

**A physics-based approach to modeling real-fuel combustion chemistry – VI. Predictive
kinetic models of gasoline fuels**

Rui Xu¹, Chiara Saggese¹, Robert Lawson², Ashkan Movaghar², Thomas Parise¹, Jiankun Shao¹,
Rishav Choudhary¹, Ji-Woong Park³, Tianfeng Lu³, Ronald K. Hanson¹, David F. Davidson¹,
Fokion N. Egolfopoulos², Allen Aradi⁴, Arjun Prakash⁴, Vivek Raja Raj Mohan⁴, Roger Cracknell⁵,
Hai Wang^{1,*}

¹*Department of Mechanical Engineering, Stanford University, Stanford, CA 94305, USA*

²*Department of Aerospace and Mechanical Engineering, University of Southern California, Los Angeles, CA
90089, USA*

³*Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269, USA*

⁴*Shell Global Solutions US Inc., 3333 Highway 6 South, Houston TX 77082, USA*

⁵*Shell Global Solutions (UK) 40 Bank Street, Canary Wharf, London E14 5NR, United Kingdom*

*Corresponding Author Email: Allen.Aradi@shell.com; haiwang@stanford.edu

S1. The evolution of the compositions of two gasoline fuels

Over the course of study, it was uncovered that the initial HyChem models developed from the fuel pyrolysis experiments were unable to reproduce the global combustion properties. The pyrolytic species measured were also found to be inconsistent with what would be expected from elemental compositions of the respective fuels. It was subsequently found that mishandlings of the fuels must have occurred during packaging and shipping: some of the low-molecular weight components have evaporated. As shown in Fig. S1, the actual compositions of the fuels (designated here as Shell A 2019 and Shell D 2019) differ from the original ones (designated here as Shell A 2017 and Shell D 2017) substantially. Some key properties of the fuels are also presented in Table S1. The original fuels were designated as E10 gasoline, containing slightly over 10% (wt) of ethanol. For the actual fuels tested, the ethanol contents had decreased significantly, to 6.7% (wt) and 5.5% (wt) in Shell A and Shell D, respectively. The reaction models proposed refer to fuels with the actual compositions tested, i.e., Shell A 2019 and Shell D 2019.

