

Final Report Certification
for
CRADA Number NFE-07-00912

Between

UT-Battelle, LLC

and

Reaction Design, Inc.

(Participant)

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Final Report for NFE-07-00912:

Development of Model Fuels Experimental Engine Data Base & Kinetic Modeling Parameter Sets A CRADA Between Oak Ridge National Laboratory and Reaction Design, Inc.

Bruce G. Bunting, Oak Ridge National Laboratory, September 28, 2012

(Document not CRADA protected)

Abstract

The automotive and engine industries are in a period of very rapid change being driven by new emission standards, new types of after treatment, new combustion strategies, the introduction of new fuels, and drive for increased fuel economy and efficiency. The rapid pace of these changes has put more pressure on the need for modeling of engine combustion and performance, in order to shorten product design and introduction cycles. New combustion strategies include homogeneous charge compression ignition (HCCI), partial-premixed combustion compression ignition (PCCI), and dilute low temperature combustion which are being developed for lower emissions and improved fuel economy. New fuels include bio-fuels such as ethanol or bio-diesel, 'drop-in' bio-derived fuels and those derived from new crude oil sources such as gas-to-liquids, coal-to-liquids, oil sands, oil shale, and wet natural gas. Kinetic modeling of the combustion process for these new combustion regimes and fuels is necessary in order to allow modeling and performance assessment for engine design purposes.

In this research covered by this CRADA, ORNL developed and supplied experimental data related to engine performance with new fuels and new combustion strategies along with interpretation and analysis of such data and consulting to Reaction Design, Inc. (RD). RD performed additional analysis of this data in order to extract important parameters and to confirm engine and kinetic models. The data generated was generally published to make it available to the engine and automotive design communities and also to the Reaction Design Model Fuels Consortium (MFC).

Background

The MFC was founded in 2006 by Reaction Design, Inc. of San Diego, CA (RD). It continued for 7 years through part 1, part 2, and an additional final year. Membership was by subscription and the number of members averaged about 10, with members joining or withdrawing as business conditions or technical goals changed. Overall, members included the following companies: Chevron, ConocoPhillips, Cummins, Dow Chemical Company, Ford Motor Company, General Motors, Honda, l'Institut Français du Pétrole, Mazda, Mitsubishi Motors, Nissan, Oak Ridge National Laboratory, Petrobras, PSA Peugeot Citroën, Saudi Aramco, Suzuki, and Toyota. As a government lab, ORNL was unable to join the consortium directly. We participated in the consortium through a CRADA with RD, with the status of work-in-kind member to the consortium. Our CRADA operated from 7/1/2007 to 12/31/2012, with funding received from the DOE EERE vehicle technologies fuels technology program. Generally, ORNL

was responsible for supplying experimental data related to engines and fuels and RD was responsible for the analysis and modeling of this data. This CRADA also gave ORNL access to RD and MFC modeling tools (Chemkin, Chemkin MFC, FORTE') and surrogate fuel design tools (MFC master mechanisms and Reaction Workbench) and to consortium meetings and reports.

During the course of the CRADA and MFC, great technical strides were made in the areas of verified master mechanisms, mechanism reduction tools, and rapid chemical solvers. Additionally, during the term of the MFC, RD also separately developed and released FORTE', a commercial software for computational fluid dynamics modeling of engines and combustion machines. This new software provides a powerful foundation for applying the MFC tools and mechanisms to combustion engines and experimental kinetic apparatus.

The CRADA agreement allowed ORNL to publish any experimental data we developed at the request of RD and much of data and analysis was jointly published with RD, and we also shared with them a large amount of data from related DOE research in fuels and combustion that was relevant to the goals and needs of the MFC. This report has been written completely using public documents, so that it should not be considered CRADA protected. The reader is referred to the original references for a more complete description of the research and for better quality copies of the figures.

CRADA related work and data

The work we performed and data we supplied to the MFC cover the span of 2007 to 2012. It is easiest to present the data by year in sequence because this also gives a sense of the progress and technical developments of the MFC. Each year of the MFC, new tools were released and previous tools were improved. Mechanisms were further improved and validated and expanded to include new species. The focus of new work for each year was determined by a combination of RD recommendations and a process of member voting.

2007

We began participating in the MFC and received funding from DOE on 7/1/2007, even though the MFC began in 2006. For 2007, our main task was to bundle existing data and transmit to RD. This data was used to help develop and test software, mechanisms, and tools. The data supplied was run on the Hatz engine converted to HCCI and included the following fuels: B20 blends of palm, soy, mustard, rape, and methyl butanoate in diesel and n-heptane base¹, 17 oil sands derived fuels and refinery intermediates ranging from 32 to 55 cetane and 17 to 43% aromatics², 11 diesel fuels ranging from 32 to 55 cetane and 17 to 43% aromatics including cetane improvers³, various blends of n-heptane, iso-octane, toluene, ethanol, butanol, and straight run naphtha⁴, and diesel secondary reference blends ranging from 17 to 73 cetane^{5 6}. RD used some of this data for development and testing of their tools and mechanisms and also to introduce ORNL to the members at the 2007 annual meeting.

2008

In 2008, RD began work on the mechanism database and published the first versions of master mechanisms for diesel and gasoline range fuels in late 2007. These master mechanisms were generated by combining, verifying, and reconciling mechanisms from open literature, research websites, and from quantum calculations. This also resulted in a large database of experimental data which could be used to validate future mechanisms and make further improvements to the existing mechanisms. The master mechanisms are very large, and became increasingly larger in subsequent years as they were improved and expanded. In 2008, the diesel master mechanism had 3560 species and included up to C16 compounds and the gasoline had 1753 species and included up to C8 compounds. We should note that most of these species are low concentration intermediates and that the mechanisms are only validated for a limited number of more common surrogate fuel components. The early MFC mechanisms were validated for n-heptane, i-octane, toluene, 1-pentene, methylcyclohexane, m-xylene, ethanol, n-decane, n-dodecane, decalin, i-cetane, and alphas-methylnaphthalene as starting or surrogate compounds. More compounds have been added each year and about 50 compounds are now validated for good or excellent kinetic representation as surrogate or starting compounds.

Initial versions were released of a surrogate blending tool that could design blends to match characteristics of commercial fuels and a tool for size reduction of the large master mechanisms to a more manageable size for kinetic calculations. Figure 1 indicates how the surrogate blend optimizer functions.

