J. Maciaszek, S. Som, and D.E. Longman, *Energy Fuels,* 24 (2010), 6283–6293.
49. - S.M. Sarathy, M.J. Thomson, W.J. Pitz, and T. Lu, *Proc. Combust. Inst.,* 33 (2011), 399-405.
50. - P. Dagaut, S. Gaïl, and M. Sahasrabudhe, *Proc. Combust. Inst.,* 31 (2007), 2955–2961.
51. - D.L. Siebers, and B.Higgins, *SAE Paper* (2001), 2001-01-0530.
52. - B.Higgins, and D.L. Siebers, *SAE Paper* (2001), 2001-01-0918.
53. - S.Som, and S.K.Aggarwal, *Combust. Flame,* 157 (2010), 1179-1193.
54. - J.G. Nerva, C.L. Genzale, J.M.G. Oliver, and L.M. Pickett, *Personal Communication*.
55. - P.K. Senecal, E. Pomraning, K.J. Richards, T.E. Briggs, C.Y. Choi, R.M. Mcdavid, and M.A. Patterson, *SAE Paper* (2003), 2003-01-0143.
56. - P.K. Senecal, K.J. Richards, E. Pomraning, T. Yang, M.Z. Dai, R.M. McDavid, M.A. Patterson, S. Hou, and T. Shethaji, *SAE Paper* (2007), 2007-01-0159.
57. - S.Som, 'Development and validation of spray models for investigating diesel engine combustion and emissions', *Ph.D Thesis*,University of Illinois at Chicago, 2009.
58. - S. Som, D.E. Longman, A.I. Ramírez, and S.K. Aggarwal, *Fuel,* 89 (2010), 4014-4024.
59. - S. Som, and D.E. Longman, *Energy Fuels* (2011), *in press*.