# Ethanolic Gasoline, a Lignocellulosic Advanced Biofuel

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# Supplementary Information

| Reaction | A ($cm^3 mol^{-1} s^{-1}$) | n | Ea ($cal mol^{-1}$) | k @ 800 K ($cm^3 mol^{-1} s^{-1}$) | Reference |
|---|---|---|---|---|---|
| ***R+O2=RO2*** | | | | | |
| EL1J+O2=EL1OO | $7.54x10^{+12}$ | 0 | 0 | $7.54x10^{+12}$ | Analogy to IC3H7+O2<=>C3H7O2 [1] |
| EL3J+O2=EL3OO | $7.54x10^{+12}$ | 0 | 0 | $7.54x10^{+12}$ | Analogy to IC3H7+O2<=>C3H7O2 [1] |
| EL4J+O2=EL4OO | $7.54x10^{+12}$ | 0 | 0 | $7.54x10^{+12}$ | Analogy to IC3H7+O2<=>C3H7O2 [1] |
| EL6J+O2=EL6OO | $7.54x10^{+12}$ | 0 | 0 | $7.54x10^{+12}$ | Analogy to IC3H7+O2<=>C3H7O2 [1] |
| EL7J+O2=EL7OO | $7.54x10^{+12}$ | 0 | 0 | $7.54x10^{+12}$ | Analogy to IC3H7+O2<=>C3H7O2 [1] |
| ***RO2=Olefin+HO2*** | | | | | |
| EL3OO=EL34D+HO2 | $8.08x10^{+12}$ | 0 | 32821 | $8.74x10^{+03}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [2] |
| *Reverse* | $5.05x10^{+10}$ | 0 | 10416 | $7.21x10^{+07}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3] |
| EL4OO=EL34D+HO2 | $8.08x10^{+12}$ | 0 | 32822 | $8.73x10^{+03}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [2] |
| *Reverse* | $5.05x10^{+10}$ | 0 | 10416 | $7.21x10^{+07}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3] |
| EL6OO=EL67D+HO2 | $1.06x10^{+13}$ | 0 | 33040 | $1.00x10^{+04}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [2] |
| Reverse | $6.22x10^{+10}$ | 0 | 8987 | $2.18x10^{+08}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [3] |
| EL7OO=EL67D+HO2 | $6.47x10^{+12}$ | 0 | 31792 | $1.34x10^{+04}$ | Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [2] |
| Reverse | $6.45x10^{+10}$ | 0 | 13000 | $1.81x10^{+07}$ | Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [3] |
| ***RO2=QOOH*** | | | | | |
| EL1OO=EL1OOH3J | $2.50x10^{+10}$ | 0 | 20450 | $6.48x10^{+04}$ | Analogy to C7H15O2-1<=>C7H14OOH1-3 [1] |
| EL3OO=EL3OOH1J | $3.75x10^{+10}$ | 0 | 24000 | $1.04x10^{+04}$ | Analogy to C7H15O2-3<=>C7H14OOH3-1 [1] |
| EL3OO=EL3OOH4J | $2.00x10^{+11}$ | 0 | 26450 | $1.19x10^{+04}$ | Analogy to C7H15O2-3<=>C7H14OOH3-4 [1] |
| EL4OO=EL4OOH3J | $4.00x10^{+11}$ | 0 | 26450 | $2.38x10^{+04}$ | Analogy to C7H15O2-4<=>C7H14OOH4-3 [1] |
| EL6OO=EL6OOH7J | $3.00x10^{+11}$ | 0 | 29000 | $3.59x10^{+03}$ | Analogy to C7H15O2-2<=>C7H14OOH2-1 [1] |
| EL7OO=EL7OOH6J | $2.00x10^{+11}$ | 0 | 26450 | $1.19x10^{+04}$ | Analogy to C7H15O2-1<=>C7H14OOH1-2 [1] |
| ***QOOH=Olefin+HO2*** | | | | | |
| EL3OOH4J=EL34D+HO2 | $1.94x10^{+13}$ | 0 | 18156 | $2.13x10^{+08}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [4] |

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|---|---|---|---|---|---|
| Reverse | $1.92\times10^{+12}$ | 0 | 10743 | $2.23\times10^{+09}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3] |
| EL4OOH3J=EL34D+HO2 | $1.94\times10^{+13}$ | 0 | 18157 | $2.13\times10^{+08}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [4] |
| Reverse | $1.92\times10^{+12}$ | 0 | 10743 | $2.23\times10^{+09}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3] |
| EL6OOH7J=EL67D+HO2 | $1.67\times10^{+13}$ | 0 | 16686 | $4.61\times10^{+08}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [4] |
| Reverse | $1.83\times10^{+12}$ | 0 | 13100 | $4.84\times10^{+08}$ | Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [3] |
| EL7OOH6J=EL67D+HO2 | $3.66\times10^{+13}$ | 0 | 19055 | $2.28\times10^{+08}$ | Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [4] |
| Reverse | $3.18\times10^{+12}$ | 0 | 13380 | $7.03\times10^{+08}$ | Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [3] |
| ***QOOH+O2=O2QOOH*** | | | | | |
| EL1OOH3J+O2=>EL1OOH3OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| EL3OOH1J+O2=>EL3OOH1OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| EL3OOH4J+O2=>EL3OOH4OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| EL4OOH3J+O2=>EL4OOH3OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| EL6OOH7J+O2=>EL6OOH7OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| EL7OOH6J+O2=>EL7OOH6OO | $4.52\times10^{+12}$ | 0 | 0 | $4.52\times10^{+12}$ | Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1] |
| ***O2QOOH=Ketohydroperoxide+OH*** | | | | | |
| EL1OOH3OO=EL1O3OOH+OH | $2.50\times10^{+10}$ | 0 | 21000 | $4.58\times10^{+04}$ | Analogy to C7H14OOH1-3O2<=>NC7KET13+OH [1] |
| EL3OOH1OO=EL3O1OOH+OH | $1.25\times10^{+10}$ | 0 | 17450 | $2.14\times10^{+05}$ | Analogy to C7H14OOH3-1O2<=>NC7KET31+OH [1] |
| EL3OOH4OO=EL3O4OOH+OH | $1.00\times10^{+11}$ | 0 | 23450 | $3.93\times10^{+04}$ | Analogy to C7H14OOH3-4O2<=>NC7KET34+OH [1] |
| EL4OOH3OO=EL4O3OOH+OH | $1.00\times10^{+11}$ | 0 | 23450 | $3.93\times10^{+04}$ | Analogy to C7H14OOH4-3O2<=>NC7KET43+OH [1] |
| EL6OOH7OO=EL6O7OOH+OH | $1.00\times10^{+11}$ | 0 | 23450 | $3.93\times10^{+04}$ | Analogy to C7H14OOH2-1O2<=>NC7KET21+OH [1] |
| EL7OOH6OO=EL7O6OOH+OH | $2.00\times10^{+11}$ | 0 | 26000 | $1.58\times10^{+04}$ | Analogy to C7H14OOH1-2O2<=>NC7KET12+OH [1] |
| ***Ketohydroperoxide Decomposition*** | | | | | |
| EL1O3OOH=OCCHO+C2H5OCOCH2CHO+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET13<=>NC4H9CHO+CH2CHO+OH [1] |
| EL3O1OOH=CH2O+C2H5OCOCH2COCOJ+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET31<=>CH2O+NC4H9COCH2+OH [1] |
| EL3O4OOH=CH3COCOJ+C2H5OCOCHO+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET34<=>NC3H7CHO+C2H5CO+OH [1] |
| EL4O3OOH=CH3COCHO+C2H5OCOCOJ+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET43<=>C2H5CHO+NC3H7CO+OH [1] |
| EL6O7OOH=CH3COC2H4COOCOJ+CH2O+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET21<=>CH2O+NC5H11CO+OH [1] |
| EL7O6OOH=CH3COC2H4COOCHO+HCO+OH | $1.00\times10^{+16}$ | 0 | 39000 | $2.22\times10^{+05}$ | Analogy to NC7KET12<=>NC5H11CHO+HCO+OH [1] |
| ***QOOH=Cyclic Ether+OH*** | | | | | |