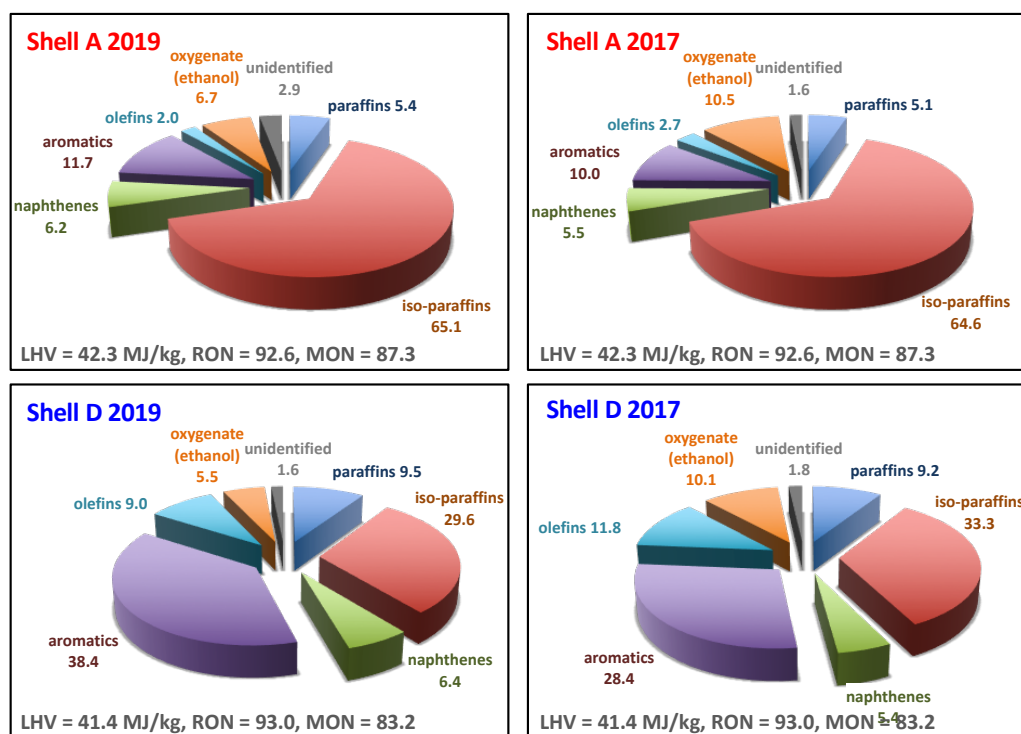


Fig. S1. Compositions (wt%) and basic properties of Shell A and D.

Table S1. Key properties of Shell A and D.

Fuel	Composition	Average formula	wt%			MW (g/mol)	Mole fraction	
			C	H	O		HC	Ethanol
Shell A	2019 ^a	C _{6.97} H _{14.36} O _{0.15}	83.3	14.4	2.3	100.5	0.855	0.145
	2017	C _{6.16} H _{13.42} O _{0.21}	81.4	14.9	3.7	90.9	0.792	0.208
Shell D	2019 ^a	C _{6.91} H _{12.36} O _{0.12}	85.3	12.8	1.9	97.4	0.883	0.117
	2017	C _{5.93} H _{11.57} O _{0.19}	82.9	13.6	3.5	85.9	0.811	0.189

^a The composition of 2019 is used for the current work.

S2. Additional physical and gas-phase thermochemical properties

We present a brief report of the thermochemical properties of the Shell gasoline A (2019) and D (2017), and their properties are listed in Table S1. The average molecular formula of each fuel is determined from the composition data (see, Table S3), including the mole fraction of ethanol and the mass fractions of C, H and O of the fuel as shown in Table S1. Also shown in the table are the mole fractions of ethanol and the hydrocarbon (HC) component of the fuel. As a supplementary information to Table S1, we present in Table S2 additional fuel physical and thermochemical properties, in Table S3 the fuel composition data in weight, volume, and molar percentages, and in Table S4 the distillation curve data of the two gasoline fuels.

For modeling purpose, we describe the fuel as an effective “two-component” mixture of ethanol and the HC component. Table S5 lists the average formula, molecular weight and heat of evaporation of the HC component of each fuel. The standard enthalpy of formation of the vapor-phase fuel may be determined from the lower heating value (LHV), enthalpy of evaporation (H_v) and molecular weight. Unfortunately, the latent enthalpy of evaporation is unavailable and has to be estimated from literature data. Following the same procedure described in the Supplementary material of Xu et al. [1], the H_v values of the HC component of each fuel are thus estimated and listed in Table S5. Then, the enthalpy of evaporation of the entire fuel ($H_{v,tot}$) can be estimated by the sum of H_v values of the HC component and ethanol, weighted by their respective mole fractions. Table S2 summarizes the lower heating values (LHV) and the vapor-phase standard enthalpy of formation of the two gasoline fuels. The H_v values are < 1% of the respective LHV values. Hence, the maximum error of 15% in an estimated H_v value leads to a negligible difference in the enthalpy of combustion of vapor-phase fuels (approximately 0.05 MJ/kg or < 0.15%).

Supplementary Materials

Table S2. Additional physical and thermochemical properties for the Shell gasoline fuels.

Fuel	Average formula	MW (g/mol)	Density @ 15°C (g/cm ³)	LHV (MJ/kg)	$H_{v,tot}^a$ (MJ/kg)	$\Delta_f H_{298}^b$ (kcal/mol)	Sulfur (wt %)
Shell A	C _{6.97} H _{14.36} O _{0.15}	100.5	0.722	42.25	0.41	-45.7	< 0.001
Shell D	C _{6.91} H _{12.36} O _{0.12}	97.4	0.744	41.36	0.43	-34.8	< 0.001

^a Estimated from the sum of enthalpy of evaporation of both ethanol and the HC component weighted by their respective mole fractions. ^b Derived from LHV, average formula and H_v .

Table S3. Composition data of Shell A and Shell D.

