Network Modeling Examples in RNFA and PNFA

The consideration of mixing and separation steps constitutes the main difference of Process Network Flux Analysis (PNFA)\(^1\) in comparison to Reaction Network Flux Analysis (RNFA).\(^2\) Figure S1 illustrates the specific differences of RNFA and PNFA flux modeling for the mole balance formulation of this study given in Eqs. 1 and 2 of the main text. In the following, the three examples of Figure S1 are explained.

Figure S1(a) shows the flux modeling of the reaction \(A + B \rightarrow C + D\). In RNFA, this is modeled as a single conversion step \(r_1\). In contrast, in PNFA, first A and B are mixed in a mixing step \(m_1\) to form the pseudo-component AB. Then, the reaction \(r_1\) takes place, which converts AB to CD. The pseudo-component CD is converted into pure C and pure D in the separation step \(t_1\). PNFA accounts for the separation of stoichiometric by-products,
Figure S1: Comparison of processing path modeling in RNFA and PNFA.

(a) Reaction $A + B \rightarrow C + D$, no solvents, inerts and high per-pass conversion $X_{r_1} \geq X_{\text{limit}}$.

(b) Reaction $E \rightarrow F$ with solvent/inert $G$ and high per-pass conversion $X_{r_2} \geq X_{\text{limit}}$.

(c) Reaction $H \rightarrow K$ without solvent/inerts and low per-pass conversion $X_{r_3} \leq X_{\text{limit}}$. 
but considers ideal separation of side products, $w_i$, that stem from parallel side reactions. This assumption is necessary since the exact properties of the side products are generally not known and hence, in these cases it is not possible to determine a valid separation step. Furthermore, in most reactions, selectivities are high, so only small amounts of side products are produced. Therefore, it is assumed that, compared to the separation of stoichiometric by-products, the separation of side products does not have a large impact on the overall process performance and can therefore be neglected.

In Figure S1(b) the reaction $E \rightarrow F$ is modeled which proceeds in the presence of the inert $G$. In RNFA, inerts and products are separated spontaneously and with full recovery, therefore, inerts do not appear in the net molar balance. In a real process, however, the inert, e.g., a solvent, is typically mixed with the reactant before the reaction takes place. After converting the reactants into products during the reaction, products and inerts (as well as unconverted reactants) are separated. PNFA assumes no loss of inerts during the reaction. Thus, the yield of inerts in the reaction is unity. This is modeled by adding the inert only after the reaction takes place in a mixing step $m_2$. Subsequently, inert and product are separated in a separation step $t_2$. In order to distinguish between the unrefined product formed after reaction and the final product gained after separation, the pseudo-component $F'$ has to be introduced which has the same physico-chemical properties as the final product $F$ but only occurs in the reaction network as an intermediate which has to be mixed with the solvent before it can be turned into final product $F$.

Figure S1(a) and S1(b) refer to reactions with high per-pass conversions $X_{r_1}, X_{r_2} \geq X_{\text{limit}}$, so it is assumed that no modeling of recycle streams is necessary. Figure S1(c) gives an example of a reaction with low per-pass conversion $X_{r_3} \leq X_{\text{limit}}$. In case of RNFA, ideal separation is assumed, therefore, irrespective of the per-pass conversion, the recycle stream does not have to be modeled explicitly. Here, the reaction yield remains $Y_{r_3} = S_{r_3}$. In PNFA, however, the mixing step $m_3$ adds unconverted reactant $H$ to the pseudo-product component $K'$ after the reaction occurred. The recycle stream is then incorporated in the separation step.
\( t_3 \) where product K and reactant H are separated. Again, to distinguish the unrefined product leaving the reactor and the purified product retrieved after separation, the pseudo-component \( K' \) is added to the reaction network.

## Reaction Parameters

Tab. S1 shows the reaction pathways that are only considered in RNFA but not PNFA, whereas Tab. S2 shows the reaction conditions of reactions considered in both RNFA and PNFA screening.

Due to the assumption of ideal recycles, yield \( Y_j \) is effectively set equal to selectivity \( S_j \) without any purges. For RNFA, only yield information \( Y_j = S_j \) is needed whereas for PNFA, conversion data, \( X_j \), solvent information, as well as pressure conditions, \( p \), are also required. The specification of the type of processing step are needed for the investment cost calculation in both RNFA and PNFA. Here, a reaction is considered a gas-phase processing step (g) if gaseous components are within the reactants since, in these cases, compression of reactants to reactor pressure and higher standards of apparatus materials lead to an increase of investment costs.

Table S1: Input for the reaction network for RNFA only. †: Assumption; ‡: selectivity is increased as it is assumed that the side products can still be recycled and turned into final product *selectivity to different product fraction already incorporated in stoichiometry.

| Reaction | \( Y_j/S_j \) [mol/mol] | \( X_j \) [mol/mol] | Solvent/inerts/non-stoichiometric compositions | \( p_j \) [bar] | Phase | Ref. |
|----------|--------------------------|---------------------|-----------------------------------------------|---------------|-------|------|
| BR72     | 0.94                     | 0.98                | excess \( H_2 \)                               | 1             | g     | 4    |
| HR18     | 1.00                     | 1.00                | nitrogen                                       | 1             | g     | 5    |
| HR19     | 0.93                     | 0.99                | nitrogen                                       | 1⇒          | g     | 6    |
| HR20     | 0.98                     | 0.28                | nitrogen                                       | 1⇒          | g     | 7    |
| HR21     | 1.00                     | 0.91                | water                                          | 2             | g     | 8    |
| HR22     | 0.94                     | 0.92                | nitrogen, water                                | 1⇒          | g     | 9    |
| HR24     | 1.00†                    | 0.92                | excess dimethoxymethane                        | 1             | l     | 9    |
| HR25     | 1.00†                    | 0.94                | excess methanol                                | 1⇒          | l     | 10   |
| HR26     | 1.00†                    | 0.91                | excess diethoxymethane                        | 1             | l     | 11   |
| HR27     | 0.85                     | 1.00†               | -                                              | 1             | g     | 12   |
| HR29     | 1.00*                    | 0.95                | -                                              | 30            | g     | 11   |
| HR31     | 1.00*                    | 1.00†               | -                                              | 8             | g     | 11   |
| HR32     | 1.00*                    | 0.86                | -                                              | 35            | 1     | 11   |
Table S2: Input for the reaction network of RNFA and PNFA. †Assumption; ‡Selectivity is increased as it is assumed that some of the side products can still be recycled and turned into final product; § recycles needed due to $X \leq X_{\text{limit}}$ *Only for cellulose, CO does not exhibit selectivity losses.

