

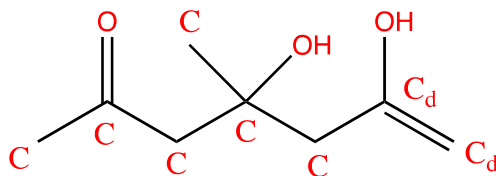
## **Supporting Information for**

# **110<sup>th</sup> Anniversary: Microkinetic Modeling of the Vapor Phase Upgrading of Biomass-Derived Oxygenates**

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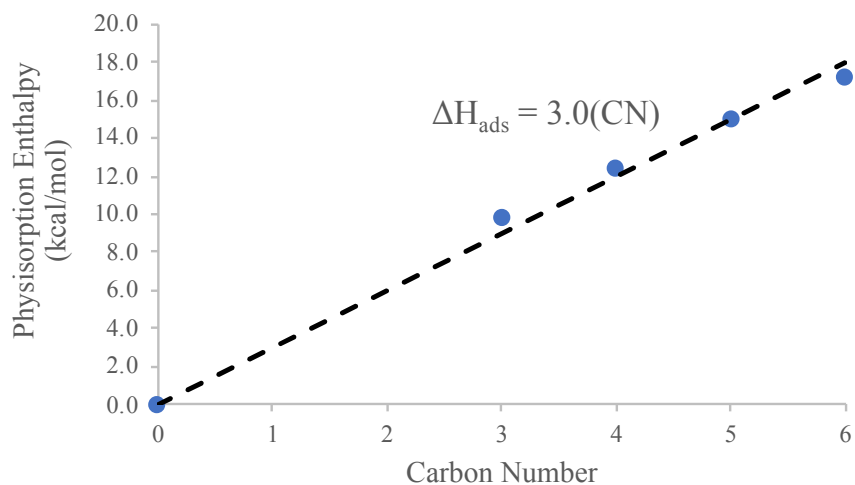
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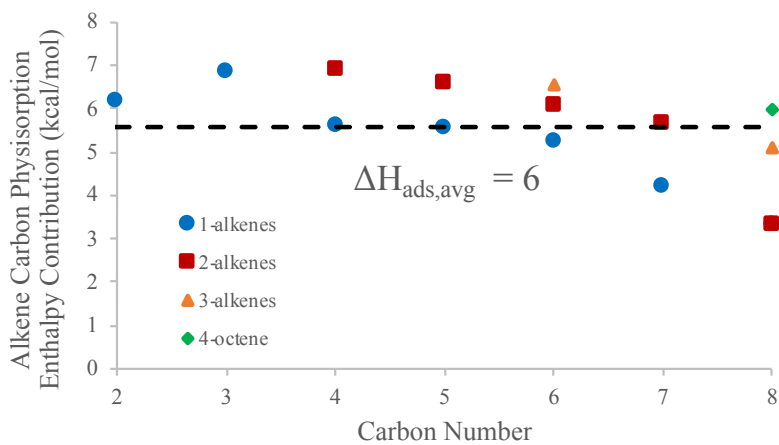
**Table S1.** Example calculation: physisorption value for molecule pictured above.

| Group           | Amount | Contribution (kcal/mol) |
|-----------------|--------|-------------------------|
| Alkane Carbon   | 6      | 3.0(6) = 18.0           |
| Alkene Carbon   | 2      | 6(2) = 12               |
| Aromatic Carbon | 0      | 2.5(0) = 0.0            |
| -OH Group       | 2      | 23(2) = 46              |
| =O Group        | 1      | 22.1(1) = 22.1          |
| -OOH Group      | 0      | 23.1(0) = 0.0           |
| Total           | 11     | 98                      |
| Final Enthalpy  |        | 98(0.6) = 59            |

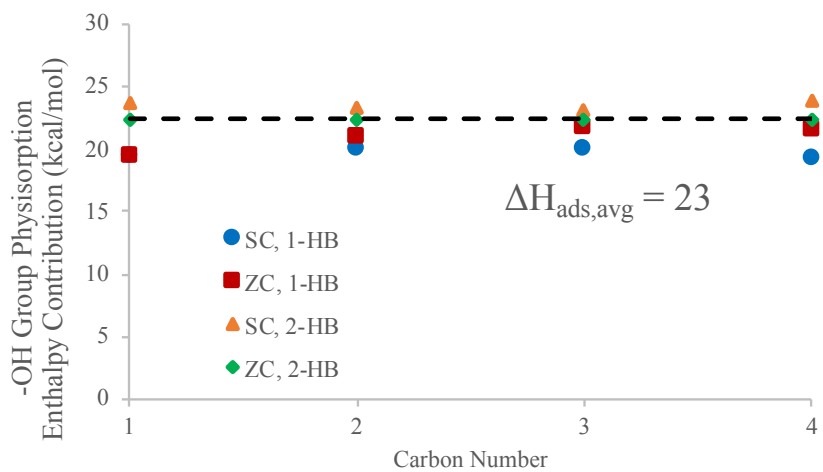
**(a) Alkane Carbon Contribution**

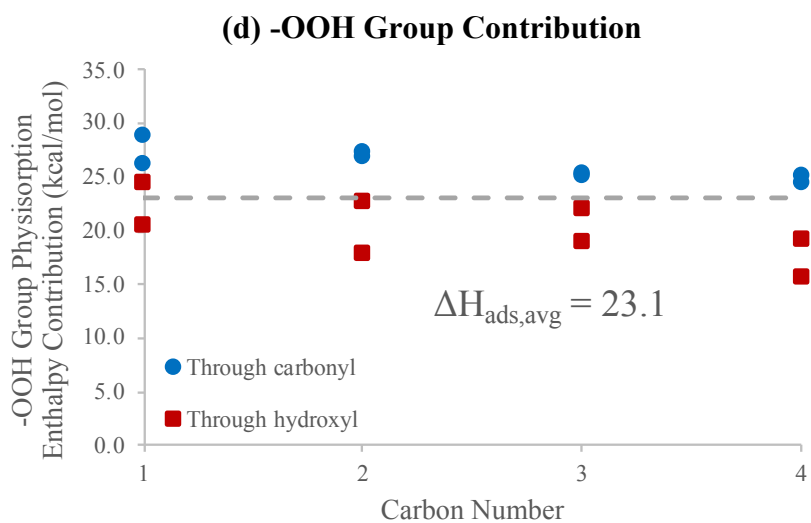


**(b) Alkene Carbon Contribution**

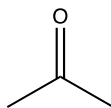


**(c) -OH Group Contribution**



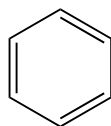


**(e) Physisorption Enthalpy Calculation for the =O Group**



$$31.07 - 3(3.0) = 22.1 \text{ kcal/mol per } =\text{O Group}$$

**(f) Physisorption Enthalpy Calculation for an Aromatic Carbon**



$$15.2/6 = 2.5 \text{ kcal/mol per aromatic carbon}$$

**Figure S1.** Determination of physisorption group contribution value for (a) alkane carbon atoms<sup>1</sup>; (b) alkene carbon atoms<sup>2</sup>; (c) -OH groups<sup>3</sup>; (d) -OOH groups<sup>4</sup>; (e) =O groups<sup>5</sup>; (f) aromatic carbon atoms<sup>6,7</sup>.