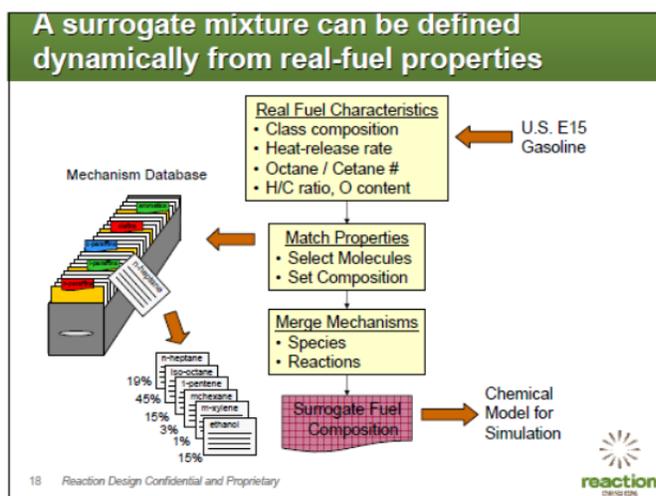


Figure 1, Early workflow for determination of surrogate fuel formulations and corresponding mechanisms to represent commercial fuel properties and chemistry.

In 2008, RD also began releasing a series of specialized input modules for Chemkin-MFC. These were developed to assist in mechanism validation and also at the request of and for use by MFC membership. These include octane and cetane calculators, single and multi-zone HCCI engines, stagnation burner, flow reactor, combustion chamber, and rapid compression machine. These

modules have also been further improved each year of the MFC, based on experience and member feedback.

ORNL experimental data supplied in 2007 was used to test and validate the kinetic mechanisms using a single zone Chemkin representation of the Hatz HCCI engine⁷. For HCCI, it is generally considered that a single zone model can accurately represent ignition timing of fuels. In this study, 5 fuels were blended to 92 RON using 5 pure components of different chemistries which also resulted in different MON. These fuels were run in the Hatz HCCI engine, and were compared to three commercial gasolines.

In this HCCI engine, ignition timing is controlled by intake air temperature, fuel rate, and fuel kinetics. At a constant fuel rate, a more energetic fuel will ignite sooner or require a lower intake temperature for the same ignition timing. As shown in Figure 2, there is quite a difference in ignition characteristics, in spite of all the fuels having the same RON.

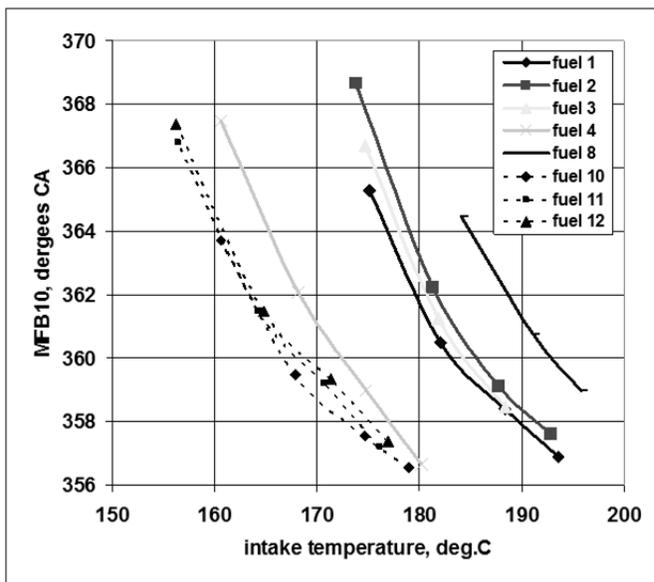


Figure 2, Relationship of ignition as characterized by MFB10 with intake air temperature for all fuels.

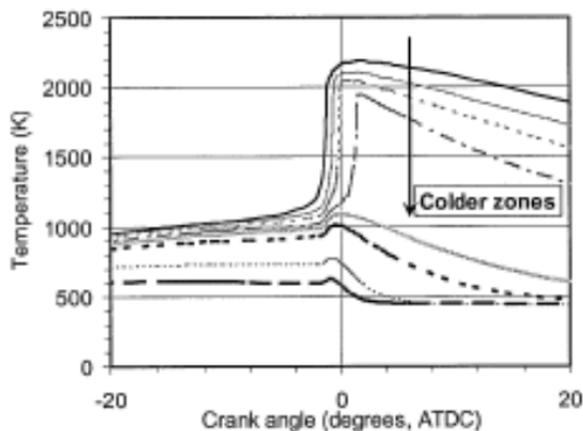
Further analysis in this experimental study indicated that ignition timing correlated more strongly to MON or to octane sensitivity, a trend noted by other researchers in this field for HCCI. Table 1 indicates how close the model and experimental data agree at one fuel rate, within 7 deg.K intake temperature to achieve equivalent combustion phasing, or better. This means that the mechanism and a single zone model provide a reasonable representation of the experimental data for ignition.

Table 1: Intake temperature for achieving MFB 10 at 362 CA degrees (interpolated values at 3 bar IMEP).

Surrogate #	Data (°K)	Model (°K)	Difference (°K)
1	452.4	451.1	1.3
2	454.9	451.1	3.8
3	453.7	448.7	5
4	441.2	448.1	-6.9
8	461.6	459.4	2.2

Multi-zone modeling was also done with the same fuels, using several multi-component surrogates matched to the based commercial gasoline in the previous study. In this study⁷, multi-zone Chemkin was used to simulate the engine. A total of 75 zones of equal mass were created. These were created by first simulating the engine with non-reacting CFD and binning the zones by temperature at a typical start of combustion angle for the engine. Heat loss fraction for each zone was then calculated from intake valve closing to exhaust valve opening for the CFD simulation, using Woschni heat transfer coefficients and % surface area was then assigned to each temperature bin based on the integrated heat losses. This resulted in the core zones showing little heat loss, some zones with moderate heat loss, and some zones with large heat loss, based mainly on proximity to the cylinder walls. Hot core zones are responsible for ignition and NO_x formation, moderate zones can generate CO due to combustion quenching during expansion, and high loss zones (typically crevice areas) are responsible for unburned fuel since combustion may not initiate at all. Figure 3 shows zonal temperatures during a Chemkin simulation with combustion.