| Reaction | $Y_j = S_j$ [mol/mol] | $X_j$ [mol/mol] | Solvent/inerts/non-stoichiometric compositions | p [bar] | Phase liquid(l)/gas(g) | Ref. |
|----------|------------------------|-----------------|-----------------------------------------------|--------|------------------------|-----|
| BR1      | 0.97                   | -               | -                                             | -      | 1                      | 1†  |
| BR4      | 1                      | 0.90            | water                                         | 1      | 1                      | 1   |
| BR5      | 1                      | 0.90            | water                                         | 1      | 1                      | 13  |
| BR6      | 0.95                   | 1.00†           | water                                         | 1      | 1                      | 14  |
| BR7      | 0.85                   | 1.00†           | water                                         | 1      | 1                      | 14  |
| BR8      | 0.70                   | 1.00†           | water                                         | 32     | 1                      | 15  |
| BR9      | 1.00                   | 1.00            | water                                         | 18     | 1                      | 15  |
| BR10     | 0.97                   | 1.00†           | -                                             | 1†     | 1                      | 16  |
| BR11     | 0.96                   | 1.00†           | water                                         | 44     | 1                      | 17  |
| BR12     | 0.99                   | 1.00†           | dimethyl sulfoxide                             | 1      | 1                      | 18  |
| BR15     | 0.90                   | 0.90            | water                                         | 60     | 1                      | 19  |
| BR16     | 0.99                   | 1.00†           | water                                         | 8      | g                      | 20  |
| BR19     | 0.96                   | 0.98            | 2-methyltetrahydrofuran                        | 50     | 1                      | 21  |
| BR25     | 0.95                   | 1.00†           | -                                             | 1      | 1                      | 22  |
| BR26     | 0.99                   | 1.00†           | -                                             | 1      | 1                      | 23  |
| BR27     | 0.99                   | 1.00†           | 1,4-dioxane                                    | 1      | 1                      | 24  |
| BR28     | 0.84                   | 1.00†           | -                                             | 1      | 1                      | 25  |
| BR29     | 1.00                   | 1.00†           | water                                         | 35     | 1                      | 26  |
| BR30     | 0.95                   | 1.00            | water                                         | 1†     | 1                      | 27  |
| BR31     | 0.68                   | 1.00†           | water, $\gamma$-butyrolactone                 | 40     | 1                      | 28  |
| BR32     | 0.60                   | 1.00†           | water                                         | 1†     | 1                      | 29  |
| BR33     | 0.55                   | 1.00†           | water, $\gamma$-butyrolactone                 | 40     | 1                      | 29  |
| BR35     | 0.98                   | 1.00†           | water                                         | 1†     | 1                      | 30  |
| BR38     | 0.75                   | 1.00†           | water                                         | 1†     | 1                      | 31  |
| BR39     | 0.76                   | 1.00†           | methylene chloride                            | 1†     | 1                      | 32  |
| BR40     | 0.72                   | 1.00†           | water                                         | 1†     | 1                      | 33  |
| BR41     | 0.94                   | 0.97            | water                                         | 1      | 1                      | 34  |
| BR42     | 0.68                   | 1.00†           | water                                         | 1†     | 1                      | 35  |
| BR43     | 0.68                   | 1.00†           | - †                                           | 1      | g                      | 36  |
| BR44     | 0.68                   | 1.00†           | - †                                           | 1      | g                      | 36  |
| BR45     | 0.77                   | 1.00†           | - †                                           | 1      | g                      | 36  |
| BR46     | 0.39                   | 1.00†           | - †                                           | 1      | g                      | 36  |
| BR52     | 0.38                   | 0.81            | water, benzene                                 | 21     | g                      | 37  |
| BR53     | 0.68                   | 1.00†           | water, benzene                                 | 21     | g                      | 38  |
| BR54     | 0.68                   | 1.00†           | tetrahydrofuran                                | 1      | g                      | 39  |
| BR57     | 0.40                   | 1.00†           | dioxane                                        | 15     | g                      | 40  |
| BR58     | 0.89                   | 1.00            | dioxane                                        | 21     | g                      | 41  |
| BR70     | 0.47                   | 1.00†           | benzene                                        | 21     | g                      | 42  |
| BR71     | 0.95                   | 0.95            | dioxane                                        | 1      | 1                      | 42  |
| BR90     | 0.60*                  | 1.00            | 2-methyltetrahydrofuran, water                 | 100    | g                      | 43,44 |
| BR91     | 1.00                   | 1.00            | 2-methyltetrahydrofuran, water                 | 50     | 1                      | 43,44 |
| BR91     | 1.00                   | 1.00            | 2-methyltetrahydrofuran, water                 | 50     | 1                      | 43,44 |
| HR1      | 0.98                   | 0.93            | small amounts of nitrogen (neglected)          | 1      | g                      | 45  |
| HR2      | 1.00                   | 0.55            | -                                              | 1      | g                      | 46  |
| HR3      | 1.00                   | 1.00            | -                                              | 3      | g                      | 47  |
| HR4      | 1.00†                  | 0.47†           | small amounts of argon (neglected)             | 184    | g                      | 48  |
| HR5      | 0.98                   | 0.143           | excess CO                                      | 100    | g                      | 49  |
| HR6      | 0.83                   | 0.99            | nitrogen, excess CH$_4$                        | 50     | g                      | 50  |
| HR7      | 0.45                   | 0.41†           | -                                              | 54     | g                      | 51  |
| HR8      | 0.95                   | 0.70†           | argon (neglected), water                       | 1      | g                      | 51  |
| HR9      | 0.95                   | 0.90            | argon (neglected), water                       | 1      | g                      | 51  |
| HR10     | 0.60                   | 0.453           | helium                                         | 1      | g                      | 52  |
| HR11     | 1.00                   | 1.00            | helium                                         | 1      | g                      | 53  |
| HR12     | 0.88                   | 0.84            | oxygen, nitrogen                               | 1†     | g                      | 54  |
| HR13     | 0.60                   | 0.433           | excess H$_2$                                    | 102    | g                      | 55  |
| HR15     | 0.99                   | 0.80            | water                                          | 10     | g                      | 56  |
| HR16     | 0.99†                  | 0.123           | -                                              | 20     | g                      | 57  |
| HR17     | 1.00†                  | 0.9              | small amounts of Ar and CO$_2$ (neglected)     | 40     | g                      | 58  |
| BHR1     | 1.00†                  | 1.00‡           | ethanol                                        | 80     | g                      | 59  |
| BHR2b    | 0.95                   | 1.00†           | excess methanol                                 | 1      | l                      | 60  |
| BHR3     | 1.00                   | 1.00            | -                                              | 1      | g                      | 61  |
Energy Requirements of Separation Steps

The energy demands of separations are determined using different models which are briefly listed in the following. The flash2 model of Aspen Plus\textsuperscript{62} is applied to calculate the energy demands of evaporation (E). Permanent gases are assumed to be separated ideally from liquid components in a flash unit (F). The energy requirements of distillation (D), heteroazeotropic distillation (HD), and pressure swing distillation (PSD) are determined with pinch-based separation models.\textsuperscript{63,64} CO\textsubscript{2} removal from a gaseous mixture is modeled by a pinch-based model for physical absorption (A)\textsuperscript{65} and a desorption distillation unit (D). Here, either methanol or propylene carbonate are used as they are suitable solvent for CO\textsubscript{2} gas removal.\textsuperscript{66} Phase splits are calculated by means of the vapor-liquid-liquid-equilibrium assuming a decanter (Dec) with no utility requirements. The energy demands of gaseous compression are determined assuming polytropic compression of an ideal gas while compression of liquids is neglected due to the much lower energy demand of pumps.

In general separation steps are incorporated in the investment cost function as a separate gas-phase processing step. In case of very simple units, i.e., a flash unit (F) or a decanter (Dec), no investment costs are assumed. In contrast, absorption steps and heat-integrated separation steps, i.e., vapor recompression columns (VRC), are counted as two units in the investment cost function as more equipment is needed.

Separations are modeled using the NRTL model for thermodynamics and the Antoine model for vapor pressure. Additionally, Henry coefficients are needed for the absorption model. NRTL parameters and Henry coefficients are taken either from Aspen Plus\textsuperscript{62} or by estimation with COSMO-RS.\textsuperscript{67} Antoine parameters are retrieved from Aspen Plus.\textsuperscript{62}

Tab. S3, S4, S5, S6, and S7 give an overview of the thermal separation steps incorporated in PNFA as well as the corresponding reactions, reactor effluent composition, type of separation, pressure, $p$, as well as heating, cooling, electricity, and refrigeration duties.

Tab. S6 refers to heat-integrated separations by means of vapor recompression while Tab. S7 gives an overview of separations needed for an concentration increase.
Table S3: Non-heat integrated energy requirement of thermal separations. Separations BT2 to BT51 are taken from Ulonska et al.¹ Heat.: Heating, Cool.: Cooling, MTHF: 2-methyltetrahydrofuran, HMF: 2,5-hydroxymethylfurfural.