**Table S2.** Experimental physisorption enthalpies for alkanes C3-C6.<sup>1</sup>

| Alkane    | Carbon Number | $\Delta H_{\text{ads}}$ (kJ/mol) | $\Delta H_{\text{ads}}$ (kcal/mol) |
|-----------|---------------|----------------------------------|------------------------------------|
| propane   | 3             | 41.0                             | 9.8                                |
| n-butane  | 4             | 52.0                             | 12.4                               |
| n-pentane | 5             | 62.5                             | 14.9                               |
| n-hexane  | 6             | 72.0                             | 17.2                               |

**Table S3.** Theoretical physisorption energies for 1/2/3/4-alkenes.<sup>2</sup> Note that the physisorption enthalpies can be taken equal to the calculated physisorption energies and can be considered independent of temperature in the range 300-800 K.

| Alkene            | Carbon Number | $\Delta E_{\text{phys}}$ (kJ/mol) | $\Delta E_{\text{phys}}$ (kcal/mol) | CD Contribution (kcal/mol) |
|-------------------|---------------|-----------------------------------|-------------------------------------|----------------------------|
| ethene            | 2             | 52                                | 12                                  | 6                          |
| propene           | 3             | 70                                | 17                                  | 7                          |
| 1-butene          | 4             | 72                                | 17                                  | 6                          |
| 1-pentene         | 5             | 84                                | 20                                  | 6                          |
| 1-hexene          | 6             | 94                                | 22                                  | 5                          |
| 1-heptene         | 7             | 98                                | 23                                  | 4                          |
| 1-octene          | 8             | 103                               | 25                                  | 3                          |
| 2-butene          | 4             | 83                                | 20                                  | 7                          |
| 2-pentene         | 5             | 93                                | 22                                  | 7                          |
| 2-hexene          | 6             | 101                               | 24                                  | 6                          |
| 2-heptene         | 7             | 110                               | 26                                  | 6                          |
| 2-octene          | 8             | 103                               | 25                                  | 3                          |
| 3-hexene          | 6             | 105                               | 25                                  | 7                          |
| 3-octene          | 8             | 118                               | 28                                  | 5                          |
| 4-octene          | 8             | 125                               | 30                                  | 6                          |
| mean contribution |               |                                   |                                     | 6                          |

**Table S4.** Theoretical physisorption enthalpies for alcohols.<sup>3</sup> Note that 1-HB is 1-hydrogen-bonded, 2-HB is 2-hydrogen-bonded, SC is in the straight channel, and ZC is in the zig-zag channel.

| Bonding           | Channel | Alcohol    | Carbon Number | $\Delta H_{\text{ads}}$ (kJ/mol) | $\Delta H_{\text{ads}}$ (kcal/mol) | OH Contribution (kcal/mol) |
|-------------------|---------|------------|---------------|----------------------------------|------------------------------------|----------------------------|
| 1-HB              | SC      | methanol   | 1             | 94                               | 22                                 | 19                         |
|                   |         | ethanol    | 2             | 109                              | 26                                 | 20                         |
|                   |         | n-propanol | 3             | 122                              | 29                                 | 20                         |
|                   |         | n-butanol  | 4             | 131                              | 31                                 | 19                         |
|                   | ZC      | methanol   | 1             | 94                               | 22                                 | 19                         |
|                   |         | ethanol    | 2             | 113                              | 27                                 | 21                         |
|                   |         | n-propanol | 3             | 129                              | 31                                 | 22                         |
|                   |         | n-butanol  | 4             | 141                              | 34                                 | 22                         |
| 2-HB              | SC      | methanol   | 1             | 112                              | 27                                 | 24                         |
|                   |         | ethanol    | 2             | 123                              | 29                                 | 23                         |
|                   |         | n-propanol | 3             | 135                              | 32                                 | 23                         |
|                   |         | n-butanol  | 4             | 150                              | 36                                 | 24                         |
|                   | ZC      | methanol   | 1             | 116                              | 28                                 | 25                         |
|                   |         | ethanol    | 2             | 131                              | 31                                 | 25                         |
|                   |         | n-propanol | 3             | 146                              | 35                                 | 26                         |
|                   |         | n-butanol  | 4             | 161                              | 38                                 | 27                         |
| mean contribution |         |            |               |                                  |                                    | 23                         |

**Table S5.** Theoretical physisorption enthalpies for carboxylic acids.<sup>4</sup> Note that there were two modes of bonding, which are depicted by Li and coworkers. Additionally, physisorption was conducted through the carbonyl oxygen and the hydroxyl oxygen.

| Adsorption              | Bonding | Carboxylic Acid | Carbon Number | $\Delta E_{\text{phys}}$ (kJ/mol) | $\Delta E_{\text{phys}}$ (kcal/mol) | OOH Contribution (kcal/mol) |
|-------------------------|---------|-----------------|---------------|-----------------------------------|-------------------------------------|-----------------------------|
| Through carbonyl oxygen | Mode A  | formic acid     | 1             | 121.8                             | 29.1                                | 26.1                        |
|                         |         | acetic acid     | 2             | 136.8                             | 32.7                                | 26.7                        |
|                         |         | propionic acid  | 3             | 143.0                             | 34.2                                | 25.2                        |
|                         |         | butyric acid    | 4             | 154.8                             | 37.0                                | 25.0                        |
|                         | Mode B  | formic acid     | 1             | 133.2                             | 31.8                                | 28.8                        |
|                         |         | acetic acid     | 2             | 139.0                             | 33.2                                | 27.2                        |
|                         |         | propionic acid  | 3             | 142.5                             | 34.1                                | 25.1                        |
|                         |         | butyric acid    | 4             | 152.5                             | 36.4                                | 24.5                        |
| Through hydroxyl oxygen | Mode A  | formic acid     | 1             | 114.8                             | 27.4                                | 24.4                        |
|                         |         | acetic acid     | 2             | 119.4                             | 28.5                                | 22.6                        |
|                         |         | propionic acid  | 3             | 129.4                             | 30.9                                | 22.0                        |
|                         |         | butyric acid    | 4             | 129.6                             | 31.0                                | 19.0                        |
|                         | Mode B  | formic acid     | 1             | 97.7                              | 23.4                                | 20.4                        |
|                         |         | acetic acid     | 2             | 99.3                              | 23.7                                | 17.8                        |
|                         |         | propionic acid  | 3             | 116.2                             | 27.8                                | 18.8                        |
|                         |         | butyric acid    | 4             | 115.5                             | 27.6                                | 15.6                        |
| mean contribution       |         |                 |               |                                   |                                     | 23.1                        |

**Table S6.** Chemisorption energies, proton affinities, and stabilization energies for various 1-alkenes.

| Alkene    | Carbon Number | $\Delta E_{\text{chem}}$ (kJ/mol) | $\Delta E_{\text{chem}}$ (kcal/mol) | PA(alkene) (kJ/mol) | PA(alkene) (kcal/mol) | $\Delta q$ (kcal/mol) |
|-----------|---------------|-----------------------------------|-------------------------------------|---------------------|-----------------------|-----------------------|
| ethene    | 2             | -130 <sup>a</sup>                 | -31                                 | 704 <sup>b</sup>    | 168                   | 152                   |
| propene   | 3             | -141 <sup>a</sup>                 | -34                                 | 752 <sup>c</sup>    | 180                   | 143                   |
| 1-butene  | 4             | -147 <sup>a</sup>                 | -35                                 | 773 <sup>b</sup>    | 185                   | 140                   |
| 1-pentene | 5             | -156 <sup>a</sup>                 | -37                                 | 787 <sup>b</sup>    | 188                   | 139                   |
| 1-hexene  | 6             | -155 <sup>a</sup>                 | -37                                 | 805 <sup>c</sup>    | 192                   | 134                   |
| 1-octene  | 8             | -167 <sup>a</sup>                 | -40                                 | 799 <sup>b</sup>    | 191                   | 138                   |
| 1-nonene  | 9             | -170 <sup>d</sup>                 | -41                                 | 799 <sup>e</sup>    | 191                   | 139                   |
| isobutene | 4             | -72 <sup>f</sup>                  | -17                                 | 802 <sup>c</sup>    | 192                   | 115                   |