Figure 3, Temperature profiles of the different zones close to TDC, for a representative case.



This modeling work also provided good agreement for ignition and burning characteristics, NO_x, HC, and CO. However, multi-zone combustion models have to be tuned very closely to provide good CO and HC calculations, because they do not include zonal mixing. Generally, multi-zone should be used mainly for ignition and NO_x calculations if extrapolating beyond experimental data.

2009

2009 marked the beginning of the MFC2, a second 3 year project, with slightly adjusted membership and goals to further improve mechanisms, develop rapid chemistry solvers to allow calculation with larger mechanisms, further improve surrogate formulation tools, and to develop and tune kinetics for soot formation and oxidation in the kinetic mechanisms.

The gasoline data modeled in 2008 was also evaluated at ORNL as part of a thesis project, using a 5 zone Chemkin model⁸. In this work, data for the 3 fuels were kinetically modeled with a common model adjusted for experimental conditions and using a single fuel mechanism containing 1747 species and 8487 reactions. Zones were defined to provide reasonable agreement to experimental data and then were left constant for all the modeling runs. Results were compared by plotting modeled vs. experimental data values for all the fuels and timing sweep points. Table 2 shows how the model was able to reproduce experimental data. In this comparison, a 1.0 slope indicates that the model reproduced the same trend as the experimental data and an R2 of 1.0 indicates a very close match across all the data points.

Table 2, Match of experimental and modeling results for multi-zone kinetic modeling.

VARIABLE	SLOPE	R ²	NOTES
Our goal	1.0	1.0	Perfection!
MFB50, deg. CA	0.54	0.79	
CA10-90, deg. CA	0.12	0.40	
Peak pressure, bar	0.21	0.33	
Peak temperature, K	0.37	0.50	
Work, dyne-cm	1.18	0.85	HPL vs. HPL+LPL
Charge mass, gm.	0.80	0.80	
Oxygen, %	0.81	0.78	Wet vs. dry (≈3.5% corr.)
Carbon dioxide, %	0.82	0.88	Wet vs. dry (≈3.5% corr.)
Nitrogen oxides, ppm	0.53	0.88	Wet vs. wet
Carbon monoxide, ppm	-0.01	0.01	Wet vs. wet
Hydrocarbons, ppm	0.05	0.01	Wet vs. wet
Formaldehyde, ppm	-0.28	0.38	
Acetaldehyde, ppm	-0.16	0.37	

Conclusions from this study indicate that use of a simple, 5 zone engine model for kinetic modeling of complete fuel effects is not practical. The model gave fairly good results and trends for work, charge mass, O₂, CO₂, NO_x, and MFB50. CO and HC proved very difficult to reproduce with a simple model, since CO destruction is too rapid and temperature sensitive and HC can remain after combustion in a wall quench zone, but this does not completely represent actual in-cylinder processes. Improved kinetic modeling of detailed fuel effects is likely to require CFD modeling to better represent in-cylinder processes.

ORNL was also requested to provide data related to detailed exhaust speciation and particulate measurements to support the development of particulate formation and oxidation kinetic models. Combustion of fuels results in a large number of intermediate species and trace exhaust chemistry compounds from incomplete combustion. At more retarded combustion phasing, intermediate reactions can be quenched, resulting in these compounds coming out in the engine exhaust. In this study⁹, three gasoline range surrogates were blended from iso-octane, n-heptane, toluene, and ethanol and evaluated in the HCCI engine. Measurements included conventional emissions, NO_x, HC, and CO, detailed particulate characterization, FTIR for aldehydes, and GC for fuel components. At a constant fuel energy input, conventional emissions behaved as expected with HC and CO increasing and NO_x decreasing at later combustion phasing. Oxygenated emissions were dominated by aldehydes, primarily formaldehyde and acetaldehyde, with formaldehyde concentrations 1.5 to 3 times higher than acetaldehyde. Hydrocarbons increased at later combustion phasing and were dominated by raw fuel. Overall, unburned fuel composed about 90% of the HC emissions and the profile of fuel chemistry was maintained in the emissions, per Table 2.

Table 3, Profiles of fuel chemistry and exhaust hydrocarbon chemistry.

FUEL	COMPONENTS COUNT % OF TOTAL CANISTER	MEASUREMENT	n-heptane	iso-octane	toluene	ethanol
PRF	87%	WT% IN FUEL	13%	87%	na	na
		WT% IN FUEL PORTION OF CANISTER	16%	84%	na	na
TRF	87%	WT% IN FUEL	27%	na	73%	na
		WT% IN FUEL PORTION OF CANISTER	33%	na	67%	na
TRF-E	91%	WT% IN FUEL	9%	54%	na	33%
		WT% IN FUEL PORTION OF CANISTER	13%	60%	na	28%

Particulate measurements indicated a large number of particles in the 13 to 30 nm range, most likely condensed fuel aerosols because of the relatively high unburned fuel emissions.

In addition to this data, ORNL also ran five of the CRC FACE fuels (Fuels for Advanced Combustion Engines) and surrogates for them and provided data to RD.

2010

In 2010, RD began the commercial development and release of CFD modeling software, FORTE', independently of the MFC. Interested MFC members were given the opportunity to use FORTE' in their research, in order to allow better engine modeling and to provide feedback and evaluation of the package. The software has also been continuously improved and released in subsequent years. An early application of this software included the analysis of gasoline data previously modeled with multi-zone Chemkin¹⁰. The fuel for this study was 33 wt% ethanol, 8.7 wt% n-heptane, and 58.3 wt% iso-octane with a RON of 105. Three experimental cases for the Hatz HCCI engine were selected for modeling at a constant fuel rate (9.1 gm/min) and 3

different charge temperatures, resulting in three combustion timings. A kinetic mechanism of 428 species and 2378 reactions was extracted and reduced from the MFC master mechanism which, at that time, contained 3553 species and 14904 reactions. This reduction was performed using a single zone Chemkin model with Direct Relation Graph (DRG) method to match ignition time (MFB10) and emissions of interest including NO, NO₂, CO, ethanol, n-heptane, iso-octane, CH₂O, CH₃CHO, CH₄, C₂H₄, C₃H₆ and iso-butylene within specified tolerances. A 15 degree sector mesh was used for the CFD grid to reduce computation time because the HCCI combustion chamber is symmetrical. The final mesh had 53,800 CFD cells at intake valve closure. This problem size could be solved at the rate of about one per day on a multi-processor desk top personal computer, using dynamic cell clustering, automatic re-meshing, and dynamic adaptive chemistry techniques. Figures 4 and % indicate match of cylinder pressure, heat release, and HC, NO_x, and CO emissions between the model and the experimental data.