| Sep. | Reaction | Comp. 1 | Comp. 2 | Comp. 3 | x₁ | x₂ | x₃ | x₄ | Type | p [bar] | Heat. (kJ/mol) | Cool. (kJ/mol) |
|------|----------|---------|---------|---------|----|----|----|----|------|--------|---------------|---------------|
| BT2  | BR4, BR5 | water   | ethanol | CO₂     | 0.957 | 0.201 | 0.201 | - | F, PSD | 1/10 | 30 | 29 |
| BT3  | BR12     | HMF     | dimethyl sulfoxide | water | 0.071 | 0.718 | 214 | - | D | 48 | 46 |
| BT4  | BR12     | water   | dimethyl sulfoxide | - | 0.231 | 0.769 | - | D | 1 | 20 | 15 |
| BT5  | BR8      | HMF     | water   | - | 0.040 | 0.960 | - | D | 1 | 40 | 40 |
| BT6  | BR19     | furfurylalcohol | MTHF | CO | 0.002 | 0.219 | 0.02 | - | F | 1 | 2 | 18 |
| BT9  | BR16     | furfurylalcohol | water | - | 0.018 | 0.982 | - | D | 1 | 133 | 132 |
| BT10 | BR10     | ethyl levulinate | water | ethanol | 0.333 | 0.334 | 0.333 | - | D | 1 | 38 | 28 |
| BT11 | BR10     | ethyl levulinate | water | - | 0.500 | 0.500 | - | PSD | 1/10 | 690 | 690 |
| BT12 | BR25     | ethyl levulinate | ethanol | - | 0.029 | 0.971 | - | - | D | 1 | 39 | 39 |
| BT14 | BR26     | ethyl levulinate | ethanol | CO | 0.040 | 0.920 | 0.040 | - | F, D | 1 | 37 | 36 |
| BT15 | BR28     | ethyl levulinate | formic acid | water | ethanol | 0.004 | 0.004 | 0.008 | 0.984 | D | 1 | 51 | 51 |
| BT16 | BR28     | formic acid | water | ethanol | - | 0.004 | 0.008 | 0.986 | - | D | 5 | 107 | 107 |
| BT17 | BR28     | ethanol | water | - | 0.902 | 0.008 | - | - | D | 1/10 | 217 | 217 |
| BT18 | BR9      | levulinic acid | formic acid | water | - | 0.048 | 0.048 | 0.904 | - | D | 1 | 40 | 38 |
| BT19 | BR9      | formic acid | water | - | 0.050 | 0.950 | - | - | D | 9 | 234 | 234 |
| BT20 | BR30     | levulinic acid | formic acid | water | - | 0.017 | 0.017 | 0.966 | - | D | 1 | 41 | 40 |
| BT21 | BR30     | formic acid | water | - | 0.018 | 0.982 | - | - | D | 9 | 240 | 240 |
| BT22 | BR32     | levulinic acid | formic acid | water | - | 0.003 | 0.003 | 0.994 | - | D | 1 | 41 | 41 |
| BT24 | BR32     | formic acid | water | - | 0.003 | 0.007 | - | - | D | 9 | 239 | 239 |
| BT25 | BR40     | levulinic acid | formic acid | water | - | 0.007 | 0.057 | 0.986 | - | D | 1 | 41 | 41 |
| BT27 | BR40     | formic acid | water | - | 0.007 | 0.993 | - | - | D | 9 | 241 | 241 |
| BT30 | BR27     | γ-valerolactone | ethanol | dioxane | CO₂ | 0.071 | 0.071 | 0.786 | 0.071 | F, D | 1 | 33 | 32 |
| BT31 | BR27     | ethanol | dioxane | - | 0.083 | 0.917 | - | - | D | 2 | 22 | 22 |
| BT32 | BR29     | γ-valerolactone | water | CO₂ | 0.027 | 0.946 | 0.027 | - | F, D | 1 | 94 | 93 |
| BT35 | BR31, BR33 | γ-valerolactone | γ-butyrolactone | water | CO₂ | 0.023 | 0.442 | 0.512 | 0.023 | F, D | 1 | 35 | 28 |
| BT36 | BR31, BR33 | γ-valerolactone | γ-butyrolactone | - | 0.050 | 0.950 | - | - | D | 1 | 894 | 894 |
| BT38 | BR38     | iso-butanol | water | CO₂ | 0.004 | 0.080 | 0.013 | - | F, HD | 1 | 6 | 5 |
| BT41 | BR37     | 2-butanone | methylene chloride | hydrogen | - | 0.016 | 0.669 | 0.016 | - | F, D | 1 | 30 | 30 |
| BT43 | BR39     | 2-butanone | methylene chloride | hydrogen | - | 0.003 | 0.994 | 0.003 | - | F, D | 1 | 30 | 30 |
| BT44 | BR41     | 2-butanone | water | - | 0.167 | 0.833 | - | - | HD | 3 | 40 | 39 |
| BT46 | BR42     | 2-butanone | water | CO₂ | 0.003 | 0.994 | 0.003 | - | F, HD | 0.5 | 7 | 5 |
| BT47 | BR35     | 2,3-butanediol | water | CO₂ | 0.019 | 0.944 | 0.037 | - | D | 1 | 49 | 48 |
| BT49 | BR11     | fructose | water | - | 0.002 | 0.998 | - | - | E | 1 | 48 | 0 |
| BT55 | BR57     | 2,5-dimethylfuran | water | tetrahydrofuran | - | 0.004 | 0.020 | 0.976 | - | D | 1 | 31 | 31 |
| BT56 | BR57     | water | tetrahydrofuran | dioxane | - | 0.027 | 0.054 | 0.919 | - | D | 1 | 41 | 41 |
| BT57 | BR58     | 2,5-dimethylfuran | water | dioxane | - | 0.056 | 0.944 | - | - | PSD | 1/0.4 | 44 | 44 |
| BT58 | BR58     | water | dioxane | - | 0.056 | 0.944 | - | - | PSD | 1/0.4 | 49 | 49 |
| BT59 | BR52, BR53 | methylfurfural | water | benzene | - | 0.006 | 0.693 | 0.300 | - | Dec | 1 | 0 | 0 |
| BT60 | BR52, BR53 | methylfurfural | water | - | 0.013 | 0.987 | - | - | D | 1 | 33 | 30 |
| BT61 | BR52, BR53 | benzene | benzene | - | 0.004 | 0.996 | - | - | D | 1 | 40 | 40 |
| BT62 | BR53a    | methylfurfural | water | benzene | - | 0.009 | 0.802 | 0.190 | - | Dec | 1 | 0 | 0 |
| BT63 | BR53a    | methylfurfural | benzene | - | 0.020 | 0.983 | - | - | D | 1 | 43 | 30 |
| BT64 | BR53a    | methylfurfural | water | - | 0.006 | 0.994 | - | - | D | 1 | 40 | 40 |
Table S4: Non-heat integrated energy requirement of thermal separations (continued), †: physical solvent: methanol ‡: physical solvent: propylene carbonate; *: modeled as methyl oleate; Heat.: Heating, Cool.: Cooling, Elec.: Electricity, Refrig.: Refrigeration, MTHF: 2-methyltetrahydrofuran, DEM: diethoxymethane.

