Supporting Information

Combustion Mechanisms and Kinetics of Fuel Additive: A ReaxFF Molecular Simulation

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The force field used in this work

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Reactive MD-force field: Combustion C/H/O force field - September 7, 2016
 39            ! Number of general parameters
    50.0000 !p(boc1)
     9.5469 !p(boc2)
    26.5405 !p(coa2)
     0.6863 !p(trip4)
     2.7295 !p(trip3)
    70.0000 !kc2
     1.0588 !p(ovun6)
     4.1262 !p(trip2)
    12.1176 !p(ovun7)
    13.3056 !p(ovun8)
   -68.9784 !p(trip1)
     0.0000 !Lower Taper-radius (swa)
    10.0000 !Upper Taper-radius (swb)
     0.0000 !not used
    33.8667 !p(val7)
     6.0891 !p(lp1)
     1.0563 !p(val9)
     2.0384 !p(val10)
     6.1431 !not used
     6.9290 !p(pen2)
     0.3989 !p(pen3)
     3.9954 !p(pen4)
     0.0000 !not used
     5.7796 !p(tor2)
    10.0000 !p(tor3)
     1.9487 !p(tor4)
     0.0000 !not used
     2.1645 !p(cot2)
     1.5591 !p(vdW1)
     0.1000 !Cutoff for bond order*100 (cutoff)
     2.1365 !p(coa4)
     0.6991 !p(ovun4)
    50.0000 !p(ovun3)
     1.8512 !p(val8)
     0.0000 !not used
     0.0000 !not used
     0.0000 !not used
     1.0000 !not used
     2.6962 !p(coa3)
 3       ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma
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                alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
                ro(pipi);p(lp2);Heat increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
                p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.
C       1.3674    4.0000   12.0000    2.0453    0.1444    0.9500    1.1706    4.0000
        9.0000    1.5000    4.0000   27.5134   79.5548    5.0191    7.0500    0.0000
        1.1168    0.0000  181.0000   14.2732   24.4406    6.7313    0.8563    0.0000
       -4.1021    5.0000    1.0564    4.0000    2.9663    0.0000    0.0000    0.0000
H       0.9479    1.0000    1.0080    1.1364    0.0232    0.9900   -0.1000    1.0000
        9.0643    4.7746    1.0000    0.0000  121.1250    4.7757    9.7732    1.0000
       -0.1000    0.0000   62.4879    2.5194    2.3785    0.2223    1.0698    0.0000
      -15.7683    2.1488    1.0338    1.0000    2.8793    0.0000    0.0000    0.0000
O       1.1939    2.0000   15.9990    1.9289    0.1201    0.9900    1.0981    6.0000
       10.4842    8.2916    4.0000   28.8967  116.0768    7.9703    7.0500    2.0000
        1.0479   20.0000   60.8726   10.0338    2.2024    0.9942    0.9745    0.0000
       -3.6141    2.7025    1.0493    4.0000    2.9225    0.0000    0.0000    0.0000
6         ! Nr of bonds; at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(b
                                  p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
  1   1   80.8865  107.9944   52.0636    0.5218   -0.3636    1.0000   34.9876    0.7769
          6.1244   -0.1693    8.0804    1.0000   -0.0586    8.1850    1.0000    0.0000