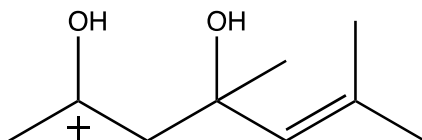
<sup>a</sup>From Nguyen and coworkers.<sup>2</sup> <sup>b</sup>From De Moor and coworkers.<sup>8</sup> <sup>c</sup>From NIST webbook.<sup>9</sup> <sup>d</sup>Extrapolated from a linear trend of propene and other 1-alkenes. <sup>e</sup>Assumed equal to the proton affinity for 1-octene. <sup>f</sup>From Nguyen and coworkers.<sup>10</sup>

**Table S7.** Chemisorption energies, proton affinities, and stabilization energies for various n-alcohols.

| Alcohol  | Carbon Number | $\Delta E_{\text{chem}}$ (kJ/mol) | $\Delta E_{\text{chem}}$ (kcal/mol) | PA(alcohol) (kJ/mol) | PA(alcohol) (kcal/mol) | $\Delta q$ (kcal/mol) |
|----------|---------------|-----------------------------------|-------------------------------------|----------------------|------------------------|-----------------------|
| methanol | 1             | -117 <sup>a</sup>                 | -28                                 | 754 <sup>b</sup>     | 180                    | 137                   |
| ethanol  | 2             | -135 <sup>a</sup>                 | -32                                 | 776 <sup>b</sup>     | 185                    | 136                   |
| propanol | 3             | -150 <sup>a</sup>                 | -36                                 | 787 <sup>b</sup>     | 188                    | 137                   |
| butanol  | 4             | -166 <sup>a</sup>                 | -40                                 | 789 <sup>b</sup>     | 189                    | 141                   |
| pentanol | 5             | -183 <sup>c</sup>                 | -44                                 | 795 <sup>d</sup>     | 190                    | 143                   |
| hexanol  | 6             | -199 <sup>c</sup>                 | -47                                 | 799 <sup>d</sup>     | 191                    | 146                   |
| heptanol | 7             | -215 <sup>c</sup>                 | -51                                 | 799 <sup>d</sup>     | 191                    | 150                   |
| octanol  | 8             | -231 <sup>c</sup>                 | -55                                 | 799 <sup>d</sup>     | 191                    | 154                   |
| nonanol  | 9             | -247 <sup>c</sup>                 | -59                                 | 799 <sup>e</sup>     | 191                    | 158                   |

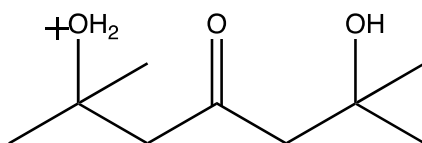
<sup>a</sup>From Nguyen and coworkers.<sup>3</sup> Note that the zig-zag channel was chosen. <sup>b</sup>From Denayer and coworkers.<sup>11</sup> <sup>c</sup>Extrapolated from linear trend of n-alcohols with carbon numbers 1-4. <sup>d</sup>From NIST webbook.<sup>9</sup> <sup>e</sup>Assumed equal to the proton affinity for hexanol, heptanol, and octanol.





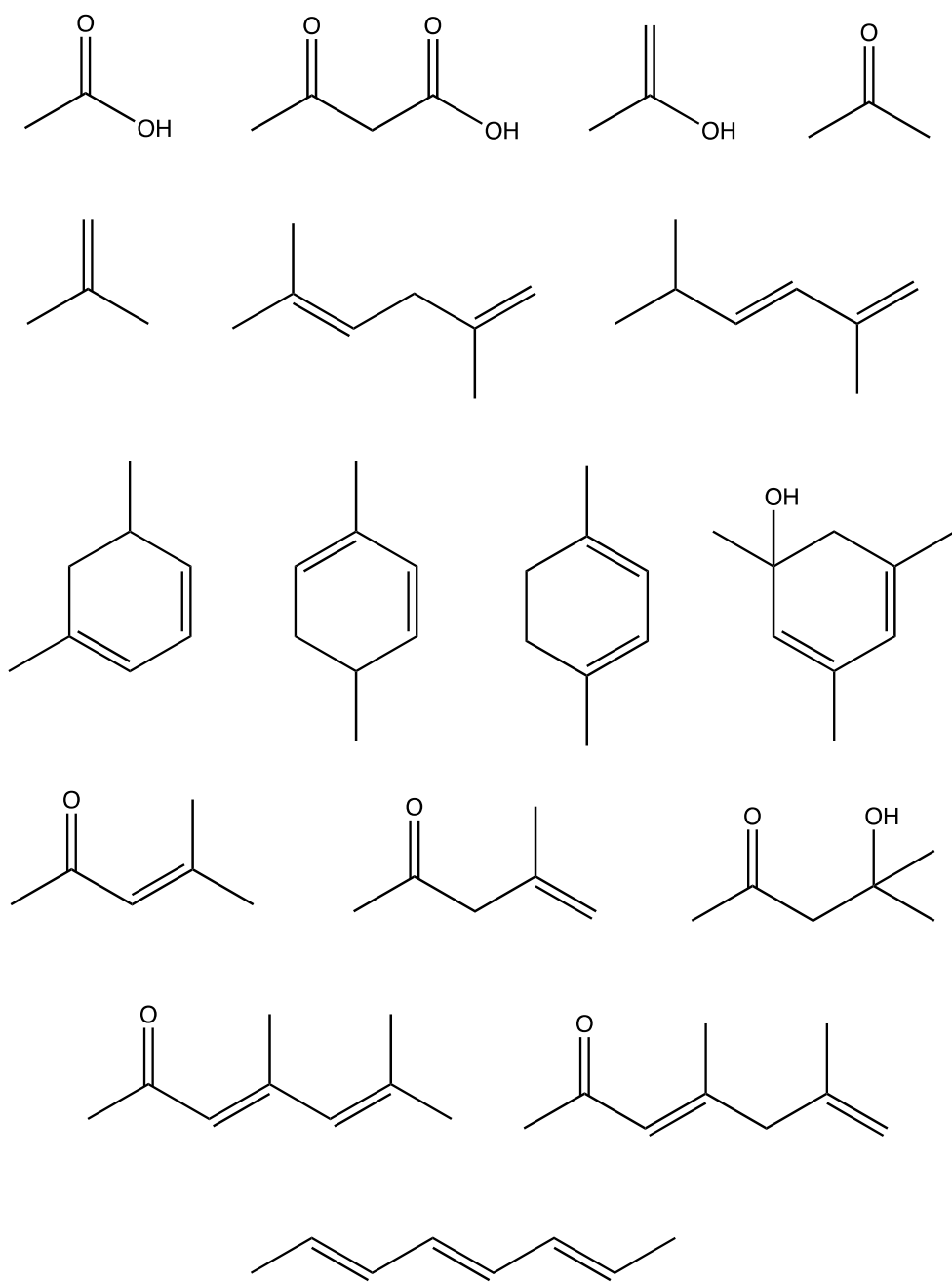
**Table S8.** Example calculation for the stabilization energy of the carbenium ion depicted above.