| Sep | Reaction | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | x1     | x2     | x3     | x4     | Type | p [bar] | Heat. | Cool. | Elec. | Refrig. |
|-----|----------|---------|---------|---------|---------|--------|--------|--------|--------|------|--------|-------|-------|-------|---------|
| BT65| BR70     | methylfurfural | water   | benzene | -       | 0.008  | 0.815  | 0.177  | -      | Dec  | 1      | 0     | 0     | 0     | 0       |
| BT66| BR70     | methylfurfural | benzene | -       | -       | 0.019  | 0.981  | -      | -      | D    | 1      | 34    | 30    | 0     | 0       |
| BT67| BR70     | methylfurfural | water   | -       | -       | 0.006  | 0.994  | -      | -      | D    | 1      | 40    | 40    | 0     | 0       |
| BT68| BR71     | 2-methylfuran | CO      | dioxane | -       | 0.017  | 0.177  | 0.967  | -      | F,D  | 1      | 16    | 16    | 0     | 0       |
| BT69| BR90     | methylfurfural | water   | MTHF    | CO2    | 0.037  | 0.444  | 0.481  | 0.037  | F,Dec| 1      | 0     | 0     | 0     | 0       |
| BT70| BR91     | 2-methylfuran | water   | MTHF    | CO     | 0.042  | 0.367  | 0.549  | 0.042  | D    | 1      | 1     | 0     | 0     | 0       |
| BT71| BR91     | 2-methylfuran | water   | -       | -       | 0.830  | 0.167  | -      | -      | HD   | 1      | 1369  | 739   | 0     | 0       |
| BHT1| BHR1     | DEM      | ethanol | water   | -       | 0.020  | 0.939  | 0.041  | -      | D    | 9.9    | 157   | 157   | 0     | 0       |
| BHT2| BHR1     | DEM      | ethanol | -       | -       | 0.026  | 0.974  | -      | -      | D    | 14.8   | 216   | 216   | 0     | 0       |
| BHT3| BHR1     | ethanol   | water   | -       | -       | 0.818  | 0.182  | -      | -      | PSD  | 1/10   | 1116  | 1110  | 0     | 0       |
| BHT6| BHR2b    | methanol | glycerol| FAME*   | -       | 0.692  | 0.077  | 0.231  | -      | HD   | 1      | 19    | 16    | 0     | 0       |
| BHT7| BHR2b    | methanol | glycerol| FAME*   | -       | 0.502  | 0.038  | 0.459  | -      | HD   | 1      | 123   | 24    | 0     | 0       |
| HT1 | HR1      | methane  | water   | -       | -       | 0.333  | 0.667  | -      | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT2 | HR2      | CO       | hydrogen| CO2     | water   | 0.275  | 0.225  | 0.225  | 0.275  | F    | 1      | 0     | 0     | 0     | 0       |
| HT3 | HR2      | CO       | hydrogen| CO2     | -       | 0.379  | 0.311  | 0.311  | -      | F    | 10     | 0     | 0     | 0     | 0       |
| HT30| HR2      | CO       | hydrogen| CO2     | -       | 0.549  | 0.451  | -      | -      | F    | 10     | 0     | 0     | 0     | 0       |
| HT4 | HR3      | methane  | water   | -       | -       | 0.500  | 0.500  | -      | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT6 | HR4      | water    | methanol| hydrogen| CO2    | 0.154  | 0.154  | 0.519  | 0.174  | F    | 1      | 0     | 0     | 0     | 0       |
| HT7 | HR4      | water    | methanol| hydrogen| CO2    | 0.500  | 0.500  | -      | -      | D    | 1      | 33    | 32    | 0     | 0       |
| HT8 | HR5      | methanol | CO      | hydrogen| -      | 0.078  | 0.500  | 0.422  | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT9 | HR6      | methanol | methane | nitrogen| -      | 0.111  | 0.667  | 0.222  | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT10| HR6      | methanol | methane | nitrogen| -      | 0.75   | 0.25   | -      | -      | D    | 4      | 1     | 0     | 5     | 7       |
| HT11| HR7      | ethanol  | water   | hydrogen| CO     | 0.092  | 0.092  | 0.543  | 0.272  | F,PSD| 1/10   | 128   | 127   | 0     | 0       |
| HT22| HR8      | ethanol  | water   | hydrogen| CO2    | 0.275  | 0.537  | 0.451  | 0.568  | F    | 1      | 5     | 4     | 0     | 0       |
| HT28| HR8      | hydrogen | CO2     | -       | -       | 0.520  | 0.471  | -      | -      | A,D  | 42/1   | 28    | 19    | 1      | 0       |
| HT13| HR8/9    | ethanol  | water   | CO2     | -       | 0.018  | 0.946  | 0.036  | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT14| HR8/9    | ethanol  | water   | hydrogen| -      | 0.019  | 0.981  | -      | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HT15| HR13     | hydrogen | CO      | ethane  | CO2    | 0.653  | 0.222  | 0.042  | 0.084  | F,PSD| 1/10   | 25    | 25    | 0     | 0       |
| HT16| HR13     | hydrogen | CO      | ethane  | -      | 0.712  | 0.242  | 0.046  | -      | D    | 4      | 1     | 0     | 5     | 3       |
| HT17| HR13     | hydrogen | CO      | -       | -       | 0.746  | 0.254  | -      | -      | E    | 10     | 0     | 0     | 10    | 8       |
| HR17| HR15     | dimethyl ether| water | -       | 0.448  | 0.556  | -      | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HR18| HR16     | dimethyl ether| water | CO2     | hydrogen| 0.016  | 0.049  | 0.234  | 0.701  | F    | 1      | 0     | 0     | 0     | 0       |
| HR19| HR16     | dimethyl ether| water | CO2     | hydrogen| 0.017  | 0.246  | 0.737  | -      | F    | 1      | 0     | 0     | 0     | 0       |
| HR27| HR4,HT18 | hydrogen | CO2     | -       | -       | 0.750  | 0.250  | -      | -      | A,D  | 42/1   | 23    | 19    | 0      | 0       |
| HR29| HR17     | CO2      | hydrogen| dimethyl ether| -       | 0.238  | 0.524  | 0.238  | -      | D    | 1      | 5     | 0     | 0     | 10      |
Table S5: Non-heat integrated energy requirement of thermal separations (continued), †: physical solvent: methanol Heat.: Heating, Elec.: Electricity, Refrig.: Refrigeration.

| Sep.  | Reaction | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | x1    | x2    | x3    | x4    | x5    | Type | p [bar] | Heat. [kJ mol⁻¹] | Cool. [kJ mol⁻¹] | Elec. [kJ mol⁻¹] | Refrig. [kJ mol⁻¹] |
|-------|----------|---------|---------|---------|---------|-------|-------|-------|-------|-------|-------|--------|----------------|-----------------|----------------|----------------|----------------|
| HT21  | HR10     | ethylene| water   | helium  | methane | oxygen| 0.011 | 0.021 | 0.930 | 0.026 | 0.013 | P     | 1      | 0                 | 0               | 0               | 0               | 0               |
| HT22  | HR10     | ethylene| helium  | methane | oxygen  | -     | 0.011 | 0.950 | 0.026 | 0.013 | -     | E     | 10     | 0                 | 0               | 0               | 10              | 14              |
| HT34  | HR10     | helium  | methane | oxygen  | -       | -     | 0.960 | 0.026 | 0.013 | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 5               |
| HT35  | HR10     | helium  | oxygen  | -       | -       | 0.986 | 0.014 | -     | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 5               |
| HT36  | HR10     | helium  | methane | oxygen  | -       | -     | 0.960 | 0.026 | 0.013 | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 5               |
| HT37  | HR10     | methane | oxygen  | -       | -       | 0.667 | 0.334 | -     | -     | -     | E     | 10     | 0                 | 0               | 5               | 8               |
| HT23  | HR11     | ethylene| helium  | water   | -       | 0.037 | 0.926 | 0.037 | -     | -     | F     | 1      | 0                 | 0               | 0               | 0               |
| HT24  | HR11     | ethylene| helium  | -       | -       | 0.038 | 0.962 | -     | -     | -     | E     | 1      | 0                 | 0               | 0               | 0               |
| HT25  | HR12     | ethylene| oxygen  | nitrogen| water   | -     | 0.095 | 0.048 | 0.762 | 0.095 | -     | F     | 1      | 0                 | 0               | 0               | 0               |
| HT26  | HR12     | ethylene| oxygen  | nitrogen| -       | -     | 0.105 | 0.053 | 0.842 | -     | -     | D     | 4      | 1                 | 0               | 5               | 4               |
| HT38  | BR43-44  | hydrogen| CO      | CO₂     | -       | 0.586 | 0.241 | 0.172 | -     | -     | A, D  | 42/1   | 17               | 0               | 19              | 0               |
| HT41  | BR43-44  | hydrogen| CO      | -       | -       | 0.708 | 0.292 | -     | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 8               |
| HT39  | BR45     | hydrogen| CO      | CO₂     | -       | 0.583 | 0.250 | 0.167 | -     | -     | A, D  | 42/1   | 17               | 0               | 19              | 0               |
| HT42  | BR45     | hydrogen| CO      | -       | -       | 0.700 | 0.300 | -     | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 8               |
| HT40  | BR46     | hydrogen| CO      | CO₂     | -       | 0.643 | 0.179 | 0.179 | -     | -     | A, D  | 42/1   | 19               | 0               | 19              | 0               |
| HT43  | BR46     | hydrogen| CO      | -       | -       | 0.783 | 0.217 | -     | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 7               |
| HT44  | BR43-46  | hydrogen| CO      | -       | -       | 0.952 | 0.048 | -     | -     | -     | E     | 10     | 0                 | 0               | 0               | 10              | 6               |
Table S6: Energy requirement for heat-integrated thermal separation by means of VRC. Only separations for which VRC is an efficient technique for heat integration are presented. VRC2 to VRC49 are taken from Ulonska et al.,"Electricity, Refrig.; Refrigeration, MTHF: 2-methyltetrahydrofuran, HMF: 2,5-hydroxymethylfurfural.