  1   2  179.5195    0.0000    0.0000   -0.5242    0.0000    1.0000    6.0000    0.7187
          5.4740    1.0000    0.0000    1.0000   -0.1144    6.7029    0.0000    0.0000
  2   2  113.9232    0.0000    0.0000   -0.5971    0.0000    1.0000    6.0000    0.9093
          1.7152    1.0000    0.0000    1.0000   -0.0450    6.0710    0.0000    0.0000
  1   3  136.4945  164.1201    5.5000   -0.9159   -0.1075    1.0000   10.6519    0.8644
          0.6858   -0.4602    9.5754    1.0000   -0.1745    4.5987    0.0000    0.0000
  3   3  148.0798  155.2406   20.1160   -1.0000   -0.1254    1.0000   33.0027    0.7790
          0.7673   -0.1697    7.0028    1.0000   -0.1300    5.1959    1.0000    0.0000
  2   3  169.1351    0.0000    0.0000   -0.8810    0.0000    1.0000    6.0000    0.5757
          1.5482    1.0000    0.0000    1.0000   -0.1788    4.6622    0.0000    0.0000
3       ! Nr of off-diagonal terms. at1;at2;Dij;RvdW;alfa;ro(sigma);r
  1   2     0.1253    1.5717    9.9736    1.2057   -1.0000   -1.0000
  2   3     0.1125    1.6311    8.7528    1.0929   -1.0000   -1.0000
  1   3     0.0953    1.7397    8.8986    1.4256    1.1067    1.1265
18        ! Nr of angles. at1;at2;at3;Thetao,o;p(val1);p(val2);p(coa1);
  1   1   1   76.1370   34.6920    1.1328    0.0000    0.0050    0.3556    1.8065
  1   1   2   68.0572    9.9461    4.7000    0.0000    0.4566    0.0000    1.8532
  2   1   2   65.6815   35.0000    1.8622    0.0000    0.0490    0.0000    1.0937
  1   2   2    0.0000    4.0000    7.2043    0.0000    0.0000    0.0000    1.0728
  1   2   1    0.0000    3.4110    7.7350    0.0000    0.0000    0.0000    1.0400
  2   2   2    0.0000   30.0000    5.6235    0.0000    0.0000    0.0000    1.0400
  1   1   3   78.3624   13.0773    9.0480    0.0000    0.1270   52.1129    2.3964
  3   1   3   76.7101   24.3833    5.8613  -21.8559    2.6395  -32.6534    3.6179
  2   1   3   79.1288   30.0000    1.4632    0.0000    0.2065    0.0000    2.0000
  1   3   1   80.7352   16.4130    4.9987    0.0000    0.0843    0.0000    1.0137
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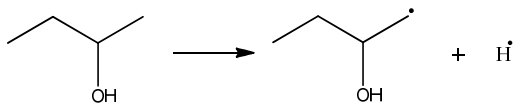
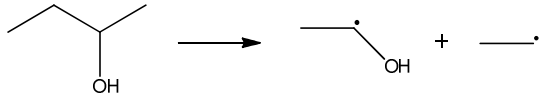
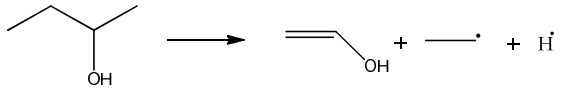
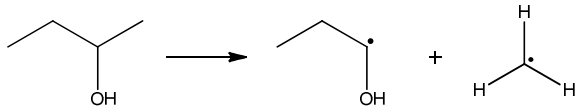
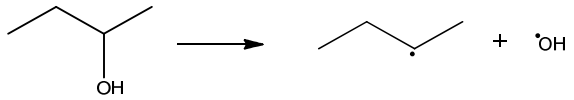
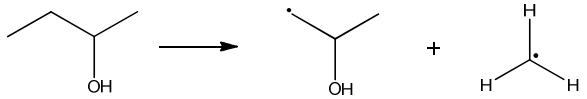
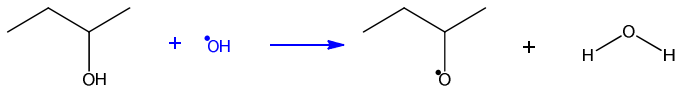
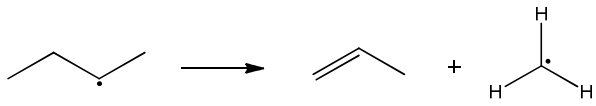
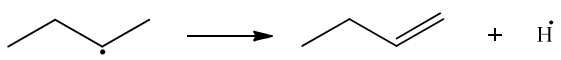
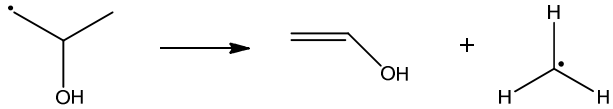
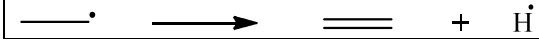
  1   3   3   85.4436   14.4937    3.9928    0.0000    1.4350   44.5320    1.1348
  3   3   3   89.9282   32.1199    2.7181    0.0000    0.3323   57.6122    1.0000
  1   3   2   82.9640   32.4874    0.8777    0.0000    0.9627    0.0000    1.0010
  2   3   3   85.7838   17.3139    1.9157    0.0000    3.6306    0.0000    2.1858
  2   3   2   84.2527   33.1226    0.6730    0.0000    0.7238    0.0000    2.4348