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|---|---|---|---|---|---|
| EL1OOH3J=EL13CY+OH | $7.50 \times 10^{+10}$ | 0 | 15250 | $5.12 \times 10^{+06}$ | Analogy to C7H14OOH1-3<=>C7H14O1-3+OH [1] |
| EL3OOH1J=EL13CY+OH | $7.50 \times 10^{+10}$ | 0 | 15250 | $5.12 \times 10^{+06}$ | Analogy to C7H14OOH3-1<=>C7H14O1-3+OH [1] |
| EL3OOH4J=EL34CY+OH | $6.00 \times 10^{+11}$ | 0 | 22000 | $5.86 \times 10^{+05}$ | Analogy to C7H14OOH3-4<=>C7H14O3-4+OH [1] |
| EL4OOH3J=EL34CY+OH | $6.00 \times 10^{+11}$ | 0 | 22000 | $5.86 \times 10^{+05}$ | Analogy to C7H14OOH4-3<=>C7H14O3-4+OH [1] |
| EL6OOH7J=EL67CY+OH | $6.00 \times 10^{+11}$ | 0 | 22000 | $5.86 \times 10^{+05}$ | Analogy to C7H14OOH2-1<=>C7H14O1-2+OH [1] |
| EL7OOH6J=EL67CY+OH | $6.00 \times 10^{+11}$ | 0 | 22000 | $5.86 \times 10^{+05}$ | Analogy to C7H14OOH1-2<=>C7H14O1-2+OH [1] |
| ***Cyclic Ether Decomposition*** | | | | | |
| EL13CY+OH=C2H5OCOCH2CHO+HCCO+H2O | $2.50 \times 10^{+12}$ | 0 | 0 | $2.50 \times 10^{+12}$ | Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1] |
| EL34CY+OH=C2H5OCOCH2CHO+HCCO+H2O | $2.50 \times 10^{+12}$ | 0 | 0 | $2.50 \times 10^{+12}$ | Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1] |
| EL67CY+OH=C5H7O3-OJ+CH2CO+H2O | $2.50 \times 10^{+12}$ | 0 | 0 | $2.50 \times 10^{+12}$ | Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1] |
| EL13CY+HO2=C2H5OCOCH2CHO+HCCO+H2O2 | $5.00 \times 10^{+12}$ | 0 | 17700 | $7.31 \times 10^{+07}$ | Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O2 [1] |
| EL34CY+HO2=C2H5OCOCH2CHO+HCCO+H2O2 | $5.00 \times 10^{+12}$ | 0 | 17700 | $7.31 \times 10^{+07}$ | Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O3 [1] |
| EL67CY+HO2=C5H7O3-OJ+CH2CO+H2O2 | $5.00 \times 10^{+12}$ | 0 | 17700 | $7.31 \times 10^{+07}$ | Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O4 [1] |
| EL13CY+CH3=C2H5OCOCH2CHO+HCCO+CH4 | $2.00 \times 10^{+11}$ | 0 | 10000 | $3.71 \times 10^{+08}$ | Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH4 [1] |
| EL34CY+CH3=C2H5OCOCH2CHO+HCCO+CH4 | $2.00 \times 10^{+11}$ | 0 | 10000 | $3.71 \times 10^{+08}$ | Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH5 [1] |
| EL67CY+CH3=C5H7O3-OJ+CH2CO+CH4 | $2.00 \times 10^{+11}$ | 0 | 10000 | $3.71 \times 10^{+08}$ | Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH6 [1] |
| ***Hydrogen Abstraction from Olefin*** | | | | | |
| EL34D+H=EL34D4J+H2 | $6.02 \times 10^{+05}$ | 2.4 | 2583 | $1.10 \times 10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+H=EL67D6J+H2 | $6.02 \times 10^{+05}$ | 2.4 | 2583 | $1.10 \times 10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+OH=EL34D4J+H2O | $2.93 \times 10^{+04}$ | 2.53 | -1659 | $1.85 \times 10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+OH=EL67D6J+H2O | $2.93 \times 10^{+04}$ | 2.53 | -1659 | $1.85 \times 10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+CH3=EL34D4J+CH4 | $9.04 \times 10^{-01}$ | 3.46 | 4598 | $5.56 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+CH3=EL67D6J+CH4 | $9.04 \times 10^{-01}$ | 3.46 | 4598 | $5.56 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+CH3O=EL34D4J+CH3OH | $1.90 \times 10^{+10}$ | 0 | 2800 | $3.26 \times 10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+CH3O=EL67D6J+CH3OH | $1.90 \times 10^{+10}$ | 0 | 2800 | $3.26 \times 10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+CH3O2=EL34D4J+CH3O2H | $1.37 \times 10^{+02}$ | 3.12 | 13190 | $3.89 \times 10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+CH3O2=EL67D6J+CH3O2H | $1.37 \times 10^{+02}$ | 3.12 | 13190 | $3.89 \times 10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+HO2=EL34D4J+H2O2 | $4.33 \times 10^{+02}$ | 3.01 | 12090 | $1.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+HO2=EL67D6J+H2O2 | $4.33 \times 10^{+02}$ | 3.01 | 12090 | $1.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+O=EL34D4J+OH | $1.97 \times 10^{+05}$ | 2.40 | 1150 | $8.98 \times 10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+O=EL67D6J+OH | $1.97 \times 10^{+05}$ | 2.40 | 1150 | $8.98 \times 10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+O2=EL34D4J+HO2 | $1.00 \times 10^{+13}$ | 0 | 48200 | $6.80 \times 10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+O2=EL67D6J+HO2 | $1.00 \times 10^{+13}$ | 0 | 48200 | $6.80 \times 10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C2H5=EL34D4J+C2H6 | $1.00 \times 10^{+11}$ | 0 | 7900 | $6.95 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+C2H5=EL67D6J+C2H6 | $1.00 \times 10^{+11}$ | 0 | 7900 | $6.95 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C2H5O=EL34D4J+C2H5OH | $5.63 \times 10^{+10}$ | 0 | 3650 | $5.66 \times 10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |

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| EL67D+C2H5O=EL67D6J+C2H5OH | $5.63\times10^{+10}$ | 0 | 3650 | $5.66\times10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C2H3=EL34D4J+C2H4 | $2.50\times10^{+11}$ | 0 | 15450 | $1.50\times10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+C2H3=EL67D6J+C2H4 | $2.50\times10^{+11}$ | 0 | 15450 | $1.50\times10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C2H5O2=EL34D4J+C2H5O2H | $2.80\times10^{+12}$ | 0 | 16000 | $1.19\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+C2H5O2=EL67D6J+C2H5O2H | $2.80\times10^{+12}$ | 0 | 16000 | $1.19\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+CH3CO3=EL34D4J+CH3CO3H | $2.80\times10^{+12}$ | 0 | 16000 | $1.19\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+CH3CO3=EL67D6J+CH3CO3H | $2.80\times10^{+12}$ | 0 | 16000 | $1.19\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+O2CHO=EL34D4J+HO2CHO | $2.80\times10^{+12}$ | 0 | 16010 | $1.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+O2CHO=EL67D6J+HO2CHO | $2.80\times10^{+12}$ | 0 | 16010 | $1.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C4H9OaOO=EL34D4J+C4H9OaOOH | $1.81\times10^{-01}$ | 3.98 | 9058 | $2.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+C4H9OaOO=EL67D6J+C4H9OaOOH | $1.81\times10^{-01}$ | 3.98 | 9058 | $2.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL34D+C4H9ObOO=EL34D4J+C4H9ObOOH | $1.81\times10^{-01}$ | 3.98 | 9058 | $2.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| EL67D+C4H9ObOO=EL67D6J+C4H9ObOOH | $1.81\times10^{-01}$ | 3.98 | 9058 | $2.18\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| ***Olefin Radical Decomposition by Beta-bond Scission*** | | | | | |
| EL34D4J=>CH3COCHCCO+C2H5O | $2.64\times10^{+14}$ | 0 | 53796 | $5.30\times10^{-01}$ | Analogy to reverse of CH3COCH2CHCO + C2H5O = EL4J [5] |
| CH3COCHCCO=>CH3CO+CO+C2H | $7.71\times10^{+12}$ | 0 | 26385 | $4.78\times10^{+05}$ | Analogy to reverse of CH3CO+C2H3COOH = C5H7O3-2J [5] |
| EL67D6J=>CH3COCH2CH2COJ+CO+CH2 | $1.13\times10^{+21}$ | -1.73 | 40550 | $8.95\times10^{+04}$ | Analogy to reverse of CH3CHO + CH3COCH2CH2COJ = EL6J [5] |
| ***Hydrogen Abstraction from Minor Species*** | | | | | |
| C2H5OCOCH2CHO+H=C2H5OCOCH2COJ+H2 | $6.02\times10^{+05}$ | 2.4 | 2583 | $1.10\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+H=C2H5OCOCOJ+H2 | $6.02\times10^{+05}$ | 2.4 | 2583 | $1.10\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+H=CH3COCOJ+H2 | $6.02\times10^{+05}$ | 2.4 | 2583 | $1.10\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+H=CH3COC2H4COOCOJ+H2 | $6.02\times10^{+05}$ | 2.4 | 2583 | $1.10\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+OH=C2H5OCOCH2COJ+H2O | $2.93\times10^{+04}$ | 2.53 | -1659 | $1.85\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+OH=C2H5OCOCOJ+H2O | $2.93\times10^{+04}$ | 2.53 | -1659 | $1.85\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+OH=CH3COCOJ+H2O | $2.93\times10^{+04}$ | 2.53 | -1659 | $1.85\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+OH=CH3COC2H4COOCOJ+H2O | $2.93\times10^{+04}$ | 2.53 | -1659 | $1.85\times10^{+12}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+CH3=C2H5OCOCH2COJ+CH4 | $9.04\times10^{-01}$ | 3.46 | 4598 | $5.56\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+CH3=C2H5OCOCOJ+CH4 | $9.04\times10^{-01}$ | 3.46 | 4598 | $5.56\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+CH3=CH3COCOJ+CH4 | $9.04\times10^{-01}$ | 3.46 | 4598 | $5.56\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+CH3=CH3COC2H4COOCOJ+CH4 | $9.04\times10^{-01}$ | 3.46 | 4598 | $5.56\times10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+CH3O=C2H5OCOCH2COJ+CH3OH | $1.90\times10^{+10}$ | 0 | 2800 | $3.26\times10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+CH3O=C2H5OCOCOJ+CH3OH | $1.90\times10^{+10}$ | 0 | 2800 | $3.26\times10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+CH3O=CH3COCOJ+CH3OH | $1.90\times10^{+10}$ | 0 | 2800 | $3.26\times10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+CH3O=CH3COC2H4COOCOJ+CH3OH | $1.90\times10^{+10}$ | 0 | 2800 | $3.26\times10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+CH3O2=C2H5OCOCH2COJ+CH3O2H | $1.37\times10^{+02}$ | 3.12 | 13190 | $3.89\times10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+CH3O2=C2H5OCOCOJ+CH3O2H | $1.37\times10^{+02}$ | 3.12 | 13190 | $3.89\times10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |

| | | | | | |
|---|---|---|---|---|---|
| CH3COCHO+CH3O2=CH3COCOJ+CH3O2H | $1.37x10^{+02}$ | 3.12 | 13190 | $3.89x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+CH3O2=CH3COC2H4COOCOJ+CH3O2H | $1.37x10^{+02}$ | 3.12 | 13190 | $3.89x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+HO2=C2H5OCOCH2COJ+H2O2 | $4.33x10^{+02}$ | 3.01 | 12090 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+HO2=C2H5OCOCOJ+H2O2 | $4.33x10^{+02}$ | 3.01 | 12090 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+HO2=CH3COCOJ+H2O2 | $4.33x10^{+02}$ | 3.01 | 12090 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+HO2=CH3COC2H4COOCOJ+H2O2 | $4.33x10^{+02}$ | 3.01 | 12090 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+O=C2H5OCOCH2COJ+OH | $1.97x10^{+05}$ | 2.40 | 1150 | $8.98x10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+O=C2H5OCOCOJ+OH | $1.97x10^{+05}$ | 2.40 | 1150 | $8.98x10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+O=CH3COCOJ+OH | $1.97x10^{+05}$ | 2.40 | 1150 | $8.98x10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+O=CH3COC2H4COOCOJ+OH | $1.97x10^{+05}$ | 2.40 | 1150 | $8.98x10^{+11}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+O2=C2H5OCOCH2COJ+HO2 | $1.00x10^{+13}$ | 0 | 48200 | $6.80x10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+O2=C2H5OCOCOJ+HO2 | $1.00x10^{+13}$ | 0 | 48200 | $6.80x10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+O2=CH3COCOJ+HO2 | $1.00x10^{+13}$ | 0 | 48200 | $6.80x10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+O2=CH3COC2H4COOCOJ+HO2 | $1.00x10^{+13}$ | 0 | 48200 | $6.80x10^{-01}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C2H5=C2H5OCOCH2COJ+C2H6 | $1.00x10^{+11}$ | 0 | 7900 | $6.95x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C2H5=C2H5OCOCOJ+C2H6 | $1.00x10^{+11}$ | 0 | 7900 | $6.95x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C2H5=CH3COCOJ+C2H6 | $1.00x10^{+11}$ | 0 | 7900 | $6.95x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C2H5=CH3COC2H4COOCOJ+C2H6 | $1.00x10^{+11}$ | 0 | 7900 | $6.95x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C2H5O=C2H5OCOCH2COJ+C2H5OH | $5.63x10^{+10}$ | 0 | 3650 | $5.66x10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C2H5O=C2H5OCOCOJ+C2H5OH | $5.63x10^{+10}$ | 0 | 3650 | $5.66x10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C2H5O=CH3COCOJ+C2H5OH | $5.63x10^{+10}$ | 0 | 3650 | $5.66x10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C2H5O=CH3COC2H4COOCOJ+C2H5OH | $5.63x10^{+10}$ | 0 | 3650 | $5.66x10^{+09}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C2H5O=C2H5OCOCH2COJ+C2H5OH | $2.50x10^{+11}$ | 0 | 15450 | $1.50x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C2H5O=C2H5OCOCOJ+C2H5OH | $2.50x10^{+11}$ | 0 | 15450 | $1.50x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C2H5O=CH3COCOJ+C2H5OH | $2.50x10^{+11}$ | 0 | 15450 | $1.50x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C2H5O=CH3COC2H4COOCOJ+C2H5OH | $2.50x10^{+11}$ | 0 | 15450 | $1.50x10^{+07}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C2H5O2=C2H5OCOCH2COJ+C2H5O2H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C2H5O2=C2H5OCOCOJ+C2H5O2H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C2H5O2=CH3COCOJ+C2H5O2H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C2H5O2=CH3COC2H4COOCOJ+C2H5O2H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+CH3CO3=C2H5OCOCH2COJ+CH3CO3H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+CH3CO3=C2H5OCOCOJ+CH3CO3H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+CH3CO3=CH3COCOJ+CH3CO3H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+CH3CO3=CH3COC2H4COOCOJ+CH3CO3H | $2.80x10^{+12}$ | 0 | 16000 | $1.19x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+O2CHO=C2H5OCOCH2COJ+HO2CHO | $2.80x10^{+12}$ | 0 | 16010 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+O2CHO=C2H5OCOCOJ+HO2CHO | $2.80x10^{+12}$ | 0 | 16010 | $1.18x10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |

| | | | | | |
|---|---|---|---|---|---|
| CH3COCHO+O2CHO=CH3COCOJ+HO2CHO | $2.80 \times 10^{+12}$ | 0 | 16010 | $1.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+O2CHO=CH3COC2H4COOCOJ+HO2CHO | $2.80 \times 10^{+12}$ | 0 | 16010 | $1.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C4H9OaOO=C2H5OCOCH2COJ+C4H9OaOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C4H9OaOO=C2H5OCOCOJ+C4H9OaOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C4H9OaOO=CH3COCOJ+C4H9OaOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C4H9OaOO=CH3COC2H4COOCOJ+C4H9OaOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCH2CHO+C4H9ObOO=C2H5OCOCH2COJ+C4H9ObOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| C2H5OCOCHO+C4H9ObOO=C2H5OCOCOJ+C4H9ObOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COCHO+C4H9ObOO=CH3COCOJ+C4H9ObOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| CH3COC2H4COOCHO+C4H9ObOO=CH3COC2H4COOCOJ+C4H9ObOOH | $1.81 \times 10^{-01}$ | 3.98 | 9058 | $2.18 \times 10^{+08}$ | Assumed to be equal to hydrogen abstraction from tertiary carbon |
| ***Decomposition of Minor Species Beta-bond Scission*** | | | | | |
| C2H5OCOCH2COJ=EFF+CO+CH2 | $8.83 \times 10^{+14}$ | -0.67 | 35550 | $1.95 \times 10^{+04}$ | Analogy to reverse of C2H3COCH3 + EFF = EL3J [5] |
| C2H5OCOCH2COCOJ=EE2J+CO+CO | $2.63 \times 10^{+10}$ | 0.84 | 26100 | $5.35 \times 10^{+05}$ | Analogy to reverse of CH2CO + EE2J = ELCOJ [5] |
| CH3COCOJ=CH3+CO+CO | $1.00 \times 10^{+14}$ | 0 | 31000 | $3.40 \times 10^{+05}$ | Analogy to reverse of CH3 + COCHCH2CO2CH2CH3 = EL3J [5] |
| C2H5OCOCOJ=C2H5O+CO+CO | $6.82 \times 10^{+16}$ | -1.34 | 26930 | $3.86 \times 10^{+05}$ | Analogy to reverse of CH3COCH2CHCO + C2H5O = EL4J [5] |
| CH3COC2H4COOCOJ=CH3COCH2CH2COJ+CO2 | $1.13 \times 10^{+21}$ | -1.73 | 40550 | $8.95 \times 10^{+04}$ | Analogy to reverse of CH3CHO + CH3COCH2CH2COJ = EL6J [5] |

Table S1. Reaction pathways, estimated rate constants and sources for the reactions of the low temperature ethyl levulinate sub model. Rate coefficients are in the form $k = AT^n \exp^{(-Ea/RT)}$.

| Mixture # | $X_{Ethanol}$ | $X_{Diethyl\ Ether}$ | $X_{Ethyl\ Levulinate}$ | IDT (ms) | Standard Deviation (ms) | Measured DCN | Standard Deviation |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 0.75 | 0.25 | 2.73 | 0.04 | 77.31 | 1.78 |
| 2 | 0 | 0.5 | 0.5 | 4.28 | 0.04 | 48.07 | 0.41 |
| 3 | 0 | 0.37 | 0.63 | 6.42 | 0.1 | 33.42 | 0.63 |
| 4 | 0 | 0.25 | 0.75 | 12.18 | 0.32 | 21.25 | 0.35 |
| 5 | 0 | 0.1 | 0.9 | 47.84 | 3.75 | 10.3 | 0.36 |
| 6 | 0.1 | 0.2 | 0.7 | 15.89 | 1.6 | 18.18 | 1.2 |
| 7 | 0.1 | 0.5 | 0.4 | 3.01 | 0.07 | 67.83 | 1.65 |
| 8 | 0.1 | 0.4 | 0.5 | 4.46 | 0.08 | 46.36 | 0.78 |
| 9 | 0.1 | 0.7 | 0.2 | 2.91 | 0.05 | 70.88 | 1.55 |
| 10 | 0.25 | 0.65 | 0.1 | 3.17 | 0.07 | 63.83 | 1.65 |
| 11 | 0.25 | 0.5 | 0.25 | 4.38 | 0.05 | 47.1 | 0.53 |
| 12 | 0.25 | 0.25 | 0.5 | 11.81 | 0.74 | 21.69 | 0.8 |
| 13 | 0.25 | 0.1 | 0.65 | 71.39 | 6.86 | 8.71 | 0.32 |
| 14 | 0.25 | 0 | 0.75 | 139.72 | 5.77 | 6.83 | 0.09 |
| 15 | 0.4 | 0.5 | 0.1 | 4.49 | 0.08 | 46.01 | 0.73 |
| 16 | 0.5 | 0.4 | 0.1 | 6.48 | 0.1 | 32.8 | 0.56 |
| 17 | 0.5 | 0.25 | 0.25 | 17.47 | 0.59 | 17.13 | 0.32 |
| 18 | 0.5 | 0.1 | 0.4 | 98.29 | 9.89 | 7.72 | 0.34 |
| 19 | 0.5 | 0 | 0.5 | 136.53 | 10.46 | 6.89 | 0.17 |
| 20 | 0.75 | 0.2 | 0.05 | 63.65 | 4.15 | 9.11 | 0.26 |
| 21 | 0.75 | 0.1 | 0.15 | 101.04 | 7.9 | 7.63 | 0.21 |
| 22 | 0.75 | 0 | 0.25 | 133.99 | 5.31 | 6.92 | 0.09 |

Table S2. Mixture mole fractions, ignition delay times and ignition quality tester measured derived cetane numbers.

| Initial Pressure (bar) | Initial Temperature (K) | Compressed Pressure (bar) | Compressed Temperature (K) | Ignition Delay Time (ms) |
|---|---|---|---|---|
| Reaction Mixture (Mole Fractions) Ethyl Levulinate/Diethyl Ether/Ethanol/$O_2$/$N_2$ = 0.0124/0.0095/0.0134/0.2026/0.7621 Φ= 1.0 | | | | |
| 0.64 | 338 | 20.13 | 765 | 426.8 |
| 0.63 | 338 | 20.2 | 765 | 391.4 |
| 0.63 | 338 | 20.19 | 765 | 404.2 |
| 0.63 | 353 | 19.99 | 793 | 107.5 |
| 0.63 | 353 | 20.06 | 793 | 105.1 |
| 0.63 | 353 | 19.88 | 792 | 109.7 |
| 0.63 | 368 | 19.54 | 817 | 40.7 |
| 0.63 | 368 | 19.61 | 817 | 40.7 |
| 0.63 | 368 | 19.51 | 817 | 40.4 |
| 0.63 | 383 | 19.36 | 844 | 17.6 |
| 0.63 | 383 | 19.64 | 846 | 17.1 |
| 0.63 | 383 | 19.36 | 844 | 17.7 |
| 0.63 | 398 | 19.28 | 870 | 8.2 |
| 0.63 | 398 | 19.32 | 871 | 8.1 |
| 0.63 | 398 | 19.22 | 870 | 8.1 |
| 0.63 | 413 | 19.15 | 897 | 4.0 |
| 0.63 | 413 | 19.12 | 897 | 3.9 |
| 0.63 | 413 | 19.18 | 897 | 3.9 |
| 1.22 | 323 | 39.99 | 741 | 185.6 |
| 1.22 | 323 | 40.10 | 741 | 179.6 |
| 1.22 | 323 | 40.03 | 741 | 178.9 |
| 1.22 | 338 | 39.64 | 769 | 70.4 |
| 1.22 | 338 | 39.64 | 768 | 69.9 |
| 1.22 | 338 | 39.52 | 768 | 70.3 |
| 1.22 | 353 | 39.35 | 796 | 29.6 |
| 1.22 | 353 | 39.31 | 796 | 27.2 |
| 1.22 | 353 | 39.31 | 796 | 29.1 |
| 1.22 | 368 | 38.65 | 821 | 13.3 |
| 1.23 | 368 | 39.11 | 823 | 13.0 |
| 1.23 | 368 | 39.12 | 823 | 13.1 |
| 1.23 | 383 | 38.50 | 848 | 5.8 |
| 1.23 | 383 | 38.66 | 849 | 5.7 |
| 1.23 | 383 | 38.79 | 849 | 5.8 |
| 1.23 | 398 | 38.70 | 876 | 2.4 |
| 1.23 | 398 | 38.44 | 875 | 2.0 |
| 1.23 | 398 | 38.58 | 876 | 2.3 |