| Sep. | Reaction | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | x1     | x2     | x3     | x4     | Type | p [bar] | Heat. | Elec. |
|------|----------|---------|---------|---------|---------|--------|--------|--------|--------|------|--------|-------|-------|
| VRCBHT1 | BHR1 | DEM | ethanol | water | - | 0.020 | 0.939 | 0.041 | - | D | 9.9 | 0.027 | 6.3 |
| VRCBHT2 | BHR1 | DEM | ethanol | water | - | 0.026 | 0.974 | - | - | D | 14.8 | 0 | 29 |
| VRCBHT3 | BHR1 | DEM | ethanol | CO₂ | - | 0.957 | 0.021 | 0.021 | - | D | 1 | 5 | 5 |
| VRC2 | BR4, BR5 | water | ethanol | CO₂ | - | 0.231 | 0.769 | - | - | D | 1 | 5 | 5 |
| VRC4 | BR12 | water | dimethyl sulfoxide | - | - | 0.040 | 0.960 | - | - | D | 1 | 5 | 5 |
| VRC5 | BR8 | HMF | water | - | - | 0.018 | 0.982 | - | - | D | 1 | 5 | 5 |
| VRC9 | BR16 | furfurylalcohol | water | - | - | 0.500 | 0.500 | - | - | PSD | 1/10 | 4 | 52 |
| VRC11 | BR10 | ethanol | water | - | - | 0.029 | 0.971 | - | - | D | 1 | 1 | 18 |
| VRC12 | BR25 | ethyl levulinate | ethanol | - | - | 0.040 | 0.920 | 0.040 | - | F,D | 1 | 1 | 16 |
| VRC14 | BR26 | ethyl levulinate | ethanol | CO | - | 0.004 | 0.004 | 0.008 | 0.984 | D | 1 | 0 | 24 |
| VRC16 | BR28 | formic acid | water | ethanol | - | 0.004 | 0.008 | 0.988 | - | D | 5 | 0 | 15 |
| VRC17 | BR28 | ethanol | water | - | - | 0.992 | 0.008 | - | - | D | 1/10 | 19 | 4 |
| VRC19 | BR9 | formic acid | water | - | - | 0.050 | 0.950 | - | - | D | 9 | 0 | 15 |
| VRC21 | BR30 | formic acid | water | - | - | 0.188 | 0.983 | - | - | D | 9 | 0 | 15 |
| VRC24 | BR32 | formic acid | water | - | - | 0.003 | 0.997 | - | - | D | 9 | 0 | 15 |
| VRC27 | BR40 | formic acid | water | - | - | 0.007 | 0.993 | - | - | D | 9 | 0 | 15 |
| VRC31 | BR27 | ethanol | dioxane | - | - | 0.083 | 0.917 | - | - | D | 2 | 0 | 3 |
| VRC33 | BR29 | γ-valerolactone | water | CO₂ | - | 0.027 | 0.946 | 0.027 | - | F,D | 1 | 1 | 40 |
| VRC35 | BR31, BR33 | γ-valerolactone | γ-butyrolactone | water | CO₂ | 0.023 | 0.442 | 0.512 | 0.023 | F,D | 1 | 7 | 12 |
| VRC36 | BR31, BR33 | γ-valerolactone | γ-butyrolactone | water | CO₂ | 0.050 | 0.950 | - | - | D | 1 | 0 | 22 |
| VRC41 | BR37 | 2-butanone | methylene chloride | H₂ | - | 0.016 | 0.969 | 0.016 | - | F,D | 1 | 0 | 5 |
| VRC43 | BR39 | 2-butanone | methylene chloride | H₂ | - | 0.003 | 0.994 | 0.003 | - | F,D | 1 | 0 | 5 |
| VRC47 | BR35 | 2,3-butanediol | water | CO₂ | - | 0.019 | 0.944 | 0.037 | - | F,D | 1 | 1 | 15 |
| VRC49 | BR11 | fructose | water | - | - | 0.002 | 0.998 | - | - | F | 1/0.3 | 22 | 2 |
| VRC77 | HR4 | water | methanol | - | - | 0.500 | 0.500 | - | - | D | 1 | 1 | 5 |
| VRC78 | HR6 | methane | nitrogen | - | - | 0.75 | 0.25 | - | - | D | 1/10 | 0 | 10 |
| VRC79 | HR7 | ethanol | water | hydrogen | CO | 0.092 | 0.092 | 0.543 | 0.272 | F,P,S,D | 1/10 | 1 | 52 |
| VRC80 | HR8/9 | ethanol | water | - | - | 0.019 | 0.981 | - | - | PSD | 1/10 | 1 | 2 |
Table S7: Energy requirement for concentration increase is presented associated with the respective reactions. BT6, VRC6, BT22, VRC22, BT25, VRC25, BT28, VRC28, BT48, and VRC48 taken from Ulonska et al.\textsuperscript{1} Heat.: Heating, Cool.: Cooling, Elec.: Electricity, HMF: 2,5-hydroxymethylfurfural.

| Sep. | Reaction | Target R. | Comp. 1 | Comp. 2 | Comp. 3 | x1  | x2  | x3  | Type | p | Heat. [kJ mol\textsuperscript{-1}] | Cool. [kJ mol\textsuperscript{-1}] | Elec. [kJ mol\textsuperscript{-1}] |
|------|----------|-----------|---------|---------|---------|-----|-----|-----|------|---|----------------------------------|-------------------------------|-------------------------------|
| BT6  | BR8      | BR9       | HMF     | water   | -       | 0.040 | 0.960 | -   | D    | 1 | 6                               | 6                             | 0                             |
|      | VRC6     |           |         |         |         | 0.045 | 0.955 | -   | VRC-D | 1 | 0                               | 6                             | 0                             |
| BT22 | BR30     | BR29      | levulinic acid | formic acid | water | 0.017 | 0.017 | 0.966 | D    | 1 | 611                             | 611                           | 0                             |
|      | VRC22    |           |         |         |         | 0.028 | 0.028 | 0.944 | VRC-D | 1 | 0                               | 0                             | 11                            |
| BT25 | BR32     | BR29      | levulinic acid | formic acid | water | 0.003 | 0.003 | 0.994 | D    | 1 | 108                             | 108                           | 0                             |
|      | VRC25    |           |         |         |         | 0.028 | 0.028 | 0.944 | VRC-D | 1 | 0                               | 0                             | 15                            |
| BT28 | BR40     | BR29      | levulinic acid | formic acid | water | 0.007 | 0.007 | 0.986 | D    | 1 | 251                             | 251                           | 0                             |
|      | VRC28    |           |         |         |         | 0.028 | 0.028 | 0.944 | VRC-D | 1 | 0                               | 0                             | 31                            |
| BT48 | BR35     | BR41      | 2,3-butanediol | water | CO\textsubscript{2} | 0.019 | 0.944 | 0.037 | D    | 1 | 39                              | 39                            | 0                             |
|      | VRC48    |           |         |         |         | 0.200 | 0.800 | -    | F,D  | 1 | 1                               | 1                             | 15                            |
| BT50 | BR11     | BR30      | fructose | water   | -       | 0.002 | 0.998 | -    | D    | 1 | 32                              | 32                            | 0                             |
|      | VRC50    |           |         |         |         | 0.018 | 0.982 | -    | VRC-E | 1 | 0                               | 0                             | 1                             |
| BT54 | BR11     | BR31      | fructose | water   | -       | 0.002 | 0.998 | -    | D    | 1 | 36                              | 36                            | 0                             |
|      | VRC51    |           |         |         |         | 0.048 | 0.952 | -    | VRC-E | 1 | 0                               | 0                             | 1                             |
| BT54 | BR11     | BR53      | fructose | water   | -       | 0.011 | 0.988 | -    | D    | 1 | 32                              | 32                            | 0                             |
|      | VRC53    |           |         |         |         | 0.011 | 0.988 | -    | VRC-E | 1 | 0                               | 0                             | 1                             |
Other Model Parameters

Tab. S8 gives an overview of the feedstock, auxiliary, and utility prices. Solvent and utility prices are only needed for PNFA.