| Group                                       | Contribution (kcal/mol)     |
|---|-----------------------------|
| Local interactions (ion type)               | 150                         |
| Non-local interactions from carbon atoms    | $0.6(9)^2 - 8.2(9) = -25.2$ |
| Alcohol local interaction (second neighbor) | 16.8                        |
| Final stabilization energy                  | 142                         |



**Table S9.** Example calculation for the stabilization energy of the oxonium ion depicted above.

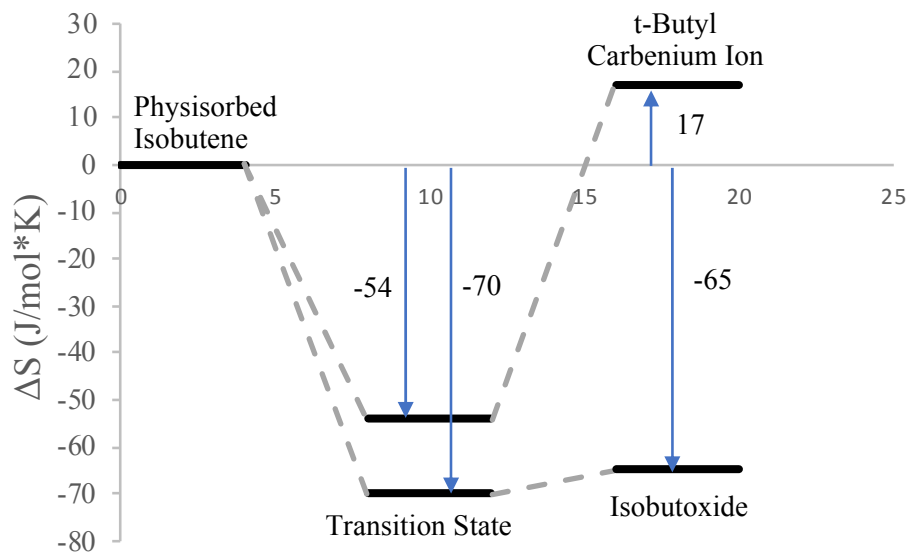
| Group                                     | Contribution (kcal/mol) |
|---|-------------------------|
| Local interactions (ion type)             | 136                     |
| Non-local interactions from carbon atoms  | $0.3(9)^2 = 24.3$       |
| Ketone local interaction (third neighbor) | -3.8                    |
| Alcohol non-local interaction             | 23                      |
| Final stabilization energy                | 180                     |



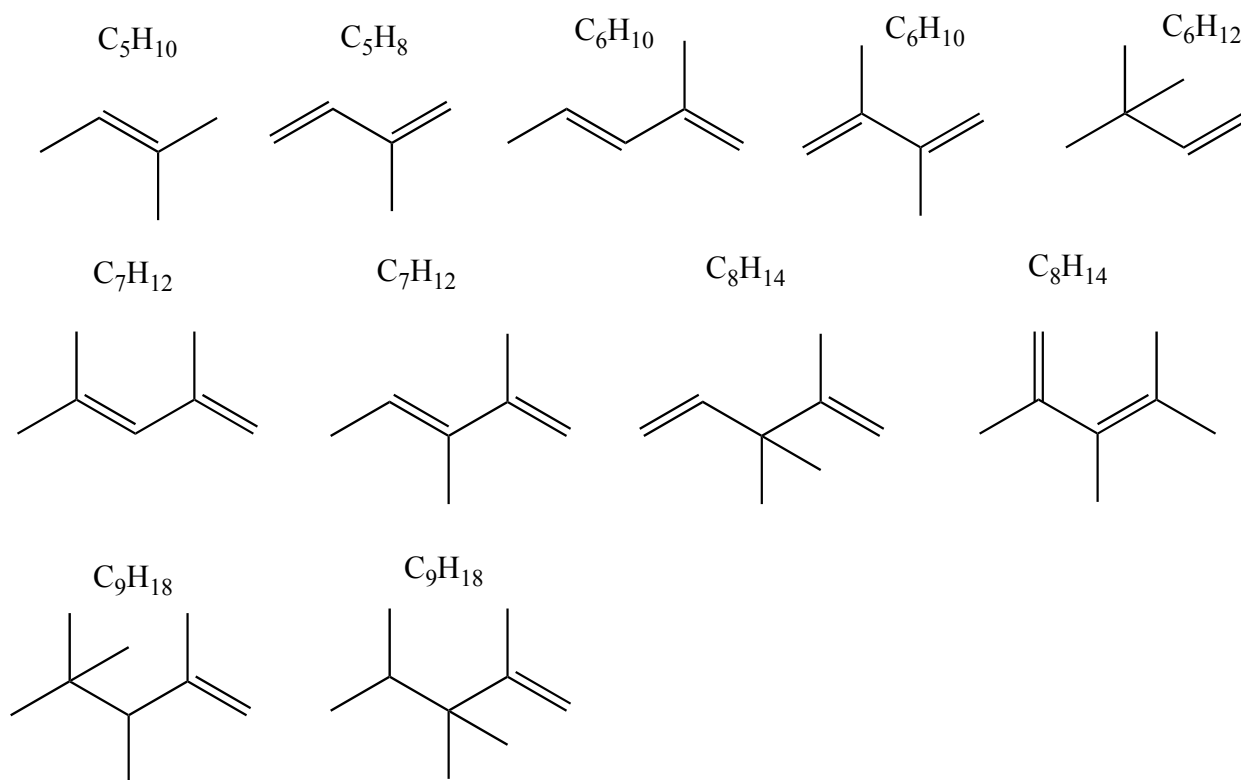
**Figure S2.** List of seed molecules.