| Reaction Mixture (Mole Fractions) Ethyl Levulinate/Diethyl Ether/Ethanol/$O_2$/$N_2$ = 0.0063/0.0049/0.0068/0.7758/0.2062 $\Phi$= 0.5 | | | | |
|---|---|---|---|---|
| 0.61 | 353 | 19.28 | 842 | 151.1 |
| 0.61 | 353 | 19.21 | 841 | 165.8 |
| 0.61 | 353 | 19.19 | 841 | 156 |
| 0.61 | 368 | 18.88 | 868 | 45.8 |
| 0.62 | 368 | 19.27 | 870 | 39.7 |
| 0.62 | 368 | 19.11 | 868 | 43.1 |
| 0.62 | 383 | 19.43 | 901 | 15.6 |
| 0.62 | 383 | 19.53 | 902 | 15.7 |
| 0.62 | 383 | 19.45 | 900 | 15.6 |
| 0.62 | 398 | 19.33 | 929 | 6.8 |
| 0.62 | 398 | 19.32 | 930 | 6.7 |
| 0.62 | 398 | 19.03 | 927 | 6.4 |
| 0.62 | 413 | 19.12 | 958 | 3.2 |
| 0.62 | 413 | 19.11 | 958 | 3 |
| 0.62 | 413 | 19.13 | 958 | 3.2 |
| 1.18 | 323 | 39.81 | 790 | 254.2 |
| 1.18 | 323 | 39.74 | 790 | 249.3 |
| 1.18 | 323 | 39.77 | 790 | 247.2 |
| 1.18 | 338 | 39.45 | 820 | 74.0 |
| 1.18 | 338 | 39.33 | 820 | 74.5 |
| 1.18 | 338 | 39.35 | 820 | 74.5 |
| 1.18 | 353 | 38.35 | 846 | 28.4 |
| 1.19 | 353 | 38.60 | 846 | 27.6 |
| 1.20 | 353 | 39.65 | 850 | 27.8 |
| 1.19 | 368 | 39.28 | 880 | 11.9 |
| 1.19 | 368 | 39.31 | 880 | 11.7 |
| 1.19 | 368 | 39.22 | 879 | 11.8 |
| 1.20 | 383 | 38.32 | 905 | 4.7 |
| 1.21 | 383 | 38.90 | 907 | 4.7 |
| 1.21 | 383 | 39.34 | 908 | 5.1 |

Table S3. Rapid compression machine initial and compressed conditions, and ignition delay times.

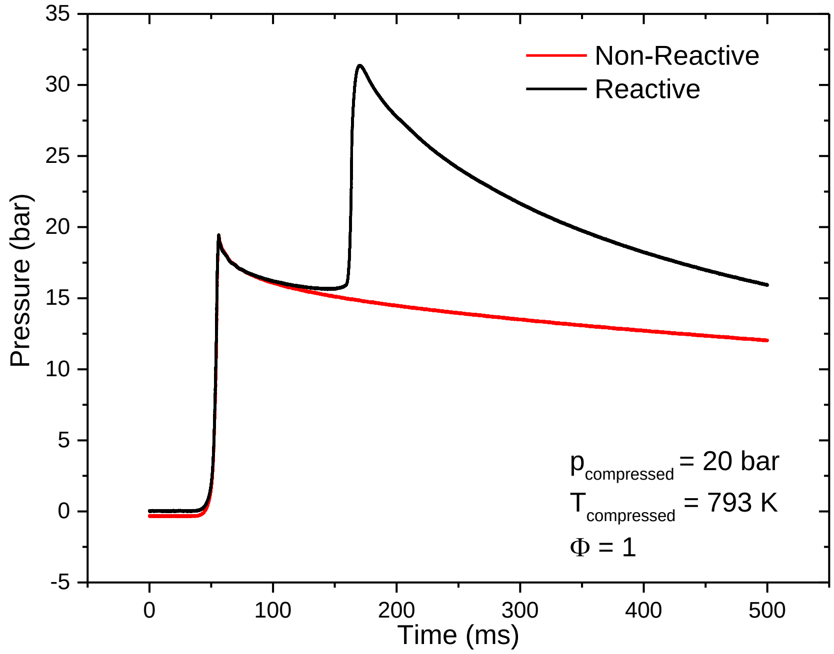


Figure S1. Exemplar rapid compression machine experimental pressure histories for the EL/DEE/EtOH Gasoline at compressed conditions of 20 bar, 793 K and Φ =1.0.