Group	Shell A			Shell D		
	Weight (%)	Volume (%)	Mole (%)	Weight (%)	Volume (%)	Mole (%)
<i>n</i> -paraffin	5.4	5.5	4.7	9.5	10.2	7.6
<i>iso</i> -paraffin	65.1	68.1	60.3	29.6	33.3	29.1
aromatics	11.7	9.7	10.2	38.4	33.4	33.8
naphthenes	6.2	5.8	5.9	6.4	6.4	6.4
olefins	2.0	2.1	2.1	9.0	9.9	9.9
oxygenate (ethanol)	6.7	6.1	14.5	5.5	5.3	11.7
unidentified	2.9	2.7	2.3	1.6	1.5	1.5

Table S4. Distillation curve data of Shell A and D.

Distillate vol. % off	Shell A Temperature (°C)	Shell D Temperature (°C)
0	26.1	26.2
5	27.3	36.3
10	63.5	60.3
15	77.2	63.4
20	88.7	70.3
25	98.5	78.2
30	98.7	87.8
35	98.9	98.3
40	99.1	105.1
45	106.2	110.4
50	109.7	110.5
55	112.4	113.5
60	113.2	124.1
65	114.3	138.3
70	117.5	144.2
75	125.0	160.7
80	143.1	167.9
85	161.7	176.1
90	176.1	187.5
95	184.0	200.4
100	207.3	235.4

Table S5. Key properties of the HC component.

Fuel	HC component		
	Average formula	MW (g/mol)	H_r^a (MJ/kg)
Shell A	$C_{7.82}H_{15.79}$	109.8	0.37
Shell D	$C_{7.57}H_{13.20}$	104.2	0.40

^a Enthalpy of evaporation at 298K, estimated from equation:
 H_r (kJ/mol) = 2.6 + 0.333 MW (g/mol) + 10.9 y_A , where y_A is the total mass fraction of the aromatic compounds in the fuel mixture.

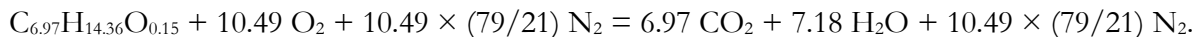
As we described in the main text, for modeling purpose, each fuel must be represented by a “binary” mixture of ethanol and the HC component given as C_mH_n where both m and n are integers. The determination of m and n are based on the considerations of both the H/C ratio, the average molecular weight, and the average formula of the HC component given in Table S6. The formula of the modeled HC component is shown in Table S6 for each fuel, along with its enthalpy of formation. The thermochemical data of the HC component are developed here using the $\Delta_f H_{298}^o$ values listed and the specific heats and entropy to be discussed later.

Table S6. Description of the modeled fuels.

Fuel	Modeled HC component					Mole fraction ^b	
	Name	Formula	MW (g/mol)	$\Delta_f H_{298}^o$ ^a (kcal/mol)	$\Delta_f H_{298}^o/\#C$ (kcal/mol)	HC	Ethanol
Shell A	SAC8H16	C_8H_{16}	112.2	-44.9	-5.62	0.852	0.148
Shell D	SDC8H14	C_8H_{14}	110.2	-33.8	-4.23	0.877	0.123

^a Derived from the $\Delta_f H_{298}^o$ of fuels and ethanol, as well as the HC and ethanol mole fractions in fuels. ^b These mole fraction values are slightly different from the actual values because of the use of approximate integer molecular formula for the HC component.

As we mentioned in the main manuscript, the use of integer molecular formula does introduce some difficulties in describing the fuel combustion chemistry, especially for gasoline fuels. In general, it is not possible to match both the equivalence ratio and mass fraction of the fuel at the same time because of small difference of the actual C/H/O ratio and the modeled C/H/O ratio. Here we take the middle ground. Specifically, using Shell A-air mixture as the example, the actual complete-combustion reaction is written as:



Decomposing the fuel into the HC component and ethanol, i.e., $0.855 C_{7.82}H_{15.79} + 0.145 C_2H_5OH$, the above formula is still exact. Replacing $C_{7.82}H_{15.79}$ by the integer formula (C_8H_{16}), we have instead $0.837 C_8H_{16} + 0.145 C_2H_5OH$ as the fuel mixture, where the value 0.837 comes from $0.855 \times$

Supplementary Materials

$MW(C_{7.82}H_{15.79})/ MW(C_8H_{16})$. The approach taken here is equivalent to matching the mass fraction of the fuel between experiment and simulation. Re-normalization of the mole fractions of the “binary” fuel components yields 0.852 C_8H_{16} + 0.148 C_2H_5OH , and these mole fraction values are given in the last two columns of Table S4.