  1   2   3    0.0000   14.4588    3.1507    0.0000    3.4571    0.0000    1.0149
  3   2   3    0.0000    0.9696    3.6303    0.0000    0.0000    0.0000    1.6987
  2   2   3    0.0000    0.5797    1.9739    0.0000    0.0000    0.0000    2.4494
21      ! Nr of torsions. at1;at2;at3;at4;;V1;V2;V3;p(tor1);p(cot1);n
  1   1   1   1    2.0474   32.6719    0.5282   -9.0000   -2.6449    0.0000    0.0000
  1   1   1   2    1.6328   78.4995   -0.1514   -6.9161   -2.9986    0.0000    0.0000
  2   1   1   2    2.4142   78.7025    0.3506   -8.8640   -6.9283    0.0000    0.0000
  1   1   1   3   -0.7104   22.6038    0.5309   -2.0000   -0.6614    0.0000    0.0000
  2   1   1   3    1.9323   52.9368    0.6554   -8.8118   -3.9854    0.0000    0.0000
  3   1   1   3   -1.2500    1.1248   -0.1230   -9.9453   -3.9000    0.0000    0.0000
  1   1   3   1   -0.6848   56.7751   -1.2733   -2.2937   -4.0000    0.0000    0.0000
  1   1   3   2   -1.4557   78.6279    0.9945   -3.2742   -2.4240    0.0000    0.0000
  2   1   3   1    0.6928   78.1546    0.5608   -3.1713   -3.7301    0.0000    0.0000
  2   1   3   2   -1.4343   77.0699    0.9875   -3.4139   -1.4053    0.0000    0.0000
  1   1   3   3    0.5153    2.1584    0.2000   -6.5859   -3.0000    0.0000    0.0000
  2   1   3   3    0.2018   80.0000    0.3778   -2.5000   -2.8750    0.0000    0.0000
  3   1   3   1   -1.9875   79.2591    1.0000   -2.4206   -3.9342    0.0000    0.0000
  3   1   3   2   -1.1000   78.8002   -1.0000   -2.6282   -4.0000    0.0000    0.0000
  3   1   3   3   -1.0000   83.5323    4.3660   -2.6805   -1.2938    0.0000    0.0000
  1   3   3   1    3.4682    0.0781    0.9887   -6.1195   -0.5004    0.0000    0.0000
  1   3   3   2    1.0000   16.5478   -1.0313   -2.0000   -2.6888    0.0000    0.0000
  2   3   3   2    4.0818   -3.2744   -0.9664   -7.1634   -3.0000    0.0000    0.0000
  1   3   3   3    4.2014  -10.0642    1.8690   -2.4805   -2.5000    0.0000    0.0000
  2   3   3   3    1.0000  -10.0500   -1.0000   -2.1946   -0.5300    0.0000    0.0000
  3   3   3   3    1.0000    1.6871    3.0000   -6.2660   -0.5500    0.0000    0.0000
 1      ! Nr of hydrogen bonds. at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3
  3   2   3    1.8130   -3.5409    2.3815   21.9463
```

Table S1 Main initial reaction pathways of ethanol in additive-fuel combustion simulations at 3000 K.

Reactions	k' (relative rate constant)
$CH_3CH_2OH \rightarrow \bullet H + \bullet CH_2CH_2OH$ (reference reaction)	1
$CH_3CH_2OH + \bullet OH \rightarrow CH_2O + \bullet CH_3 + H_2O$	1.62
$CH_3CH_2OH + \bullet OH \rightarrow H_2O + CH_3CH_2O\bullet$	5.68
$CH_3CH_2OH \rightarrow \bullet CH_3 + \bullet CH_2OH$	8.03
$\bullet CH_2CH_2OH \rightarrow C_2H_4 + \bullet OH$	3.20e+03
$CH_3CH_2O\bullet \rightarrow \bullet CH_3 + CH_2O$	6.41e+03

Table S2 Main initial reaction pathways of 2-butanol in additive-fuel combustion simulations at 3000 K.