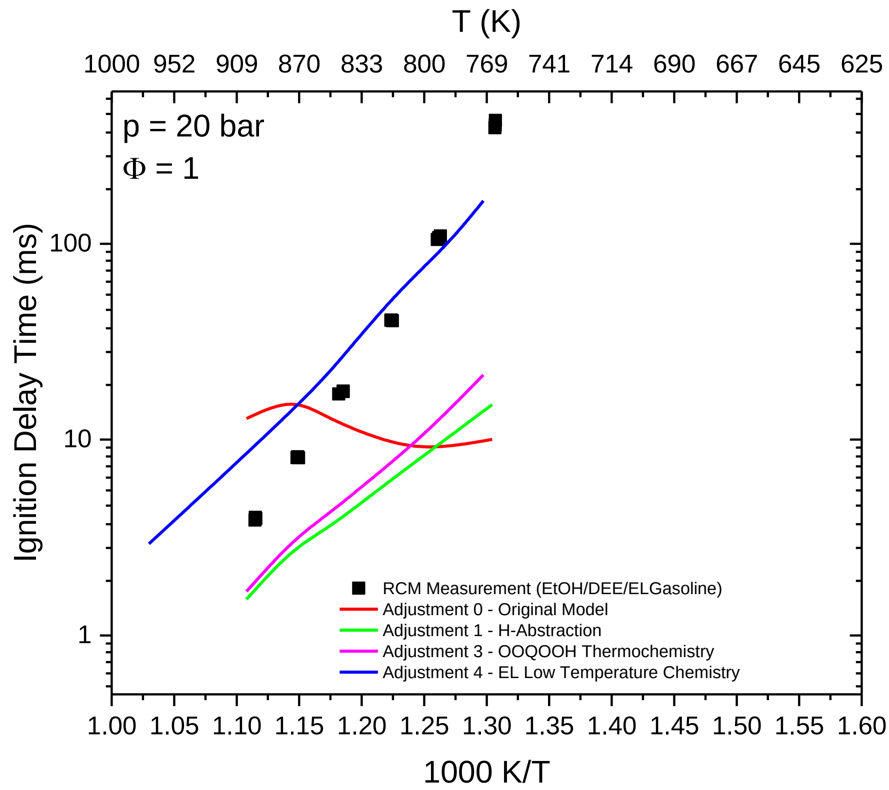


Figure S2. Comparison of modifications made to the kinetic model developed in this work. Adjustment 1 refers to the standardization of all the H-abstraction rate constants, and Adjustment 2 refers to the increasing of the formation enthalpy of the peroxy alkylhydroperoxide radicals (OOQOOH) in the diethyl ether sub model by 10 kJ/mol. Adjustment 3 refers to the addition of the EL low temperature combustion pathways.