The specific heat and entropy of each hydrocarbon may be estimated by defining a thermochemical surrogate, as shown in Table S7. For each hydrocarbon, a neat reference compound of molecular weight similar to the mean molecular weight of a class of similar compounds (e.g., *iso*-alkane) is assigned to that class. Attention has been placed on matching closely the average formula, mean molecular weight, and H/C ratio of the thermodynamic surrogate with those of the modeled hydrocarbon. Table S8 lists the thermochemical property values for the reference compounds considered (including ethanol). The thermochemical properties of the HC components of Shell A and D are listed in Tables S9 and S10, and the property data are presented in the form of NASA polynomials in Table S11.

Table S7. Thermochemical surrogate composition in mole fractions.

Hydrocarbon Name	Composition	Average Formula
SAC8H16	72.51% <i>iso</i> -octane (<i>i</i> - C_8H_{18}) + 7.09% methyl-cyclohexane (C_7H_{14}) + 12.32% toluene (C_7H_8) + 5.61% <i>n</i> -heptane (<i>n</i> - C_7H_{16}) + 2.48% 1-heptene (1- C_7H_{14})	$C_{7.73}H_{16.27}$
SDC8H14	33.50% <i>iso</i> -octane (<i>i</i> - C_8H_{18}) + 7.40% methyl-cyclohexane (C_7H_{14}) + 38.93% <i>p</i> -xylene (C_8H_{10}) + 8.77% <i>n</i> -heptane (<i>n</i> - C_7H_{16}) + 11.40% 1-heptene (1- C_7H_{14})	$C_{7.72}H_{13.96}$

Table S8. Thermochemical data of reference species.

Species	s_{298}° (cal/mol-K)	$c_p(T)$ (cal/mol-K)					Reference/ comments
		300 K	500 K	1000 K	1500 K	2000 K	
<i>iso</i> -octane	101.1	45.3	70.0	108.7	129.1	142.0	Therm [2]
methyl-cyclohexane	82.4	30.6	53.5	90.1	102.1	109.2	JetSurf 2.0 [3]
<i>p</i> -xylene	80.7	28.5	47.4	74.2	85.5	92.0	Burcat & Ruscic [4]
toluene	76.5	24.8	40.6	62.5	71.6	76.8	JetSurf 2.0 [3]
<i>n</i> -heptane	102.2	39.9	60.1	93.1	106.1	114.0	JetSurf 2.0 [3]
1-heptene	101.9	37.0	55.8	85.7	97.3	104.4	JetSurf 2.0 [3]
ethanol	67.1	15.7	22.8	34.2	39.5	42.7	Burcat & Ruscic [4]

Supplementary Materials

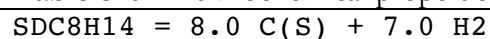
Table S9. Thermochemical properties of SAC8H16 (Fuel A Hydrocarbon)