**Table S10.** Inventory of elementary reaction steps.

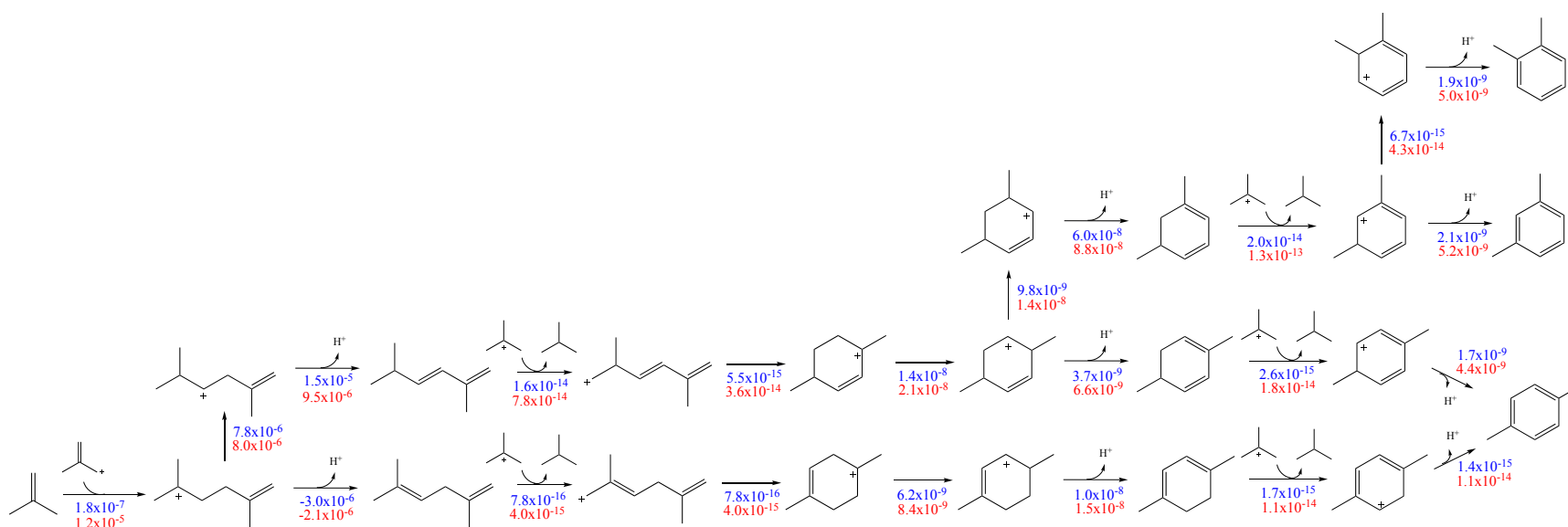
| <b>Reaction Family</b>  | <b>#</b>   |
|-------------------------|------------|
| Protonation (p, s)      | 143        |
| Protonation (t)         | 186        |
| Deprotonation (p, s)    | 143        |
| Deprotonation (t)       | 186        |
| Alcohol Protonation     | 18         |
| Oxodeprotonation        | 18         |
| Keto Protonation        | 19         |
| Alcohol Deprotonation   | 19         |
| Hydration               | 17         |
| Dehydration             | 17         |
| Aldol Condensation      | 20         |
| Retro Aldol             | 19         |
| Acylium Ion Addition    | 1          |
| Acylium Ion Removal     | 4          |
| Oligomerization         | 58         |
| $\beta$ -Scission       | 116        |
| Hydride Transfer (p, s) | 145        |
| Hydride Transfer (t)    | 36         |
| Cyclic Hydride Transfer | 13         |
| Ring Cyclization (endo) | 41         |
| Ring Cyclization (exo)  | 1          |
| 1,2-Hydride Shift       | 138        |
| 1,2-Methyl Shift        | 106        |
| $\alpha$ PCP Branching  | 31         |
| $\beta$ PCP Branching   | 36         |
| Decarboxylation         | 1          |
| Physisorption           | 314        |
| Dephysisorption         | 314        |
| <hr/> Total             | <hr/> 2160 |



**Figure S3.** Entropy changes upon protonation of physisorbed isobutene to isobutoxide and t-butyl carbenium ion.<sup>10</sup>

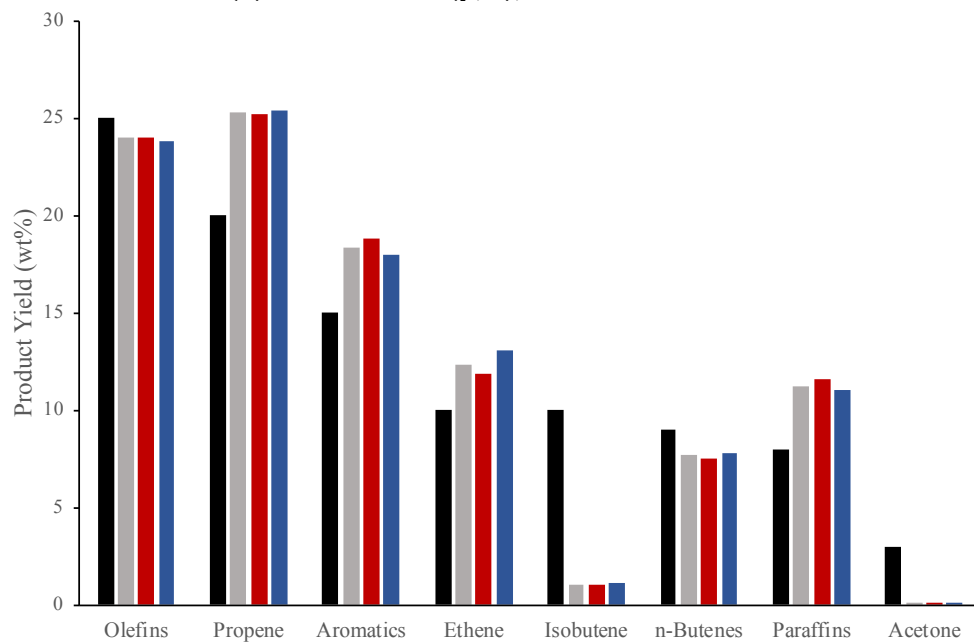


**Figure S4.** C5+ olefins with noticeable presence in the product stream in the model.

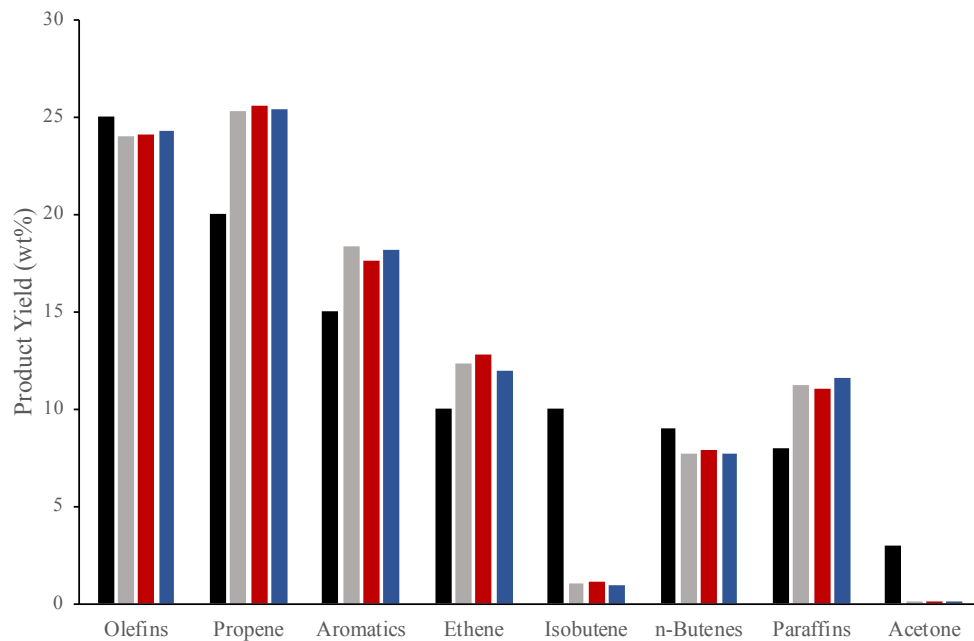


**Figure S5.** Net rate (in  $\text{s}^{-1}$ ) analysis for the pathway from isobutene to aromatics. The net rates in blue are from the transformation of acetone at  $400^\circ\text{C}$  for a space time of  $4.48 \times 10^{-1}$  g cat. h/g reactant, while the net rates in red are from the transformation of acetic acid at  $450^\circ\text{C}$  for a space time of  $2.24 \times 10^{-1}$  g cat. h/g reactant. Although they are presented in the same figure, no comparisons are made between the net rates for the transformation of acetone and acetic acid, as the space times differ. All species are either physisorbed or chemisorbed (no gas-phase species shown).