Reactions	k' (relative rate constant)
	13.23
	1.38e+02
	6.61
	1.16e+02
	4.56e+02
	75.98
	2.99
	2.06e+03
	9.06e+02
	1.87e+03
	7.37e+02

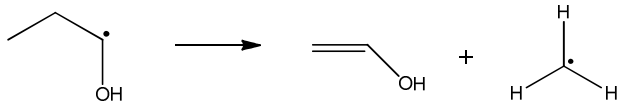
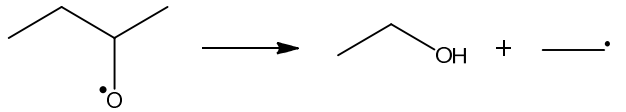
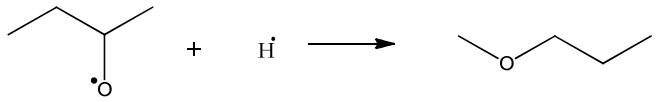
	2.42e+03
	2.89e+04
	5.25e+03

Table S3 Main initial reaction pathways of DMC in additive-fuel combustion simulations at 3000 K.

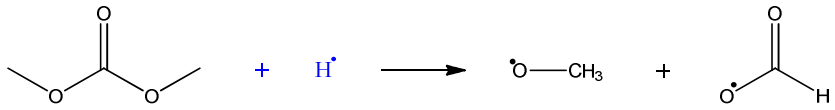
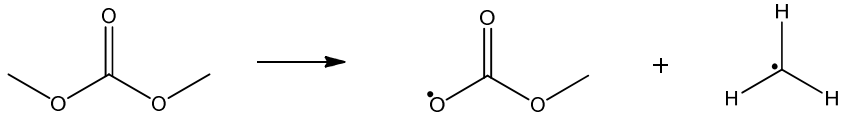
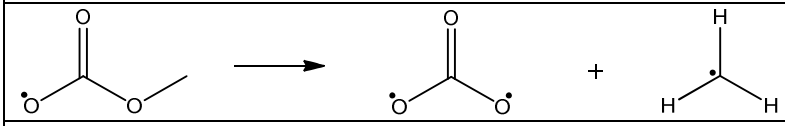
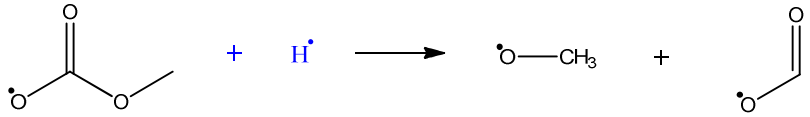
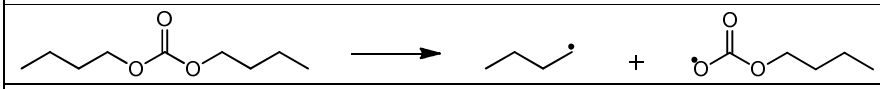
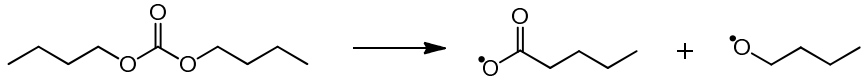
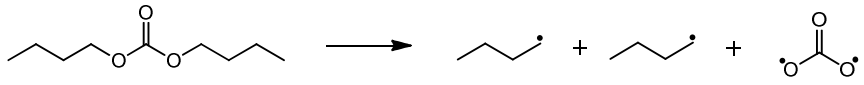
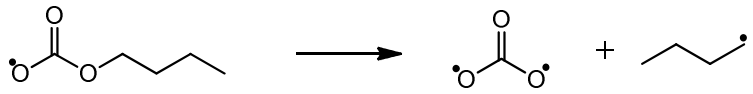
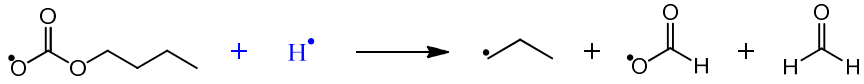
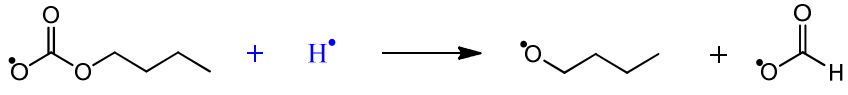
Reactions	k' (relative rate constant)
	4.26e+02
	1.17e+04
	2.60e+03
	1.37e+04

Table S4 Main initial reaction pathways of DBC in additive-fuel combustion simulations at 3000 K.