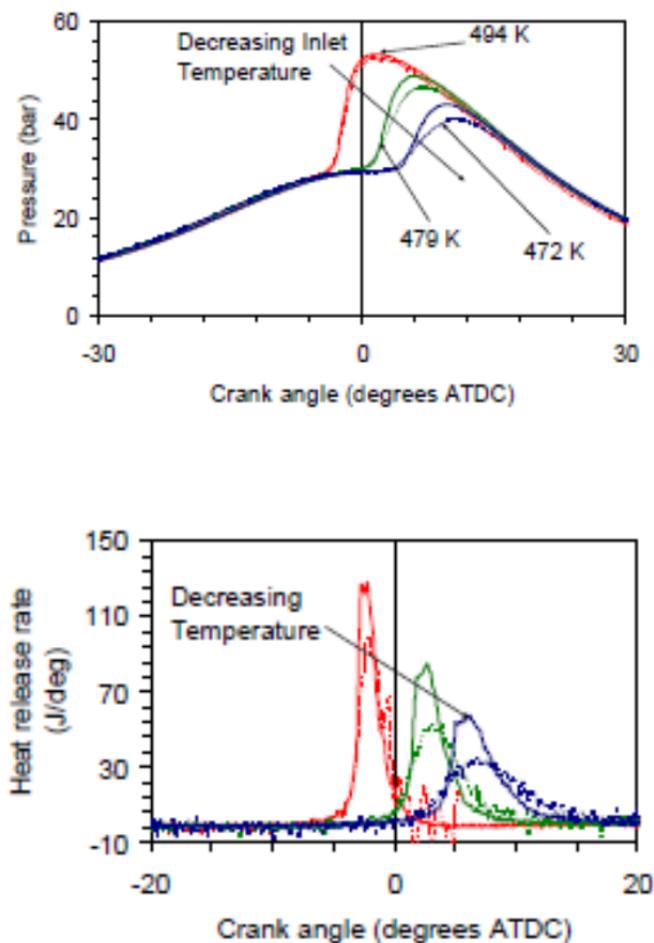


Figure 4, Match of experimental and modeled cylinder pressure and heat release for representative data points.

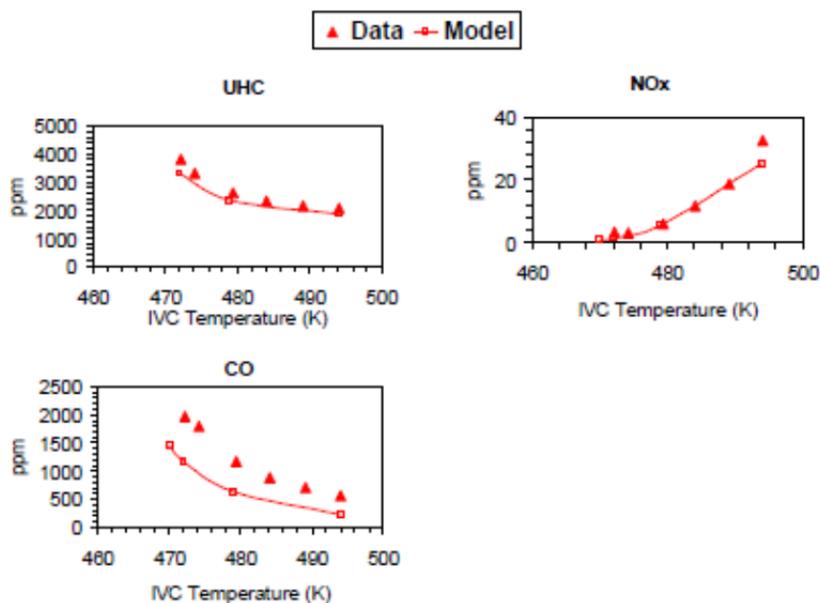


Figure 5, Match of experimental and modeled emissions for representative data points.

Overall conclusions of this work indicate that predicted combustion phasing and emissions of nine species agreed well with the engine data over a range of intake temperatures. The detailed exhaust measurements performed at ORNL have enabled the testing of the kinetic mechanism and the modeling approach. The emissions compared included NO_x , CO, formaldehyde, acetaldehyde, methane, ethylene, propene, iso-butylene and the overall unburned hydrocarbons. This framework of CFD modeling with detailed chemical kinetics sets the stage for further analysis of fuel and chemistry effects.

ORNL also supplied data for the FACE diesel fuels in HCCI combustion¹¹ so that more work could be done with the representation of real fuels using surrogates. This data covered a wide range of fuel rates (6 to 13 grams per minute) and a wide range of combustion phasing (3 to 10 degrees ATDC). Conclusions of this work indicated that response of this HCCI engine is mainly controlled by cetane number and the resulting combustion phasing. Lower cetane fuels were found to be desirable for improved fuel efficiency, but this can also result in an increase in NO_x . Higher T90 increases both CO and HC. Aromatics, when independent of cetane, did not appear to have an effect on either fuel economy or emissions.

Further exhaust chemistry measurements were done in 2010, for three diesel range fuels in HCCI¹². The fuels consisted of FACE fuel 9 and two surrogates blended to the same cetane number, one with and one without aromatics. These measurements were used to evaluate various mechanisms and tools being developed for the MFC. These measurements also included taking some TEM grids for particle characterization. A key finding was that HCCI particulate was mainly composed of partially volatile droplet aerosols. This is fundamentally different than soot

from a diesel engine and lead to the decision to convert the engine back to diesel operation in order to provide data more relevant for soot formation and oxidation.

2011

In late 2010, the Hatz engine was converted back to stock configuration diesel and a new combustion analysis system was installed. The AVL Indicom system included integrated high and low speed data acquisition and embedded software for gas exchange and energy balance calculation. This resulted in more accurate definition of cylinder conditions for CFD modeling inputs, including mass at intake valve closing, exhaust residual fraction, and heat loss calculations^{13 14 15}.