Table S8: Feedstock, auxiliary and utility prices. †Average value ‡only needed for PNFA; MTHF: 2-methyltetrahydrofuran.

| Parameter                  | Unit                     | Value | Ref. | Assumption                                                                 |
|----------------------------|--------------------------|-------|------|-----------------------------------------------------------------------------|
| \( P_{\text{lignocell. biomass}} \) | USD/\( \text{kg}_{\text{biomass}} \) | 0.05  | 68   | -                                                                           |
| \( P_{\text{H}_2} \)             | USD/\( \text{kg}_{\text{H}_2} \) | 5.8†  | 69   | electrolysis using wind power only                                          |
| \( P_{\text{waste veg. oil}} \)  | USD/\( \text{kg}_{\text{oil}} \) | 0.93† | 70   | purified waste vegetable oil; conversion rate 0.9078 EUR = 1 USD†71          |
| \( P_{\text{CO}_2} \)           | USD/\( \text{kg}_{\text{CO}_2} \) | 0.04† | 72   | capture from steel plant exhaust gases                                      |
| \( P_{\text{water}} \)‡         | USD/\( \text{kg}_{\text{water}} \) | 0.0005| 73   | -                                                                           |
| \( P_{\text{dimethyl sulfoxide}} \)‡ | USD/\( \text{kg}_{\text{dimethyl sulfoxide}} \) | 1.48  | 74   | -                                                                           |
| \( P_{\text{MTHF}} \)‡         | USD/\( \text{kg}_{\text{MTHF}} \) | 7.5   | 75   | -                                                                           |
| \( P_{\text{methylene chloride}} \)‡ | USD/\( \text{kg}_{\text{methylene chloride}} \) | 0.55  | 76   | -                                                                           |
| \( P_{\gamma-\text{butyrolactone}} \)‡ | USD/\( \text{kg}_{\text{GBL}} \) | 1.417 | 77   | -                                                                           |
| \( P_{1,4-\text{dioxane}} \)‡ | USD/\( \text{kg}_{\text{dioxane}} \) | 2.70  | 78   | -                                                                           |
| \( P_{\text{cooling water}} \)‡ | USD/\( \text{m}^3_{\text{water}} \) | 0.065 | 79   | -                                                                           |
| \( P_{\text{steam}} \)‡         | USD/\( \text{ton}_{\text{steam}} \) | 9.5   | 79   | -                                                                           |
| \( P_{\text{electricity}} \)‡   | USD/\( \text{kWh}_{\text{elec}} \) | 0.075 | 79   | fuel production uses grid electricity                                       |
| \( P_{\text{refrigeration}} \)‡ | USD/\( \text{kWh}_{\text{refrig}} \) | 0.12  | 79   | -                                                                           |
| \( P_{\text{waste}} \)‡         | USD/\( \text{kg}_{\text{waste}} \) | 0.0004| 80   | -                                                                           |

Furthermore, Tab. S9 summarizes the GWP-related parameters used in PNFA for all main feedstocks. These rely on the energy demand of the upstream chains and do not account for any transportation-related aspects. Finally, the composition of the two types of biomass, lignocellulosic biomass and waste vegetable oil, is given in Tab. S11 along with the representative molecules that are used in the modeling.
Table S9: GWP-related parameters of all main feedstocks used in PNFA.

| Parameter                        | Unit       | Value | Ref  | Assumption                                      |
|----------------------------------|------------|-------|------|------------------------------------------------|
| gwp\text{heat}                   | $^{g}$CO$_2$,eq / MJ$_{fuel}$ | 86    | 81   | German industry mix (2020)                      |
| gwp\text{elec}                   | $^{g}$CO$_2$,eq / MJ$_{fuel}$ | 152   | 81   | German industry mix (2020)                      |
| gwp\text{refrig}                 | $^{g}$CO$_2$,eq / MJ$_{fuel}$ | 179   | 81   | propane (2005)                                  |
| gwp\text{ignocell. biomass}      | $^{k}$CO$_2$,eq / kg$_{biomass}$ | 0     | 81   | residual biomass                                |
| gwp\text{waste veg. oil}         | $^{k}$CO$_2$,eq / kg$_{oil}$ | 0.18  | 82   | same GWP as for extraction and refining of fresh rapeseed oil |
| gwp\text{CO}_2                   | $^{k}$CO$_2$,eq / kg$_{CO}_2$ | 0.033 | 81,83| energy demand of carbon capture; German electricity mix (2020) |
| gwp\text{H}_2                    | $^{k}$CO$_2$,eq / kg$_{H}_2$ | 0.2556| 81,84| energy demand of electrolysis; off-shore wind power (2020) |

Additionally, other economic parameters relevant to RNFA and PNFA investment cost calculations are given in Tab. S10.

Table S10: Economic Parameters for RNFA and PNFA.

| Parameter | Unit | Value | Ref |
|-----------|------|-------|-----|
| interest rate $ir$ | yr$^{-1}$ | 0.08  | -   |
| plant run time $t$  | year | 10    | -   |
| CEPCI (2010)        | -    | 550.8 | 85  |
| CEPCI (2016)        | -    | 541.7 | 85  |
| Inv$_{11}$          | -    | 7000  | 79  |
| Inv$_{21}$          | -    | 0.68  | 79  |
| Inv$_{1g}$          | -    | 36000 | 79  |
| Inv$_{2g}$          | -    | 0.62  | 79  |

Table S11: Biomass composition and representative molecules used in RNFA and PNFA. Data of lignocellulosic biomass is taken from Voll$^{86}$ and Ulonska et al.$^{1}$

| Parameter                  | Lower bound [mol-%] | Upper bound [mol-%] | representative molecule |
|----------------------------|---------------------|---------------------|------------------------|
| Lignocellulosic biomass    |                     |                     |                        |
| cellulose                  | 0.40                | 0.75                | C$_6$H$_{10}$O$_5$     |
| hemicellulose              | 0.16                | 0.32                | C$_5$H$_{10}$O$_5$     |
| lignin                     | 0.09                | 0.23                | C$_{10}$H$_{12}$O$_3$  |
| Waste vegetable oil        |                     |                     |                        |
| Triglycerides              | 1.00                | 1.00                | C$_{57}$H$_{104}$O$_6$ |

13
Performance Curve of the Linear Combination

This section presents a derivation of the performance curve of the linear combination seen in Figure 4 of the main text. The two performance criteria in RNFA are cost and carbon loss (CL). At a fleet level, the overall production volume can be either covered by several identical hybrid plants, or by a combination of plants that either represent the minCL ($n_{\text{minCL}}$) or the minCost ($n_{\text{minCost}}$) design.

The overall performance of the linear combination is determined from the performances of minCL and minCost and their plant fraction $\lambda_{\text{minCost}} = \frac{n_{\text{minCost}}}{n_{\text{all plants}}} = 1 - \frac{n_{\text{minCL}}}{n_{\text{all plants}}} = 1 - \lambda_{\text{minCL}}$.

The specific production cost of the fleet, $\text{Cost}_{lc}$, can be determined by linear interpolation using the plant fractions $\lambda$,

$$\text{Cost}_{lc} = \frac{\text{TAC}_{\text{all plants}}}{\alpha \cdot n_{\text{all plants}}} = \frac{n_{\text{minCost}} \cdot \text{TAC}_{\text{minCost}} + n_{\text{minCL}} \cdot \text{TAC}_{\text{minCL}}}{\alpha \cdot n_{\text{all plants}}} = \lambda_{\text{minCost}} \cdot \text{Cost}_{\text{minCost}} + \lambda_{\text{minCL}} \cdot \text{Cost}_{\text{minCL}}.$$  \hspace{1cm} (S1)

with TAC being the total annual costs and $\alpha$ representing the fixed production volume of each plant in MJ per year. The carbon loss of the linear combination $\text{CL}_{lc}$ cannot be derived from a simple linear interpolation. Instead, it is calculated as follows,

$$\text{CL}_{lc} = \frac{\#C_{\text{lost, all plants}}}{\#C_{\text{input, all plants}}} = \frac{n_{\text{minCost}} \cdot \#C_{\text{lost, minCost}} + n_{\text{minCL}} \cdot \#C_{\text{lost, minCL}}}{n_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + n_{\text{minCL}} \cdot \#C_{\text{input, minCL}}} \quad \text{= } \lambda_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input, minCL}} \quad \text{(S3)}$$

$$\text{CL}_{lc} = \frac{n_{\text{all plants}} (\lambda_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input, minCL}})}{\#C_{\text{input, all plants}}} \quad \text{= } \frac{\lambda_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input, minCL}}}{\lambda_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input, minCL}}} \quad \text{(S4)}$$

$$= 1 - \frac{\lambda_{\text{minCost}} \cdot \#C_{\text{fuel, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{fuel, minCL}}}{\lambda_{\text{minCost}} \cdot \#C_{\text{input, minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input, minCL}}} \quad \text{(S5)}$$

$$= 1 - \frac{\text{CL}_{\text{minCost}} + \text{CL}_{\text{minCL}}}{\text{CL}_{\text{minCost}} + \text{CL}_{\text{minCL}}}.$$
Since the capacity of each plant is fixed to $\alpha$ and the same fuel is considered at both minCL and minCost, at each plant the same number of carbon atoms is put into the fuel, i.e., $\#C_{\text{fuel}, \text{minCL}} = \#C_{\text{fuel}, \text{minCost}} = \#C_{\text{fuel}}$. Thus, Eq. S3 can be further simplified to

$$
\text{CL}_{lc} = 1 - \frac{\#C_{\text{fuel}}}{\lambda_{\text{minCost}} \cdot \#C_{\text{input}, \text{minCost}} + \lambda_{\text{minCL}} \cdot \#C_{\text{input}, \text{minCL}}}
$$