Reactions	k' (relative rate constant)
	2.00e+04
	8.90e+04
	8.90e+04
	4.06e+03
	8.11e+02
	1.87e+04

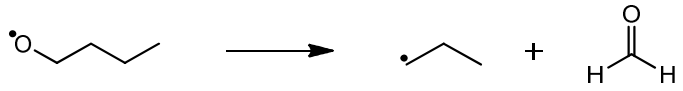
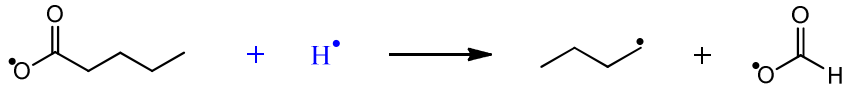
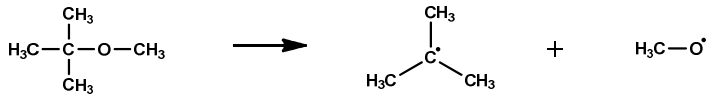
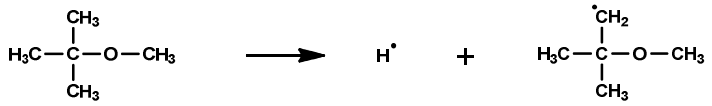
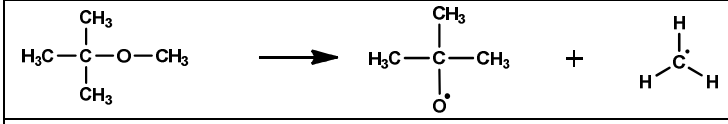
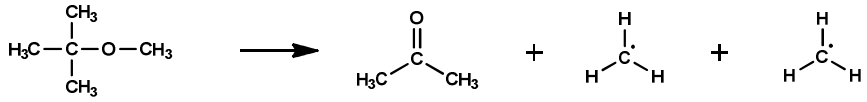
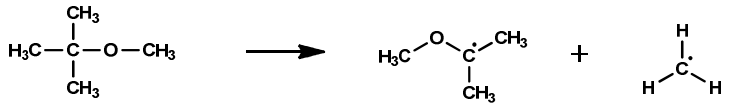
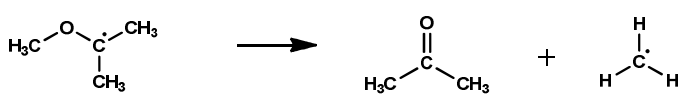
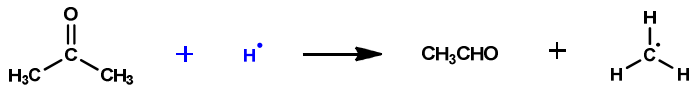
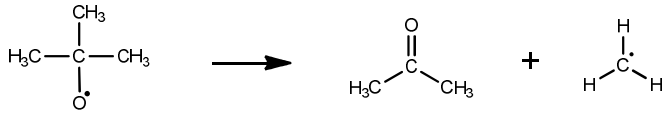
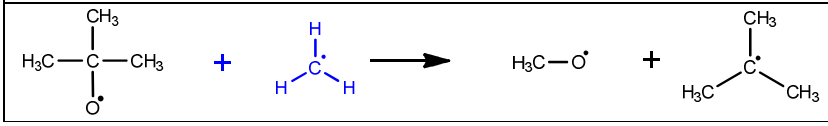
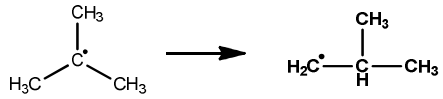
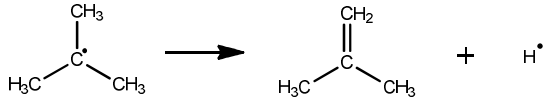
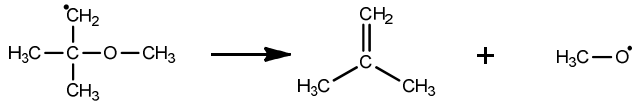
	1.29e+04
	2.30e+03
	4.72e+02
	1.96e+03

Table S5 Main initial reaction pathways of MTBE in additive-fuel combustion simulations at 3000 K.