SAC8H16 = 8.0 C(S) + 8.0 H2

T (K)	Cp (cal/mol-K)	S (cal/mol-k)	H(T)-H(298) (kcal/mol)	Hf (kcal/mol)	Gf (kcal/mol)
298.	40.953	96.841	0.000	-44.938	3.920
300.	41.207	97.115	0.082	-44.998	4.249
400.	53.392	110.665	4.821	-47.786	21.099
500.	64.318	123.779	10.718	-50.027	38.591
600.	73.784	136.365	17.636	-51.719	56.482
700.	81.797	148.358	25.427	-52.920	74.617
800.	88.569	159.734	33.954	-53.703	92.894
900.	94.520	170.515	43.113	-54.129	111.248
1000.	100.276	180.770	52.851	-54.201	129.631
1100.	104.479	190.528	63.092	-53.954	148.004
1200.	108.331	199.786	73.735	-53.484	166.345
1300.	111.856	208.598	84.747	-52.816	184.638
1400.	115.075	217.007	96.096	-51.973	202.873
1500.	118.011	225.049	107.753	-50.976	221.042
1600.	120.685	232.751	119.690	-49.844	239.141
1700.	123.114	240.142	131.882	-48.594	257.165
1800.	125.317	247.242	144.305	-47.242	275.112
1900.	127.313	254.072	156.938	-45.801	292.982
2000.	129.116	260.649	169.761	-44.286	310.773
2100.	130.741	266.989	182.755	-42.706	328.488
2200.	132.203	273.105	195.904	-41.073	346.125
2300.	133.515	279.011	209.191	-39.396	363.688
2400.	134.687	284.719	222.602	-37.683	381.177
2500.	135.732	290.239	236.124	-35.943	398.594

Supplementary Materials

Table S10. Thermochemical properties of SDC8H14 (Fuel D Hydrocarbon)



T (K)	Cp (cal/mol-K)	S (cal/mol-k)	H(T)-H(298) (kcal/mol)	Hf (kcal/mol)	Gf (kcal/mol)
298.	35.975	91.972	0.000	-33.838	7.164
300.	36.208	92.213	0.072	-33.895	7.440
400.	47.417	104.187	4.261	-36.537	21.628
500.	57.478	115.873	9.517	-38.719	36.431
600.	66.110	127.138	15.709	-40.437	51.630
700.	73.295	137.887	22.691	-41.747	67.084
800.	79.277	148.075	30.327	-42.717	82.701
900.	84.563	157.722	38.522	-43.394	98.421
1000.	89.923	166.904	47.242	-43.765	114.202
1100.	93.374	175.639	56.410	-43.866	130.005
1200.	96.538	183.901	65.908	-43.806	145.810
1300.	99.430	191.744	75.708	-43.603	161.604
1400.	102.067	199.211	85.785	-43.276	177.377
1500.	104.464	206.335	96.114	-42.840	193.124
1600.	106.636	213.148	106.670	-42.311	208.838
1700.	108.598	219.673	117.434	-41.704	224.516
1800.	110.364	225.931	128.383	-41.029	240.157
1900.	111.949	231.941	139.500	-40.300	255.759
2000.	113.366	237.720	150.767	-39.526	271.321
2100.	114.629	243.282	162.168	-38.717	286.844
2200.	115.750	248.641	173.688	-37.881	302.327
2300.	116.744	253.809	185.314	-37.026	317.772
2400.	117.621	258.796	197.033	-36.158	333.180
2500.	118.395	263.614	208.835	-35.285	348.551

Table S11. NASA Polynomials for hydrocarbons in fuels considered.

SAC8H16	S12/19C	8H	16	0	OG	298.000	3000.000	1
0.16599417E+02	0.48211332E-01	-0.17137061E-04	0.30121534E-08	-0.22484103E-12				2
-0.31723938E+05	-0.64288055E+02	0.11043806E+01	0.60797900E-01	0.39996248E-04				3
-0.94742312E-07	0.43304766E-10	-0.25833947E+05	0.23297089E+02					4
SDC8H14	S12/19C	8H	14	0	OG	298.000	3000.000	1
0.18020479E+02	0.37881661E-01	-0.12259099E-04	0.16786289E-08	-0.70531221E-13				2
-0.26540160E+05	-0.72785660E+02	0.12218976E+01	0.46767473E-01	0.64798354E-04				3
-0.12255914E-06	0.55022525E-10	-0.19829512E+05	0.23479656E+02					4

The adiabatic flame temperature (T_{ad}) is calculated for the two gasoline fuels in air at 1 atm pressure. Fig. S2 show the adiabatic flame temperature plotted as a function of the equivalence ratio. Clearly, the T_{ad} values of the two fuels are close to each other over the entire range of equivalence ratio, and peak within 2280-2305 K. Given the small difference in the adiabatic flame temperature,

it is unlikely that differences observed in the combustion behavior of these fuels, if any, is attributable to the difference in their thermochemical properties.