Once up and running, a series of diesel fuels and surrogates were evaluated with combustion, performance, and emissions measurements¹⁶. In this research, 5 of the 9 FACE diesel fuels were evaluated, along with 8 surrogates designed to represent these fuels. The surrogates were composed of 3 to 6 pure components each. Generally, the FACE fuels fell into groups for combustion phasing and heat release characteristics, based mainly on cetane value. The lower cetane fuels evaluated (fuels 1 and 3) had later start of combustion and correspondingly higher rates of heat release once combustion began, compared to the higher cetane fuels evaluated (fuels 5, 8, and 9). This behavior is shown in Figure 6 for a representative load condition. These measurements and figure also indicate that the surrogate fuels tended to track the fuels they were designed to represent.

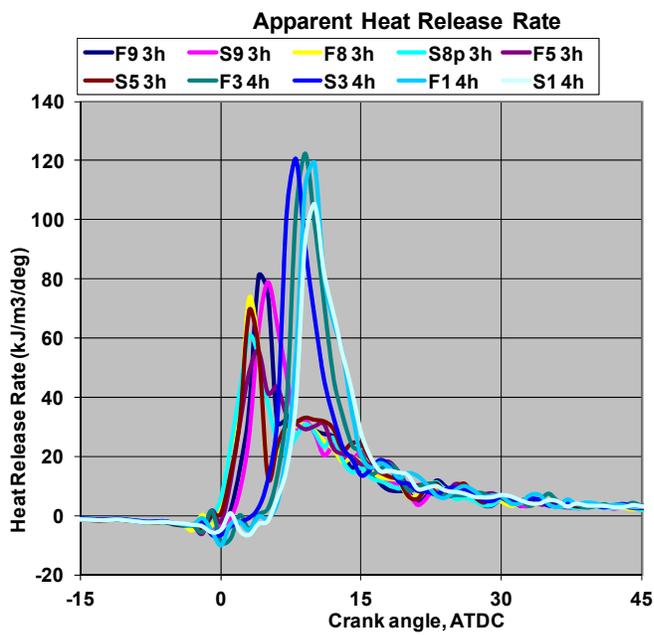
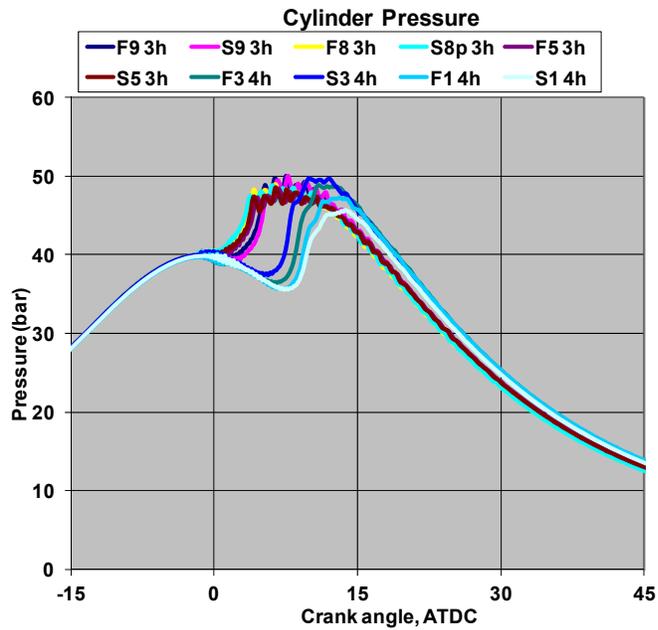
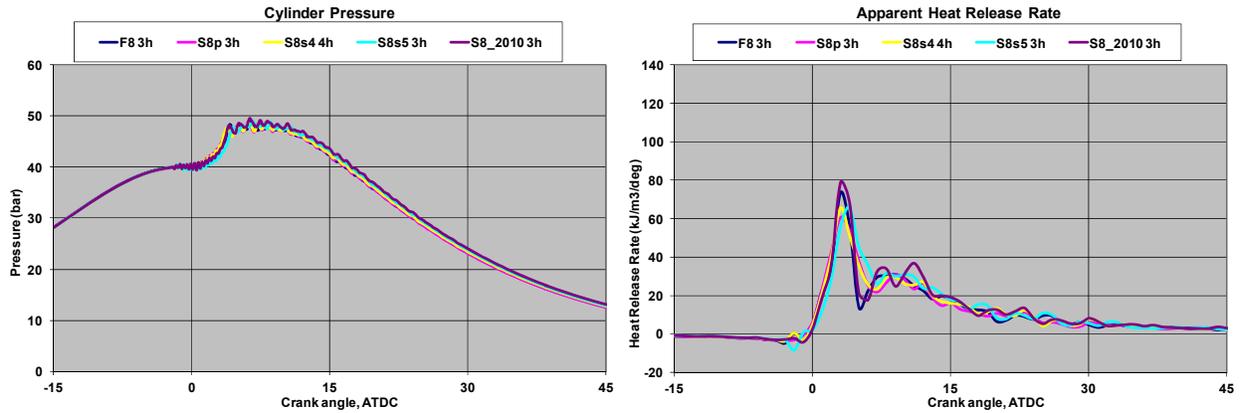


Figure 6, Cylinder pressure and heat release response of diesel engine to FACE fuels and corresponding surrogates. Only high load, heated intake data is shown.