Reactions	k' (relative rate constant)
	7.59e+02
	26.85
	1.49e+03
	80.31
	1.00e+02
	2.49e+04
	68.43
	2.32e+04
	10.47

	1.14e+03
	1.05e+03
	1.83e+04
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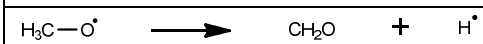
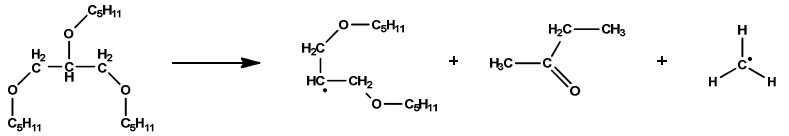
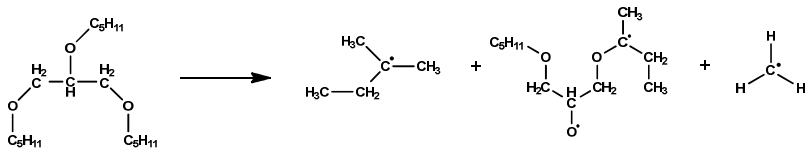
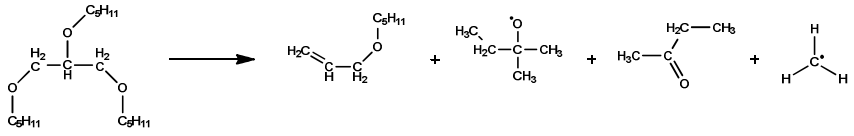
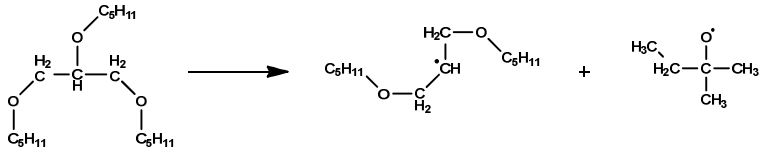
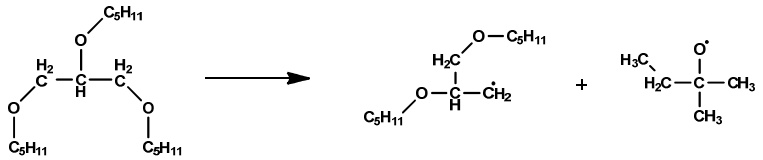
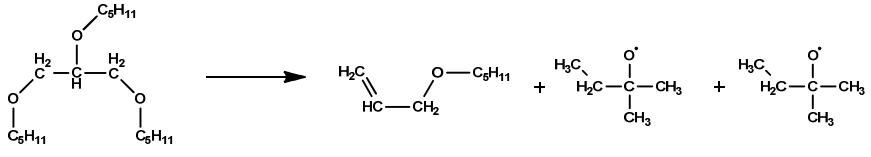
	1.65e+03

Table S6 Main initial reaction pathways of TTAG in additive-fuel combustion simulations at 3000 K.

Reactions	k' (relative rate constant)
	2.02e+02
	7.39e+02
	2.02e+02
	3.29e+02
	2.76e+02
	7.39e+02

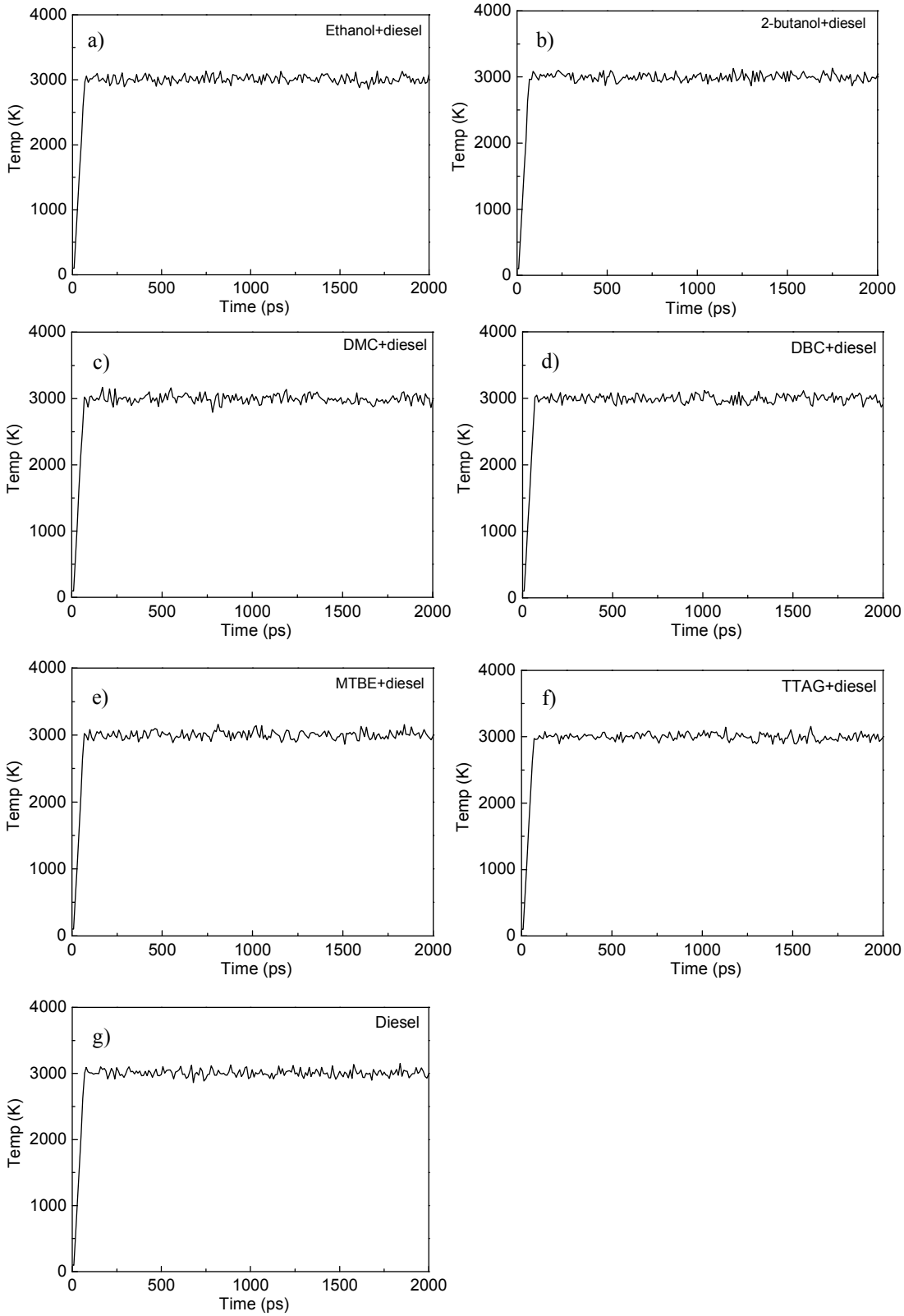
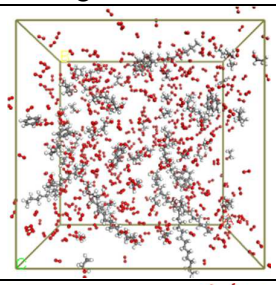
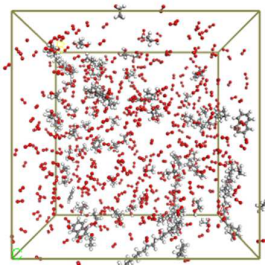
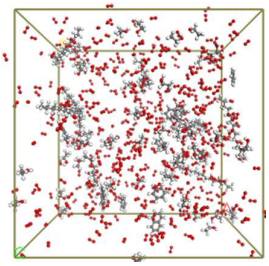
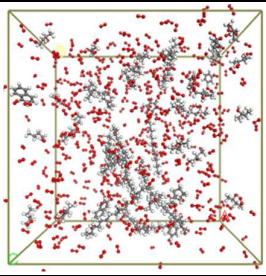
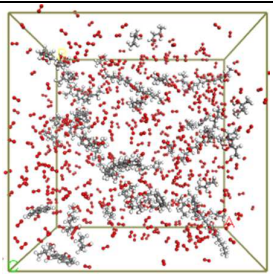
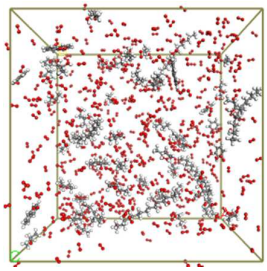