(S7)

$$
= 1 - \frac{1}{\frac{\lambda_{\text{minCost}} \cdot \#C_{\text{input}, \text{minCost}}}{\#C_{\text{input}, \text{minCost}} - \#C_{\text{lost}, \text{minCost}}} + \frac{\lambda_{\text{minCL}} \cdot \#C_{\text{input}, \text{minCL}}}{1 - \#C_{\text{input}, \text{minCL}} - \#C_{\text{lost}, \text{minCL}}}}
$$

(S8)

$$
= 1 - \frac{1}{\frac{\lambda_{\text{minCost}}}{1 - \text{CL}_{\text{minCost}}} + \frac{\lambda_{\text{minCL}}}{1 - \text{CL}_{\text{minCL}}}}.
$$

(S9)

Cost$_{lc}$ and CL$_{lc}$ are calculated for different $\lambda$ values using Eqs. S2 and S9 as well as the respective minCL and minCost values from RNFA (PNFA). For RNFA, they are plotted in Fig. 4 (dashed curve) of the main text and for PNFA, the corresponding performance curve is seen in Fig. S3 (dashed curve) of the next section.

**Cost and CL Optimization Using PNFA**

Similar to RNFA, PNFA results of CL and cost optimization are presented as Pareto fronts in Fig. S2 sorted by their respective optimal production types. Like in RNFA, FAME and uFAME obtain favorable performances while the performance of other products, e.g., DEM, has worsened relatively to the other fuels. In the following, first, the deviations between RNFA and are briefly explained. Then, it is discussed whether the synergies of hybrid designs discovered in RNFA are visible in PNFA.

In contrast to RNFA, PNFA gives a more detailed cost analysis that also includes utility costs and investment costs of downstream processing units. Thus, the production costs of PNFA, Cost$_{\text{PNFA}}$, are higher than those calculated by RNFA, Cost$_{\text{RNFA}}$.

The environmental objective, CL, is calculated in the same way in both RNFA and PNFA. Nevertheless, for many fuels, the more detailed analysis of PNFA leads to small
Figure S2: PNFA results of CL and cost optimization with Pareto fronts for each considered fuel product sorted by the active production types. Every point represents a Pareto-optimal pathway design for the considered fuel with ethanol as benchmark in every graph (△). The data points are connected by curves to guide the eye.

*: 2-MF is produced via BR90, BR91 without the use of H\textsubscript{2} directly from cellulose. Hence, even though biomass is pretreated, no biochemical pathways are present. For simplicity, it is still considered to be a BC-based route.

additional carbon losses. For example, the downstream processing steps of FAME, uFAME, γ-valerolactone, and DMF production are associated to small carbon losses. Furthermore, in PNFA, syngas fermentation steps, HR8 and HR9, are linked by the separation of the same solvent phase and can thus only be activated jointly. Due to the additional yield losses of HR9, a higher CL is determined for ethanol and fuels that require ethanol as intermediate.

Although in PNFA higher costs and carbon losses are estimated, the optimal pathway designs are typically similar to those of RNFA (cf. Tab. S12 - S15). In particular, PNFA results confirm that e-based feedstocks are preferred at minCL whereas biomass is favorable at minCost.

Exceptions concern routes that only require small amounts of H\textsubscript{2}. In V-routes, for example, e-based methanol synthesis is preferred in PNFA even at minCost. This is due to the fact that
only little methanol is needed and thus, the additional investment costs of implementing a
gasification step with subsequent gas cleaning to produce methanol from TC-routes is higher
for the given production capacity than the savings made from using a cheaper raw material.
Similar effects are visible for DMF production that requires H₂ in a hydrogenation step.

Figure S3: Pareto front of ethanol determined with PNFA (dotted curve) and comparison
to linear combination of plants (dashed curve). On the right, optimal pathway designs are
shown for the point of minimal cost (minCost), the point of minimal carbon loss (minCL) as
well as one exemplary hybrid design in the middle section of the Pareto front. For simplicity,
solvent separation or recycle steps are not visualized.

Fig. S3 shows the Pareto front for ethanol, the optimal pathway designs at minCost and
minCL, as well as a hybrid design in the middle of the Pareto front. The linear combination
metric manifests as a nonlinear curve in the Pareto graph (cf. previous section for derivation).
By comparing the Pareto front to the linear combination curve, it can be seen that the hybrid
designs show synergies. This is due to the efficient utilization of the hemicellulose fraction
and the CO₂ emitted during fermentation. In contrast, lignin gasification, which is optimal
in RNFA, is only activated in one hybrid design, next to the minCL design, in PNFA (cf.
Tab. S16), as in all other cases, the additional investment costs and the costly gas cleaning
leads to the exclusion of the route. When examining each integration option separately, it
is found that the utilization of CO₂ emitted during glucose fermentation generally leads
to better performances than hydrolysis and fermentation of hemicellulose. No additional investment costs are needed for CO₂ utilization neither does it require any additional utility costs, thus rendering it a promising low-cost CL-reduction option, especially in combination with hemicellulose hydrolysis and fermentation that provides additional CO₂.

**Active Fluxes**

Tab. S12 (alcohols, alkanes, furans, ketones) and Tab. S13 (esters, ethers) present all the active fluxes of RNFA. The pathway designs are categorized by the main feedstocks they utilize, i.e. e-based hydrogen (E), waste vegetable oil (V), lignocellulosic biomass by means of thermochemical pathways (TC), and/or lignocellulosis-based by means of biochemical pathways (BC).

Tab. S14 (alcohols, alkanes, furans) and Tab. S15 (esters, ketones, ethers) give an overview of the active fluxes of PNFA at all points of the Pareto front for all fuel products when carbon loss and cost are the objectives.

When PNFA is optimized for cost ($\text{Cost}_{\text{PNFA}}$) and global warming potential (GWP), the fluxes shown in Tab. S16 (alcohols, alkanes, furans, ketones) and S17 (esters, ethers) are activated.
Table S12: Active reaction fluxes in RNFA for all points of the Pareto curve of alcohols, alkanes, furans, and ketones. Cost \((Cost_{RNFA})\) and carbon loss (CL) are taken as objectives.