T124MBZ
O-XYLCH2
+HO2, 5%
+OH, 55%
+OH, 41%
+HO2, 10%
P-XYLCH2
+OH, 2%
HOCH3C6H3CH3 + CH3
+OH, 92%
OCH3C6H3CH3
+CH3O2, -CH3O, 9%
+HO2, -OH, 7%
+O2, 6%
O-XYLCH2OO
+HO2, 73%
+HO2, -O2, 61%
+HO2, -O2, 26%
7%
+HO2, 71%
+CH3O2, -CH3O, 9%
+HO2, -OH, 6%
O-XYLCH2O
-OH, 98%
O-XYLXH2OOH
O-CH2TOLCH2OOH
P-XYLXH2OOH
-OH, 98%
P-XYLCH2O
-HO2, 28%
C6H5C3H5-1
CPT
+OH, 93%
CYC5H9
+O2, -HO2, 3%
+O2, 95%
CYC5H8
-HO2, 62%
CPTO2J
28%
CPT1Q3J
+O2, 95%
CPTQ3QJ
C4H10
+OH, 60%
+OH, 34%
SC4H9
PC4H9
+O2, 98%
+O2, 97%
SC4H9O2
PC4H9O2
18%
-HO2, 28%
-HO2, 28%
-HO2, 17%
63%
C4H8OOH2-4
C4H8-2
C4H8-1
C4H8OOH1-3
+O2, 98%
+O2, 97%
C4H8OOH2-4O2
C4H8OOH1-3O2
C6H12-1
+OH, 56%
C6H12OH-1
+O2, 99%
O2C6H12OH-1
100%
NC4H9CHO + CH2O + OH
+OH, 16%
+OH, 9%
+OH, 9%
+OH, 5%
C6H111-3
C6H111-4
C6H111-5
C6H111-6
+HO2, 37%
+CH3O2, 12%
+C2H5O2, 11%
+O2, 34%
C6H111O1-3
C6H111O2-3
-HO2, 20%
10%
61%
9%
C6H101OOH3-4
C6H101OOH3-5
C6H101OOH3-6
-HO2, 98%
8%
+O2, 88%
+O2, 36%
63%
C6H101-3
OH+C3H6+C2H3CHO
C6H101OOH3-5O2
C6H101OOH3-6O2
VTHF + OH
+O2, 99%
C6H111O2-4
-HO2, 18%
-HO2, 33%
C6H101-4
32%
9%
8%
C6H101-3
C6H101OOH4-3
C6H101OOH4-3
C6H101OOH4-6
-HO2, 11%
88%
-HO2, 90%
7%
96%
C6H101-3
EDHF + OH
C6H101-4
C3H5-A + AC3H5OOH
CHX1Q3J
+O2, 99%
C6H111O2-5
-HO2, 8%
-HO2, 7%
80%
C6H101-4
C6H101-5
C6H101OOH5-3
95%
O2, 5%
MVOX + OH
C6H101OOH5-3O2
+O2, 100%
C6H111O2-6
-HO2, 12%
C6H101-5
54%
27%
6%
C6H101OOH6-3
C6H101OOH6-4
C6H101OOH6-5
100%
37%
O2, 61%
-HO2, 98%
VTHF + OH
ETES1 + OH
C6H101OOH6-4O2
C6H101-5
IC8H18
+OH, 29%
+OH, 20%
+OH, 23%
+OH, 20%
Isomerisation 16%
AC8H17
DC8H17
+O2, 81%
DC8H17O2
8%
29%
53%
DC8H16OOH-D
+O2, 52%
7%
41%
DC8H16OOH-DO2
NEOC5H11 + AC3H5OOH
IC8ETERDD + OH
DC8H16OOH-C
-HO2, 99%
JC8H16
DC8H16OOH-B
+O2, 56%
39%
DC8H16OOH-BO2
IC8ETERBD + OH
AC8H17
+O2, 90%
AC8H17O2
6%
IC4H4 + IC4H9
13%
45%
36%
AC8H16OOH-A
AC8H16OOH-B
AC8H16OOH-C
+O2, 13%
55%
13%
AC8H16OOH-AO2
IC4H7OOH + TC4H9
IC8ETERAA + OH
+O2, 45%
45%
AC8H16OOH-BO2
IC8ETERAB + OH
5%
95%
IC4H8 + IC4H8O2H-T
IC8ETERAC + OH
BC8H17
+O2, 98%
BC8H17O2
-HO2, 5%
IC8H16
34%
33%
20%
BC8H16OOH-A
BC8H16OOH-C
BC8H16OOH-D
+O2, 55%
31%
13%
-HO2, 33%
15%
+O2, 52%
15%
+O2, 63%
BC8H16OOH-AO2
IC8ETERAB + OH
IC3H7CHO + IC4H8 + OH
IC8H16
IC8ETERBC + OH
BC8H16OOH-CO2
IC8ETERBD + OH
BC8H16OOH-DO2
CC8H17
75%
IC4H8 + TC4H9
+O2, 23%
CC8H17O2
IC8H16
-HO2, 11%
-HO2, 20%
JC8H16
26%
19%
11%
CC8H16OOH-A
CC8H16OOH-B
CC8H16OOH-D
97%
5%
-HO2, 95%
-HO2, 100%
IC8ETERAC + OH
IC8ETERBC + OH
JC8H16
JC8H16
IC5H12
+OH, 24%
+OH, 29%
+OH, 24%
+OH, 12%
AC5H11
BC5H11
CC5H11
DC5H11
+O2, 99%
AC5H11O2
6%
32%
50%
AC5H10OOH-A
AC5H10OOH-B
AC5H10OOH-C
+O2, 77%
20%
AC5H10OOH-AO2
A-AC5H10O + OH
-HO2, 83%
AC5H10
+O2, 13%
AC5H10OOH-BO2
+O2, 88%
11%
AC5H10OOH-CO2
A-CC5H10O + OH
+HO2, -OH, 5%
BC5H11O
+O2, 93%
BC5H11O2
+HO2, -OH, 5%
BC5H11O2H
15%
-HO2, 16%
-HO2, 16%
BC5H10OOH-A
-HO2, 99%
AC5H10
28%
17%
AC5H10
BC5H10
BC5H10OOH-C
-HO2, 99%
BC5H10
BC5H10OOH-D
11%
88%
B-DC5H10O + OH
CH3COCH3 + C2H4 + OH
+O2, 100%
CC5H11O2
+HO2, -OH, 6%
CC5H11O2H
-HO2, 9%
26%
47%
5%
CC5H10OOH-A
CC5H10OOH-B
CC5H10OOH-D
+O2, 84%
13%
CC5H10OOH-AO2
OH + CH3CHO + C3H6
+O2, 44%
CC5H10OOH-BO2
-HO2, 54%
BC5H10
-HO2, 57%
CC5H10
+O2, 42%
CC5H10OOH-DO2
+O2, 96%
DC5H11O2
-HO2, 7%
CC5H10
7%
72%
12%
DC5H10OOH-A
DC5H10OOH-B
DC5H10OOH-C
+O2, 15%
85%
DC5H10OOH-AO2
A-DC5H10O + OH
+O2, 75%
25%
DC5H10OOH-BO2
B-DC5H10O + OH
+O2, 33%
-HO2, 66%
DC5H10OOH-CO2
CC5H10
C7H16-2
+OH, 20%
+OH, 18%
+OH, 15%
+OH, 14%
+OH, 19%
+OH, 10%
C7H15-2A
C7H15-2B
C7H15-2C
C7H15-2D
C7H15-2E
C7H15-2F
Isomerisation 33%
C7H15-2B
+O2, 94%
C7H15OO-1-2
8%
29%
50%
8%
C7OOH1-2B
C7OOH1-2C
C7OOH1-2D
C7OOH1-2E
82%
-HO2, 15%
C7H14O1-2-2 + OH
C7H14-1-2
8%
+O2, 92%
C7H14O1-3-2 + OH
C7OOH1-OO3-2
58%
+O2, 42%
C7H14O1-4-2 + OH
C7OOH1-OO4-2
20%
+O2, 80%
C7H14O1-5-2 + OH
C7OOH1-OO5-2
+O2, 99%
C7H15OO-2-2
-HO2, 10%
C7H14-1-2
15%
66%
11%
C7OOH2-2D
C7OOH2-2E
C7OOH3-2B
38%
+O2, 58%
77%
+O2, 23%
42%
-HO2, 54%
C7H14O2-4-2 + OH
C7OOH2-OO4-2
C7H14O2-5-2 + OH
C7OOH2-OO5-2
C7H14O2-3-2 + OH
C7H14-2-2
+O2, 99%
C7H15OO-3-2
-HO2, 6%
C7H14-3-2
59%
10%
C7OOH3-2E
C7OOH3-2F
7%
+O2, 92%
64%
+O2, 36%
C7H14O3-5-2 + OH
C7OOH3-OO5-2
C7H14O3-6-2 + OH
C7OOH3-OO6-2
+O2, 98%
C7H15OO-4-2
96%
C7OOH4-2B
+O2, 98%
C7OOH4-OO2-2
+O2, 99%
C7H15OO-5-2
79%
14%
C7OOH5-2B
C7OOH5-2C
41%
+O2, 59%
7%
+O2, 91%
C7H14O2-5-2 + OH
C7OOH5-OO2-2
C7H14O3-5-2 + OH
C7OOH5-OO3-2
+O2, 66%
C7H15OO-6-2
18%
45%
29%
C7OOH6-2B
C7OOH6-2C
C7OOH6-2D
14%
+O2, 86%
C7H14O2-6-2 + OH
C7OOH6-OO2-2
59%
+O2, 41%
C7H14O3-6-2 + OH
C7OOH6-OO3-2
7%
+O2, 93%
C7H14O4-6-2 + OH
C7OOH6-OO4-2

Figure S3. Reacting flux analysis at 65% of the ignition delay time for combustion simulation in a closed constant volume homogenous reactor, for FACE-F, at 750 K, 25 bar, and Φ=1. Oxidation reactions are highlighted in blue and elimination reactions in red.

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