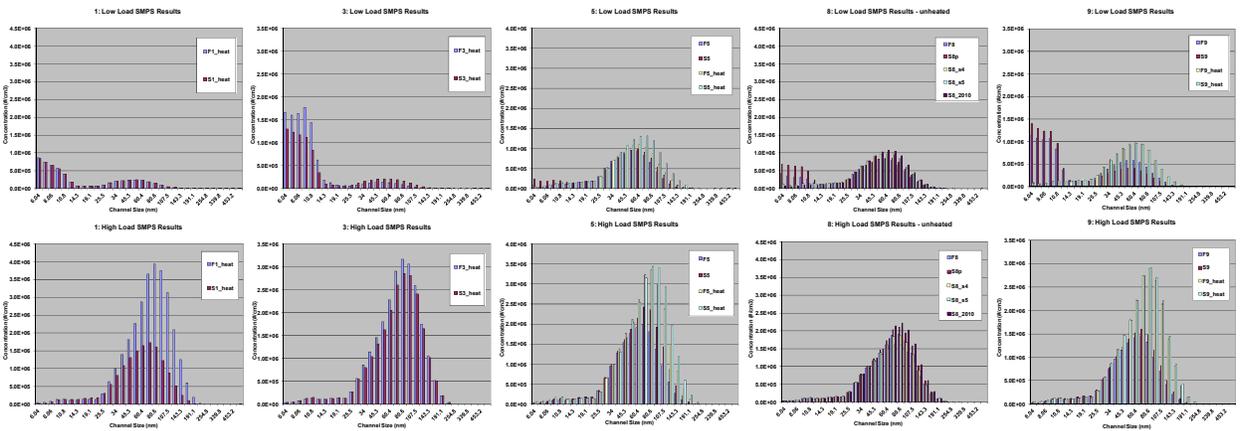
Figure 7 indicates that the 4 different surrogates designed for FACE fuel 8 all provided about equivalent combustion performance.

Figure 7, Comparison of engine response with 4 different surrogate fuel compositions mimicking FACE diesel fuel 8.



As noted, the fuels were largely grouped by cetane, with the lower cetane fuels and surrogates showing later combustion, higher CO and HC, and lower soot. These trends are consistent with more mixing time before combustion begins. The fuels also provided differing amounts of particulate, with different size distribution characteristics, as shown in Figure 8.

Figure 8, Particle size distributions for FACE fuels and surrogates. Left to right fuels 1, 3, 5, 8, and 9. Top row = light load, bottom row = high load.



Generally, the light load points (top row) showed bi-modal size distributions with both primary and secondary (small and larger) particles. The high load points showed only secondary particles. In some cases, the surrogates produced fewer particulates than the corresponding fuels, which may be because the surrogates only contained compounds up to C16, while the diesel fuels also contained larger molecules. This is an important topic for research in future studies.

2012

In 2012, data was supplied on blending characteristics of ethanol, gasoline surrogates, n-butanol, THF, and ETE to support improvements in the surrogate blend optimizer. The 3 latter fuel blending components can be manufactured using bacterial fermentation of sugars and are of current interest as drop-in biofuels. The ethanol data was developed for two DOE different projects related to octane of intermediate ethanol blends and substituting renewable hydrocarbons for ethanol in terminal blending^{17 18}. This data encompassed RON, MON, distillation, and RVP measurements on 86 blends spanning 0 to 85% ethanol in 2 gasolines and blends of n-heptane, i-octane, i-octene, and toluene. Additionally, RD requested that we evaluate a series of n-butane, tetrahydrofuran (THF), and ethyltetrahydrofurfuryl ether (ETE) in pure hydrocarbon blends. The n-butanol and ETE are intended for gasoline range fuels and were evaluated as 20% blends in various mixtures of iso-octane, n-heptane, methyl cyclohexane, and 1-hexene. The THF is intended as a diesel component and was evaluated as 20% blends in mixtures of n-hexadecane, 1-methyl naphthalene, decalin, and heptamethylnonane. Overall, 27 blends were evaluated, spanning a RON range of 80 to 101 and a cetane range of 13 to 66. It is also our intent to run some of these blends in diesel and gasoline HCCI, but this has not been completed at the time of this report.

Accurate modeling of combustion engines requires both accurate chemical representation of a fuel for combustion and also accurate physical representation of the fuel for accurate spray, evaporation, and mixing of the fuel. Surrogates are often set up with one surrogate fuel representing both chemical and physical properties, but this results in large mechanisms for diesel fuels, where fuel molecules can be large (up to about C22). FORTE' has an option to split a mechanism to a chemical and physical part by designing a mechanism to accurately represent chemistry in a homogeneous combustion system and then to assign the resulting surrogate compounds to have the physical properties of larger molecules to match physical properties. In order to demonstrate the importance of fuel reactivity and volatility, a CFD modeling study was undertaken to mimic diesel engine results with the FACE fuels, but with cetane controlled by using blends of n-heptane and benzene and T50 matched by using n-neptane, n-dodecane, or n-hexadecane for physical properties¹⁹. In this work, the surrogate fuels and kinetic modeling were able to reproduce the range and direction of fuel effects, although further model tuning was indicated to reproduce exact values. Figure 9 indicates the match of cylinder pressure for experimental data (grey) and CFD modeling (colored lines).

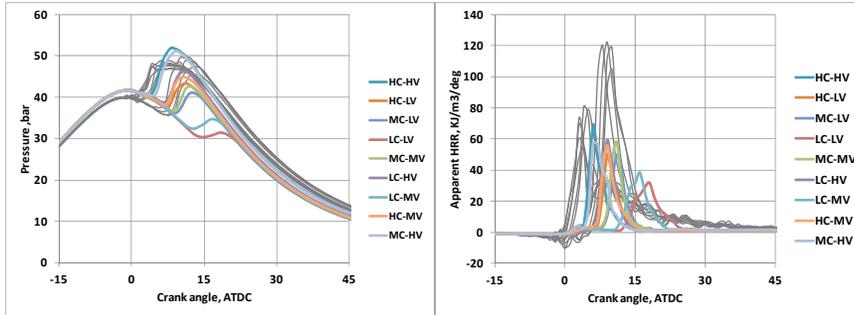


Figure 9, Match of CFD modeling to experimental data for cylinder pressure and heat release rate. HC, MC, and LC = high, medium, and low cetane and HV, MV, and LV = same for volatility.

Combustion phasing was shown to be sensitive to both cetane number and fuel volatility, with lower cetane and lower volatility (higher T50) resulting in later combustion. These trends are shown in figure 10 for MFB10, the crank angle position where 10% of the fuel has been burned.