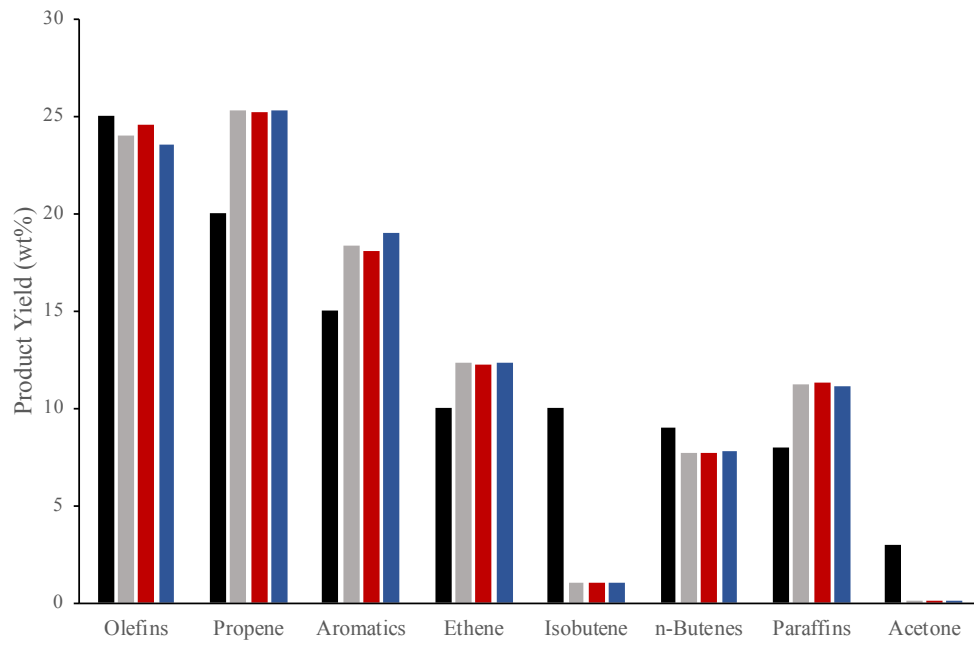
**(a) Protonation (p, s), Alcohol Protonation**



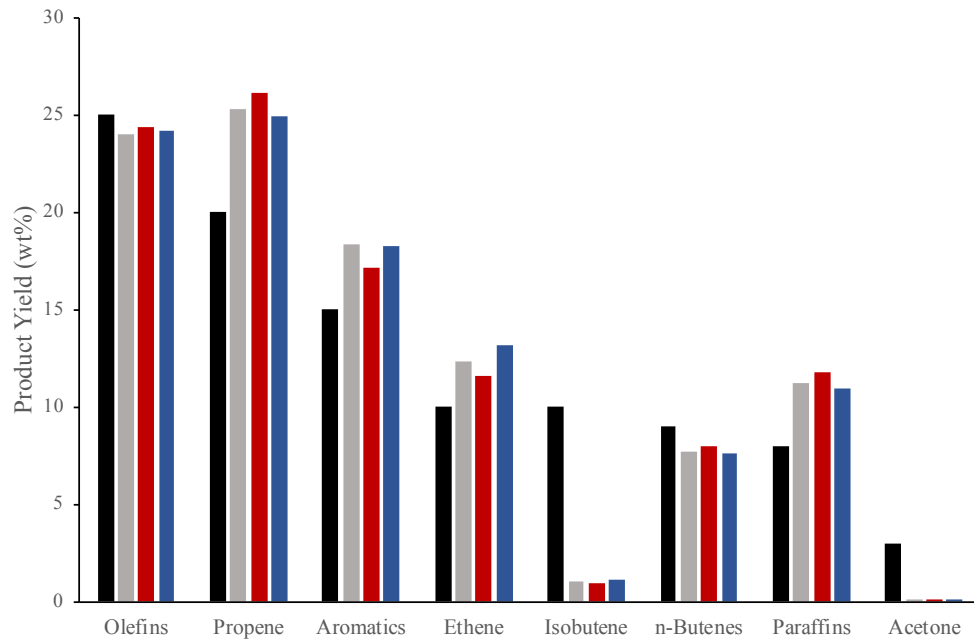
**(b) Protonation (t), Keto Protonation**