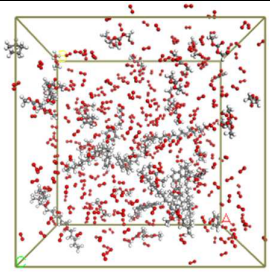
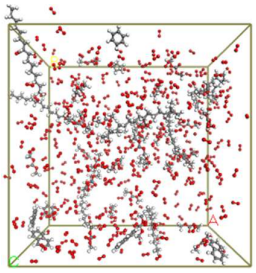
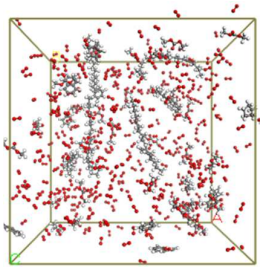
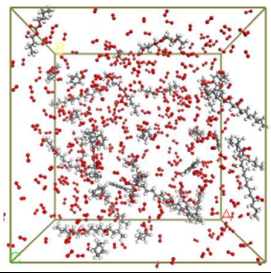
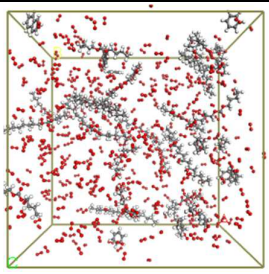
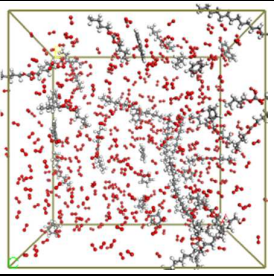
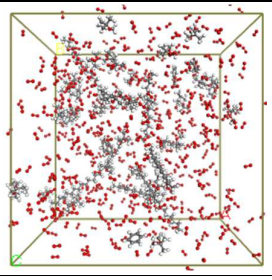
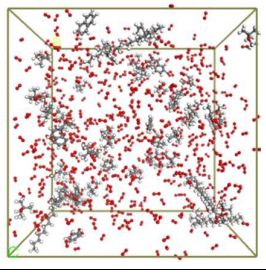
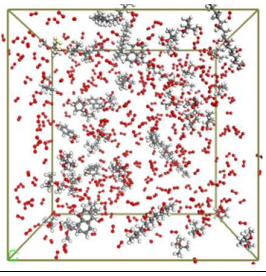


Figure S1 Time evolution of temperature in a). ethanol+diesel, b). 2-butanol+diesel, c). DMC+diesel, d). DBC+diesel, e). MTBE+diesel, f). TTAG+diesel, g). diesel systems.

The construction procedure and random settings

Table S7 The different configurations used in this work:

Systems	Configuration 1	Configuration 2	Configuration 3
Ethanol+diesel+O_2			
2-butanol+diesel+O_2			
DMC+diesel+O_2			
DBC+diesel+O_2			
MTBE+diesel+O_2			

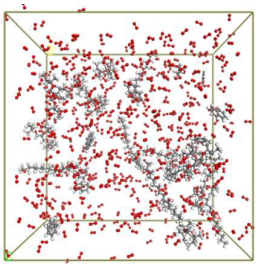
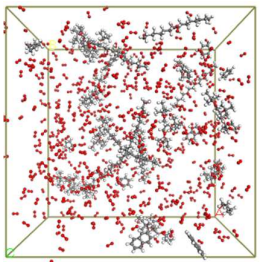
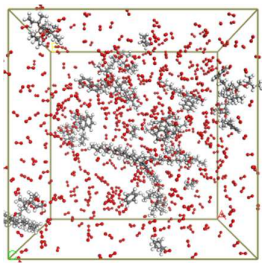
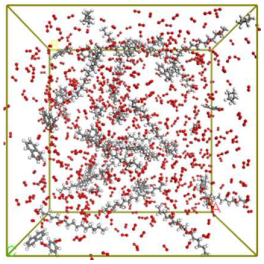
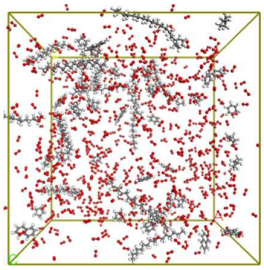
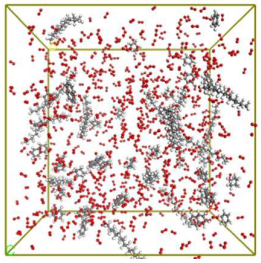
TTAG+diesel+O_2			
Diesel+O_2			

Table S8 Randomization settings and explanations

Steps	Explanations
1. Constructing three simulation boxes for each system (shown in Table S7).	The molecules were randomly placed and thus could ensure the different configurations between the simulation boxes.
2. Random seed (including the absolute value and direction) was set and adopted on each atom for the first simulation step.	The initial rate (including the absolute value and direction) is the basis of later integrals. Random initial rate will ensure the randomization of subsequent rates.
3. All the species underwent the low-temperature simulation firstly before the temperature was increased.	Enough low-temperature simulation allowed bond torsion and any other bond variation except for reactions, and thus ensure the diversity of configurations.
4. Heating the systems to target temperature.	Then reactions may occur.