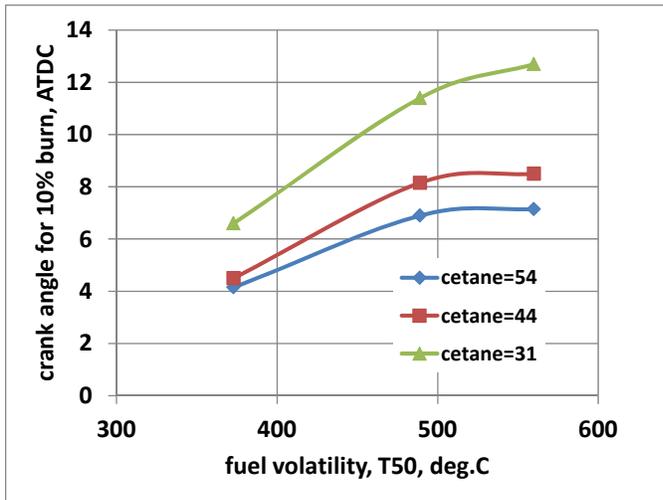


Figure 10, Trends of combustion phasing for results in Figure 9 as related to cetane and volatility.

As another application of MFC surrogate tools and kinetic modeling, a set of 7 fuels was designed, similar to the FACE diesel fuels, but designed to provide three levels and as wide a range possible of cetane, volatility, and threshold sooting index. These surrogate fuel blends are described in Table 4. The compositions for the surrogates are % by volume and the compound naming convention is the same as used by RD in the surrogate data base.

Table 4, Surrogate fuel blends designed to study cetane, sooting index, and volatility effects. Compositions are volume fractions.

BLEND	1	2	3	4	5	6	7
CETANE	L	M	H	M	M	M	M
TSI	M	M	M	L	H	M	M
T50 K	M	M	M	M	M	L	H
CETANE	40	48	60	50	50	48	50
TSI	35	34	35	10	60	35	35
T50 K	475	473	478	478	517	447	517
A2CH3	0.25	0.19	0.19	0.02	0.43	0.11	0.22
C6H5CH3	0.00	0.18	0.10	0.03	0.00	0.25	0.04
DECALIN	0.05	0.03	0.04	0.00	0.02	0.30	0.00
MCH	0.08	0.00	0.00	0.33	0.00	0.00	0.18
HMN	0.00	0.00	0.00	0.14	0.00	0.00	0.04
IC8H18	0.23	0.00	0.00	0.00	0.00	0.00	0.05
NC12H26	0.27	0.19	0.65	0.05	0.12	0.00	0.00
NC16H34	0.07	0.20	0.02	0.31	0.40	0.34	0.46
NC7H16	0.05	0.21	0.00	0.12	0.03	0.00	0.01

These surrogates were blended and run in the Hatz diesel engine and this data is also being used to support a modeling study that will be completed by year end. Results indicate that the engine responded to the fuels in an expected manner. For example, combustion phasing (5%, 10%, 50%, and 90% burn points) are plotted against 4 experimental variables in Figure 11. Combustion advances with both cetane and sooting index and retards with T50.

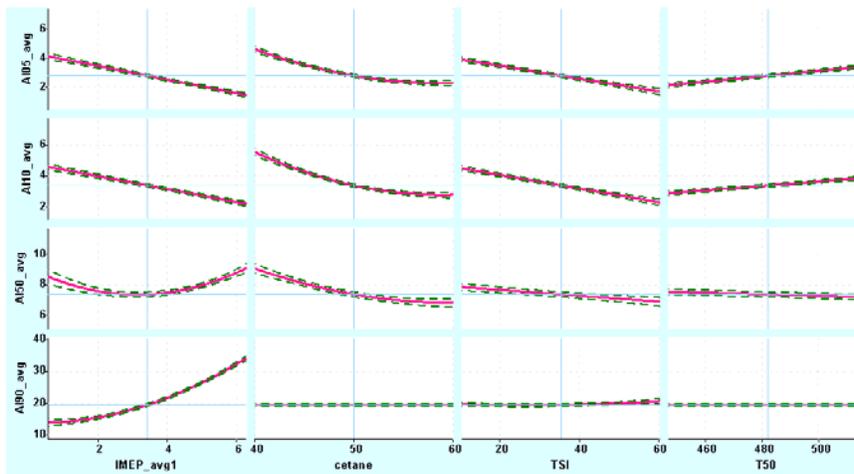


Figure 11, Combustion phasing of surrogate fuels as affected by engine load, cetane, sooting index, and T50.

Emissions also respond in a logical manner with cetane increasing NO_x and soot and decreasing HC and CO, sooting index increasing NO_x and soot, and T50 increasing NO_x. These trends can be a result of both the properties quoted and also a result of the chemistries that were used to obtain these properties. The experimental trends and results quoted are mainly of value in the

context of CFD and kinetic modeling, to see if they can be reproduced using the MFC kinetic mechanisms. This modeling work is under way, but was not completed at the time of this report being written. The goal of this modeling is to represent the entire dataset, using a single mechanism and CFD model, of sufficient complexity to reproduce the data, but of small enough size to allow modeling runs to be completed in less than 24 hours using advanced chemistry solvers, such as those incorporated in FORTE'.

Conclusions

The RD MFC is completing its 7th and probably final year of full operation, although there will be a subscription service offered for future additions to and improvements of the MFC master mechanisms. ORNL participated in the MFC through a CRADA project with RD (for the benefit of the MFC) for all but the first year of the consortium. ORNL was considered a work-in-kind member of the consortium and supplied experimental fuels and engine data, which was used to develop or test kinetic mechanisms, blending tools, and reaction models. Our data was considered to be in the public domain and was widely published, both with RD and for other purposes. This is why this CRADA report could be assembled from public sources. More details of the experiments and analysis of the results are contained in the references.

During the course of the MFC, work progressed in a logical manner and resulted in continual improvements in verified master mechanisms, tools for designing surrogate mixtures, tools for mimicking various engine and kinetic measurement equipment, improving chemical solvers to improve calculation speed, integrating these tools and mechanisms into a special version of Chemkin (Chemkin MFC), and a large data base of sources and analysis kinetic measurements from literature. Additionally, many of these tools were made compatible with FORTE', a CFD modeling software developed by RD over the same time frame. CFD allows the entire strength of the MFC tools to be applied and the mechanism reduction tools combined with fast solving techniques allows complex chemistry to be incorporated into CFD for accurate representation of fuels.

Accurate CFD and kinetic modeling requires a surrogate fuel to match both chemical characteristics and volatility characteristics to accurately mimic chemistry and mixing. This either requires surrogates to contain large molecules, resulting in longer calculation times, or it requires the ability to use smaller molecules for chemistry and larger molecules for physical properties, which is an option that RD offers in FORTE' CFD.