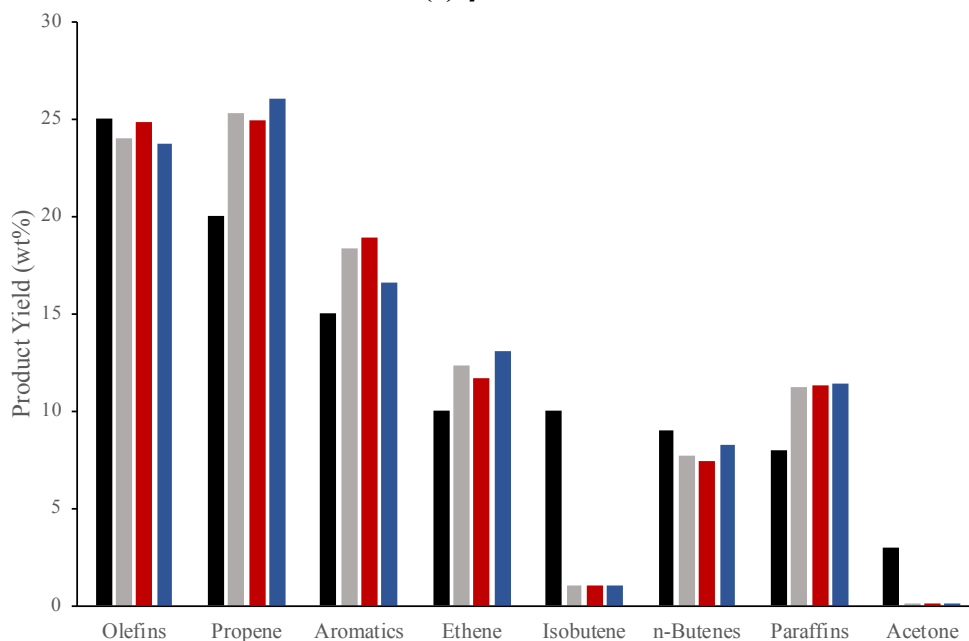
### (c) Aldol Condensation



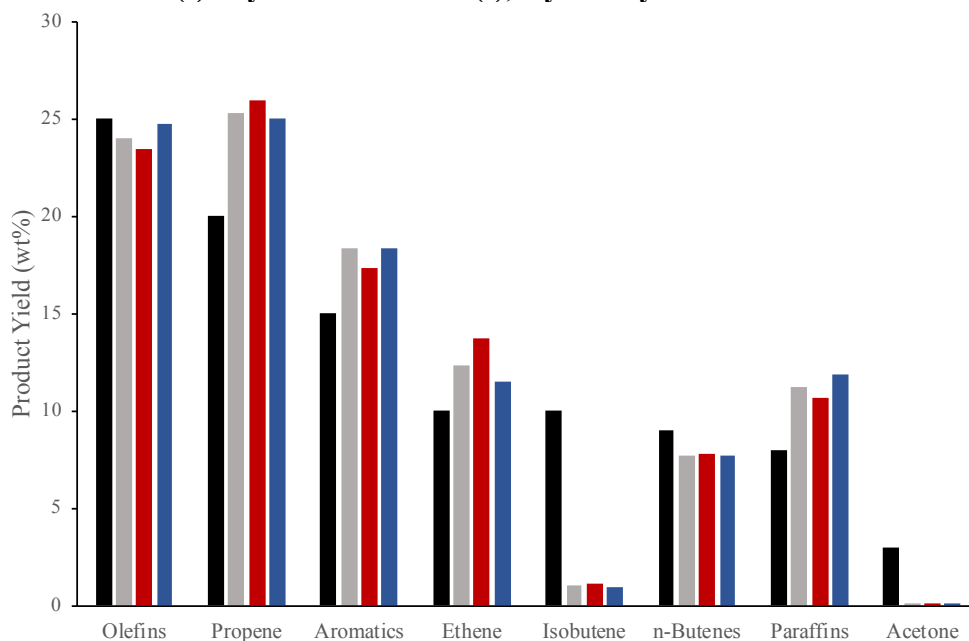
### (d) Addition



(e)  $\beta$ -Scission



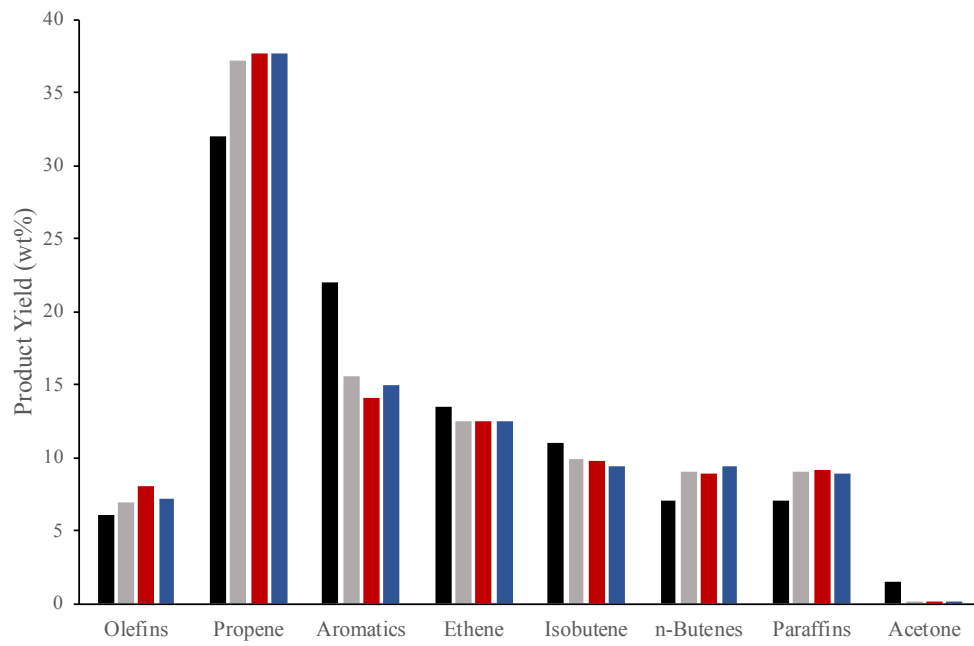
(f) Hydride Transfer (t), Cyclic Hydride Transfer



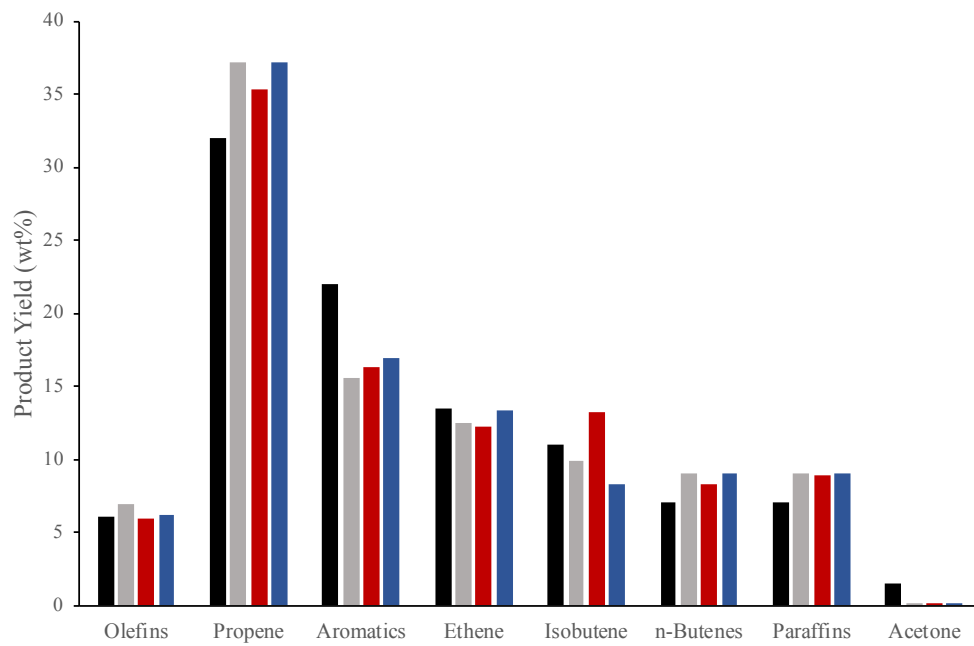
**Figure S6.** Sensitivity analysis for the conversion of acetone at 400°C, for which each optimized parameter was adjusted by +10% and -10%. Each bar graph shows the experimental product yields (black), fitted model yields (gray), predicted yields when the parameter was adjusted by +10% (red), and predicted yields when the parameter was adjusted by -10% (blue). The optimized parameters are (a) protonation (p, s), alcohol protonation; (b) protonation (t), keto protonation; (c) aldol condensation; (d) addition; (e)  $\beta$ -scission; (f) hydride transfer (t), cyclic hydride transfer.



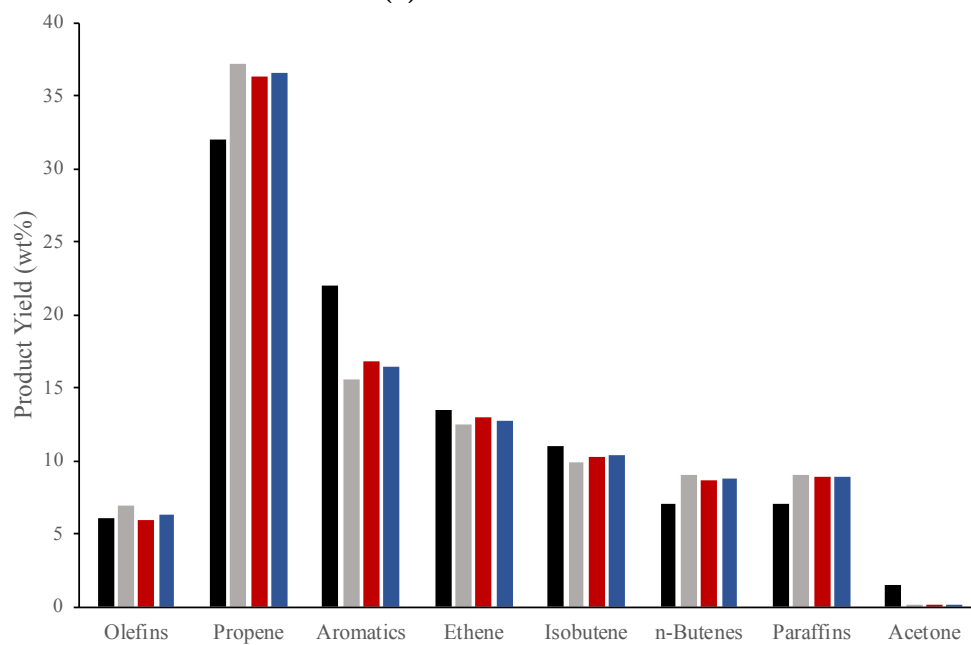
**(a) Protonation (p, s), Alcohol Protonation**