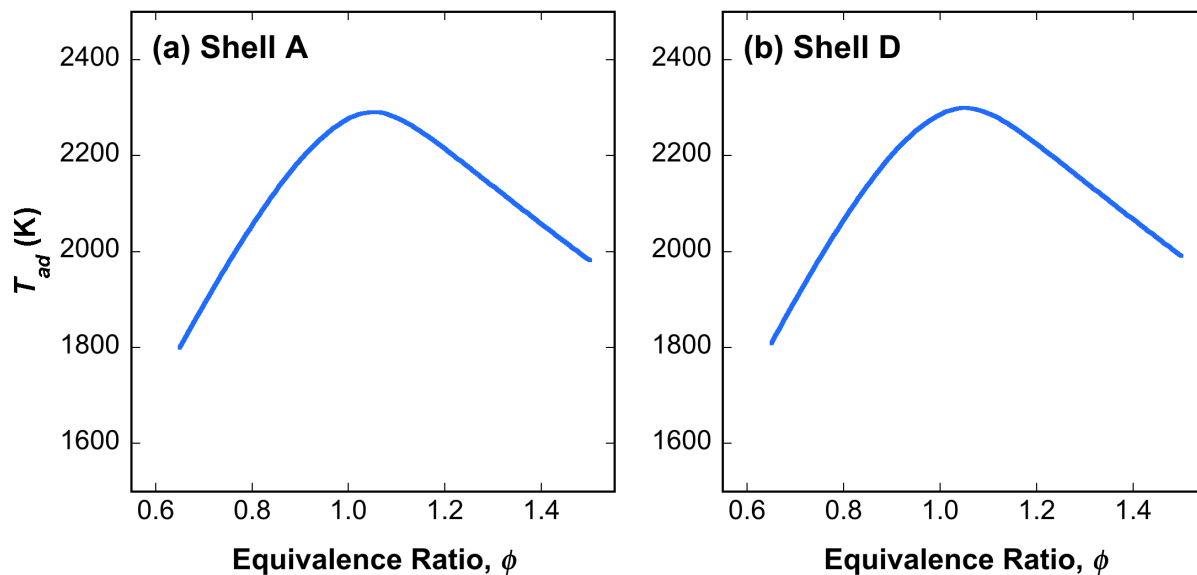


Fig. S2. Adiabatic flame temperature (T_{ad}) computed for (a) Shell A and (b) Shell D in air ($p = 1$ atm, $T_0 = 298$ K).

References

- [1] R. Xu, K. Wang, S. Banerjee, J. Shao, T. Parise, Y. Zhu, S. Wang, A. Movaghar, D.J. Lee, R. Zhao, X. Han, Y. Gao, T. Lu, K. Brezinsky, F. Egolfopoulos, D. Davidson, R. Hanson, C. Bowman, H. Wang, A physics-based approach to modeling real-fuel combustion chemistry – II. Reaction kinetic models of jet and rocket fuels, *Combust. Flame* 193 (2018) 520-537.
- [2] E.R. Ritter, J.W. Bozzelli, THERM: Thermodynamic property estimation for gas phase radicals and molecules, *Int. J. Chem. Kinet.* 23 (1991) 767-778.
- [3] H. Wang, E. Dames, B. Sirjean, D.A. Sheen, R. Tangko, A. Violi, J.Y.W. Lai, F.N. Egolfopoulos, D.F. Davidson, R.K. Hanson, C.T. Bowman, C.K. Law, W. Tsang, N.P. Cernansky, D.L. Millar, R.P. Lindstedt, A high-temperature chemical kinetic model of n -alkane (up to n -dodecane), cyclohexane, and methyl-, ethyl-, n -propyl and n -butyl-cyclohexane oxidation at high temperatures, *JetSurF* version 2.0, September 19, 2010 (<http://web.stanford.edu/group/haiwanglab/JetSurF/JetSurF2.0/index.html>), 2010.
- [4] A. Burcat, B. Ruscic, Third millenium ideal gas and condensed phase thermochemical database for combustion (with update from active thermochemical tables), Argonne National Laboratory (ANL), 2005.