The MFC mechanisms and tools, combined with CFD modeling should provide a basis for representing a wide range of fuels with a single mechanism. MFC mechanism reduction tools combined with advanced chemistry solvers will allow solution of these complex problems in a usable time. Modeling work is underway to test this premise, using a set of surrogate fuels which were designed to span a wide range of cetane, sooting index, and boiling points.

Definitions

HCCI: homogeneous compression charge ignition, a combustion style where fuel is premixed and ignited kinetically near top dead center of the combustion stroke. Location of combustion is commonly controlled by temperature, residual exhaust gas, or pressure. If done correctly, this results in efficient, low emissions combustion.

HPL, LPL: the compression / combustion revolution and the gas exchange revolution, respectively, of a 4 stroke engine.

MON: motor octane number, one measure of gasoline fuel octane.

RON: research octane number, one measure of gasoline fuel octane.

Wet vs. dry: emissions measurements can be measured in total exhaust or in exhaust with the water removed. This changes results about 5%.

¹ James P. Szybist, Joanna McFarlane, and Bruce G. Bunting, Comparison of Simulated and Experimental Combustion of Biodiesel Blends in a Single Cylinder Diesel HCCI Engine, SAE Paper 2007-01-4010, 2007.

² Bruce G. Bunting, Scott J. Eaton, John Storey, Craig Fairbridge, Ken Mitchell, Robert W. Crawford, Tom Gallant, Jim Franz, and Mikhail Alaijar, The Chemistry, Properties, and HCCI Combustion Behavior of Refinery Streams Derived from Canadian Oil Sands Crude, SAE Paper 2008-01-2406, 2006.

³ Bruce G. Bunting, Robert W. Crawford, Les R. Wolf, and Yi Xu, The Relationship of Diesel Fuel Properties, Chemistry, and HCCI Engine Performance as Determined by Principal Component Analysis, SAE Paper 2007-01-4059, 2007.

⁴ Bruce G. Bunting, Scott Eaton, Chitrakumar V. Niak, Karthik V. Puduppakkam, Chen-Pang Chou, and Ellen Meeks, A Comparison of HCCI Ignition Characteristics of Gasoline Fuels Using a Single Zone Kinetic Model with a 5 Component Surrogate Fuel, SAE Paper 2008-01-2399, 2008.

⁵ James P. Szybist and Bruce G. Bunting, Cetane Number and Engine Speed Effects on Diesel HCCI Performance and Emissions, SAE Paper 2005-01-3723, 2005.

⁶ Samuel A. Lewis, John M. Storey, Bruce Bunting, and James P. Szybist, Partial Oxidation Products and Other Hydrocarbon Species in Diesel HCCI Exhaust, SAE Paper 2005-01-3737, 2005.

⁷ Karthik V. Puduppakkam, Long Lian, Chitral V. Naik, Ellen Meeks, and Bruce G. Bunting, Combustion and Emissions Modeling of a Gasoline HCCI Engine Using Model Fuels, SAE Paper 2009-01-0669, 2009.

⁸ Bruce G. Bunting, Scott Eaton, Jerome Taylor, Ke Nguyen, Karthik Puduppakkam, and Ellen Meeks, A Comparison of HCCI Engine Performance Data and Kinetic Modeling Results over a Wide Range of Gasoline Surrogate Blends, presentation at 2009 DOE DEER Conference, Directions in Engine Efficiency and Emissions Research, 2009.

⁹ Bruce Bunting, Scott Eaton, John Storey, Sam Lewis, Teresa Barone, and Maggie Connaster, Detailed HCCI Exhaust Speciation – ORNL Reference Fuel Blends, presentation at 2009 DOE DEER Conference, Directions in Engine-Efficiency and Emissions Research, 2009

¹⁰ Karthik V. Puduppakkam, Long Lian, Anthony Shelburn, Chitrakumar V. Niak, Ellen Meeks, and Bruce G. Bunting, Predicting Emissions Using CFD Simulations of an E30 Gasoline Surrogate in an HCCI Engine with Detailed Kinetics, SAE paper 2010-01-0362, 2010.

¹¹ Bruce G. Bunting and Scott J. Eaton, Performance Evaluation and Optimization of Diesel Fuel Properties and Chemistry in an HCCI engine, SAE paper 2009-01-2645, 2009.

¹² Teresa Barone, John Storey, Bruce Bunting, Raynella Connatser, and Samuel Lewis, The Influence of Fuel Chemistry on Particulate Emissions from an Advanced Combustion Engine, American Association for Aerosol Research Annual Meeting, Minneapolis, MN, 2010.

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- ¹³ Michael Bunce, Bruce Bunting, and Gary Patterson, Unique Hardware and Software Data Acquisition and Processing Solutions in a Small Engine Test Cell for Enhanced Kinetic Modeling Accuracy, poster presentation at 2011 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2011.
- ¹⁴ Michael Bunce, Bruce Bunting, Robert Crawford, and Jun Wang, Experimental and Statistical Comparison of Engine Response as a Function of Fuel Chemistry and Properties in CI and HCCI Engines, SAE Paper 2012-01-0857, 2012.
- ¹⁵ Bruce G. Bunting and Michael Bunce, ORNL Fuels Research on Behalf of Reaction Design Model Fuels Consortium, presentation at Reaction Design MFC Annual Meeting, San Diego, CA, Nov 14-15, 2011.
- ¹⁶ Karthik V. Puduppakkam, Bruce Bunting, Michael Bunce, and Ellen Meeks, Modeling Fuel Effects under Diesel Direct-Injection and HCCI Conditions, Using Multi-Component Fuel Surrogates in CFD, submitted for 2013 SAE International Congress, 2013.
- ¹⁷ Kukwon Cho, Bruce G. Bunting, and Brian H. West, High Level Blend Octane Study, poster presentation at 2011 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2011.
- ¹⁸ Bruce G. Bunting, The Use of Renewable Hydrocarbons as a Partial Substitution for ethanol in Gasoline terminal Blending, poster presentation at 2012 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2012.
- ¹⁹ Bruce Bunting, Michael Bunce, Karthik Puduppakkam, and Chitralkumar Niak, Kinetic Modeling of Fuel Effects Over a Wide Range of Chemistry, Properties, and Sources, International Conference on Sustainable Automobile Technologies 2012, Melbourne, AU, March 21-23, 2012.