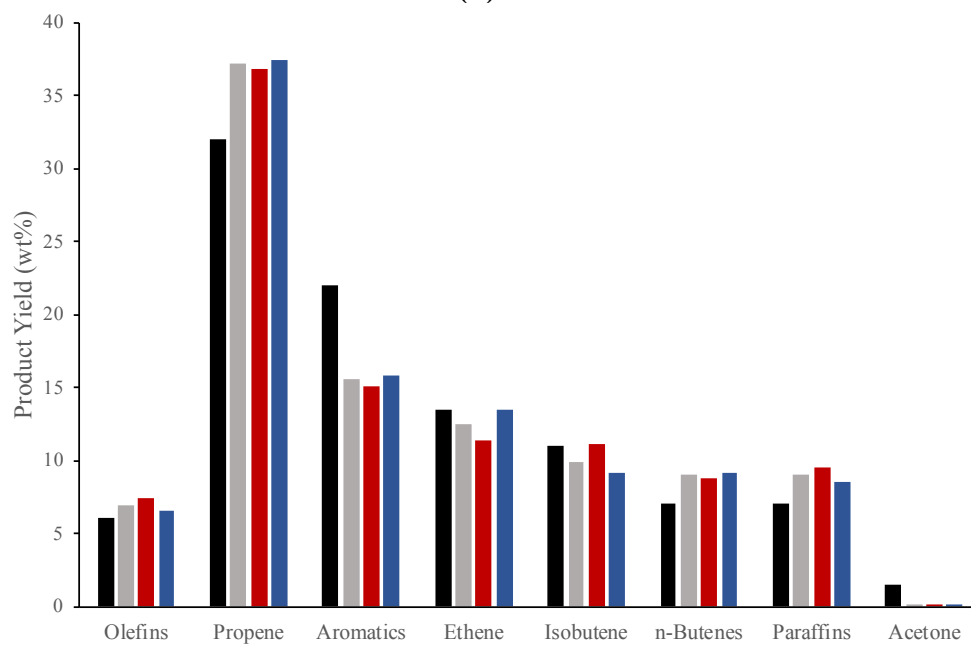
**(b) Protonation (t), Keto Protonation**



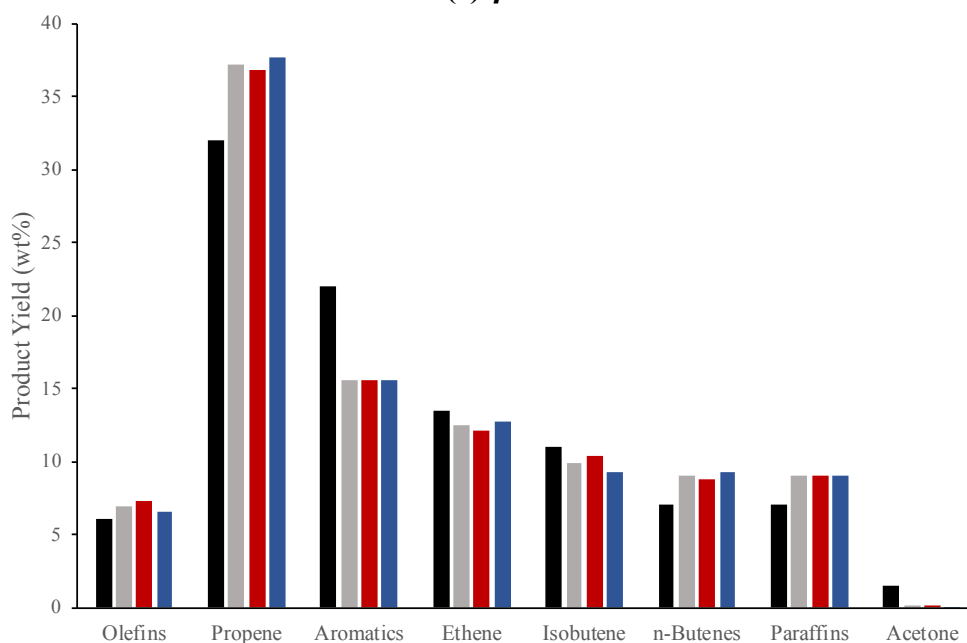
### (c) Aldol Condensation



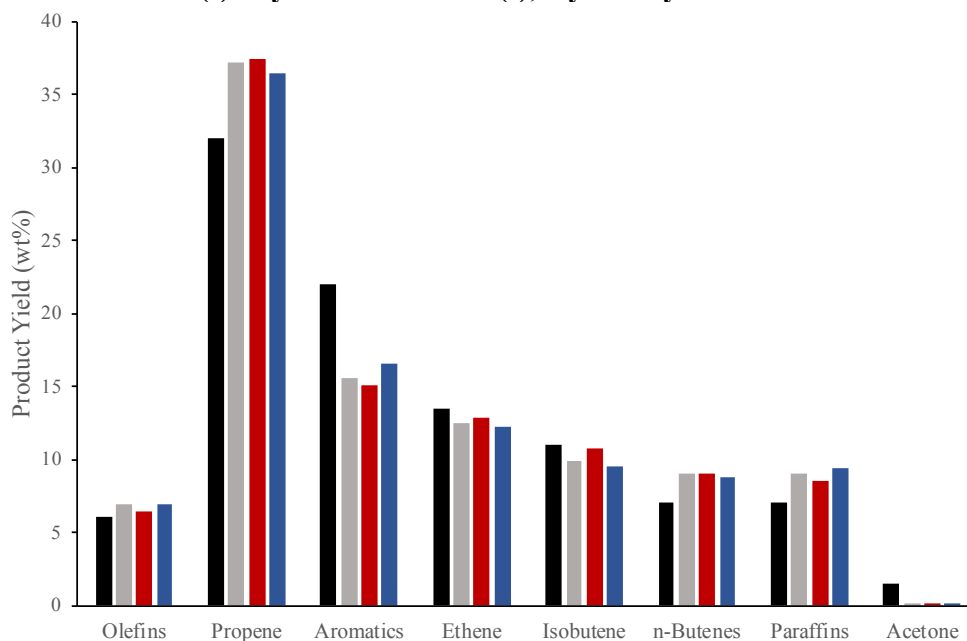
### (d) Addition



(e)  $\beta$ -Scission



(f) Hydride Transfer (t), Cyclic Hydride Transfer



**Figure S7.** Sensitivity analysis for the conversion of acetic acid at 450°C, for which each optimized parameter was adjusted by +10% and -10%. Each bar graph shows the experimental product yields (black), fitted model yields (gray), predicted yields when the parameter was adjusted by +10% (red), and predicted yields when the parameter was adjusted by -10% (blue). The optimized parameters are (a) protonation (p, s), alcohol protonation; (b) protonation (t), keto protonation; (c) aldol condensation; (d) addition; (e)  $\beta$ -scission; (f) hydride transfer (t), cyclic hydride transfer.

## References

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