| Fuel      | min Cost (1) | 2       | 3       | 4       | 5       | min CL (6) |
|-----------|--------------|---------|---------|---------|---------|------------|
| alcohols  |              |         |         |         |         |            |
| methanol  | TC (BR43, HR5) | E, TC (BR43, HR4, HR5) | E, TC (BR43, HR4, HR5) | E, TC (BR43, HR4, HR5) | E, TC (BR43, HR4, HR5) | E (HR4) |
| ethanol   | BC (BR1, BR5, BR6) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, HR8) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, HR8) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, HR8) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, HR8, HR9) | E (HR8) |
| iso-butanol | BC (BR1, BR5, BR38) | BC (BR1, BR5, BR38) | BC (BR1, BR5, BR38) | BC (BR1, BR5, BR38) | BC (BR1, BR5, BR38) | BC (BR1, BR5, BR38) |
| alkanes   |              |         |         |         |         |            |
| methane   | TC (BR43, HR3) | TC, E (BR43, HR2, HR3) | TC, E (BR43, HR2, HR3) | TC, E (BR43, HR2, HR3) | TC, E (BR43, HR2, HR3) | E (HR2, HR3) |
| FT-gasoline | TC (BR43, HR30) | TC, E (BR43, HR2, HR30) | TC, E (BR43, HR2, HR30) | TC, E (BR43, HR2, HR30) | TC, E (BR43, HR2, HR30) | E (HR2, HR30) |
| FT-diesel | TC (BR43, HR29, HR32) | TC, E (BR43, HR2, HR29, HR32) | TC, E (BR43, HR2, HR29, HR32) | TC, E (BR43, HR2, HR29, HR32) | TC, E (BR43, HR2, HR29, HR32) | E (HR2, HR29, HR32) |
| furans    |              |         |         |         |         |            |
| 2-MF      | BC, TC (BR1, BR5, BR11, BR12, BR19, BR46, BR72) | BC, TC (BR1, BR5, BR11, BR12, BR19, BR46, BR72) | BC, TC (BR1, BR5, BR11, BR12, BR15, BR16, BR19, BR46, BR72) | BC, TC (BR1, BR5, BR11, BR12, BR15, BR16, BR19, BR46, BR72) | BC, TC (BR1, BR5, BR11, BR12, BR15, BR16, BR19, BR46, BR72) | BC, TC (BR1, BR5, BR11, BR12, BR15, BR16, BR19, BR46, BR72) |
| DMF       | BC, TC (BR1, BR5, BR11, BR12, BR46, BR58) | BC, TC (BR1, BR5, BR11, BR12, BR46, BR58) | BC, TC (BR1, BR5, BR11, BR12, BR45, BR46, BR58) | BC, TC (BR1, BR5, BR11, BR12, BR45, BR46, BR58) | BC, TC (BR1, BR5, BR11, BR12, BR45, BR46, BR58) | BC, TC (BR1, BR5, BR11, BR12, BR45, BR46, BR58) |
| ketones   |              |         |         |         |         |            |
| 2-butanone | BC (BR1, BR5, BR35, BR41) | BC (BR1, BR5, BR35, BR41) | BC (BR1, BR5, BR35, BR41) | BC (BR1, BR5, BR35, BR41) | BC (BR1, BR5, BR35, BR41) | BC (BR1, BR5, BR35, BR41) |
Table S13: Active reaction fluxes in RNFA for all points of the Pareto fronts of esters and ethers. Cost ($Cost_{RNFA}$) and carbon loss (CL) are taken as objectives.

| Fuel | min Cost (1) | 2 | 3 | 4 | 5 | min CL (6) |
|------|--------------|---|---|---|---|------------|
| ester |              |   |   |   |   |            |
| ethyl levulinate | BC (BR1, BR5, BR6, BR11, BR12, BR26) | BC (BR1, BR4, BR5, BR6, BR7, BR11, BR12, BR26) | BC, TC (BR1, BR4, BR5, BR6, BR7, BR11, BR12, BR26, BR46, HR9) | BC, TC, E (BR1, BR4, BR5, BR7, BR11, BR12, BR26, BR46, HR2, HR9) | BC, TC, E (BR1, BR4, BR5, BR7, BR11, BR12, BR26, BR46, HR2, HR9) | BC, TC, E (BR1, BR4, BR5, BR7, BR11, BR12, BR26, BR46, HR9) |
| γ-valerolactone | BC (BR1, BR5, BR11, BR29, BR30) | BC (BR1, BR5, BR9, BR11, BR12, BR29) | BC (BR1, BR5, BR9, BR11, BR12, BR29) | BC (BR1, BR5, BR9, BR11, BR12, BR29) | BC (BR1, BR5, BR9, BR11, BR12, BR29) | BC (BR1, BR5, BR9, BR11, BR12, BR29) |
| FAME | TC, V (BR43, BHR2b, HR5) | E, V (BHR2b, HR4) | E, V (BHR2b, HR4) | E, V (BHR2b, HR4) | E, V (BHR2b, HR4) | E, V (BHR2b, HR4) |
| uFAME | BC, TC, V (BR1, BR5, BR6, BR43, BHR2b, BHR3, HR5, HR11) | BC, E, V (BR1, BR5, BR6, BHR2b, BHR3, HR4, HR11) | BC, E, V (BR1, BR5, BR6, BHR2b, BHR3, HR4, HR11) | BC, E, V (BR1, BR4, BR5, BR6, BHR, HR11) | BC, E, V (BR1, BR4, BR5, BR6, BHR, HR11) | BC, E, V (BR1, BR4, BR5, BR6, BHR, HR11) |
| ether |              |   |   |   |   |            |
| DME | TC (BR43, HR16) | TC (BR43, HR2, HR17) | TC, E (BR43, HR16, HR17) | TC, E (BR43, HR2, HR17) | TC, E (BR43, HR2, HR17) | E (HR2, HR17) |
| DMM | TC (BR43, HR5, HR18, HR21) | TC, E (BR43, HR4, HR5, HR18, HR21) | TC, E (BR43, HR4, HR5, HR18, HR21) | TC, E (BR43, HR4, HR5, HR18, HR21) | TC, E (BR43, HR4, HR5, HR18, HR21) | E (HR4, HR18, HR21) |
| DEM | BC, TC (BR1, BR5, BR6, BR46, BHR1) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, BHR1) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, BHR1, HR8) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, BHR1, HR8) | BC, TC, E (BR1, BR4, BR5, BR6, BR7, BR46, BHR1, HR8) | E (BHR1, HR8) |
| OMDME | TC (BR43, HR5, HR18, HR20, HR25) | TC (BR43, HR4, HR5, HR18, HR20, HR25) | TC (BR43, HR4, HR5, HR18, HR20, HR25) | TC (BR43, HR4, HR5, HR18, HR20, HR25) | TC (BR43, HR4, HR5, HR18, HR20, HR25) | E (HR4, HR18, HR20, HR25) |
| OMDEE | BC, TC (BR1, BR5, BR6, BR43, BHR1, HR5, HR18, HR20, HR26) | BC, TC (BR1, BR5, BR6, BR45, BR46, BHR1, HR4, HR5, HR18, HR20, HR26) | BC, TC (BR1, BR5, BR6, BR45, BR46, BHR1, HR4, HR5, HR18, HR20, HR26) | BC, TC (BR1, BR5, BR6, BR45, BR46, BHR1, HR4, HR5, HR18, HR20, HR26) | BC, TC (BR1, BR5, BR6, BR45, BR46, BHR1, HR4, HR5, HR18, HR20, HR26) | E (BHR1, HR4, HR8, HR18, HR20, HR26) |
Table S14: Active reaction fluxes in PNFA for all points of the Pareto fronts of alcohols, alkanes, and furans. Cost ($Cost_{PNFA}$) and carbon loss (CL) are optimized. *: biomass is fractionated but no subsequent hydrolysis or fermentation occurs; for simplicity, it is still counted to the BC-route, even though no biochemical reaction occurs.

| Fuel    | min Cost (1) | 2           | 3           | 4           | 5           | min CL (6) |
|---------|--------------|-------------|-------------|-------------|-------------|------------|
| **alcohols** |              |             |             |             |             |            |
| methanol | TC (HR5, BR43, HT8, HT38) | TC, E (HR4, HR5, BR43, HT6, HT7, HT8, HT38, HT44) | TC, E (HR4, HR5, BR43, HT6, HT7, HT8, HT38, HT44) | TC, E (HR4, HR5, BR43, HT6, HT7, HT8, HT38, HT44) | E (HR4, HT6, HT7) | E (HR4, HT6, HT7) |
| ethanol  | BC (BR1, BR5, BR6, VRC2) | BC, E (HR2, HR8, HR9, BR1, BR4, BR5, BR6, BR7, VRC2, HT2, HT3, HT12, HT13, HT14) | BC, E (HR2, HR8, HR9, BR1, BR4, BR5, BR6, BR7, VRC2, HT2, HT3, HT12, HT13, HT14) | BC, E (HR2, HR8, HR9, BR1, BR4, BR5, BR6, BR7, VRC2, HT2, HT3, HT12, HT13, HT14) | E (HR2, HR8, HR9, BR1, BR4, BR5, BR6, BR7, BR46, BT2, HT2, HT3, HT12, HT13, HT14, HT40) | E (HR2, HR8, HR9, HT2, HT3, HT12, HT13, VRC HT14) |
| iso-butanol | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) |
| **alkanes** |              |             |             |             |             |            |
| methane  | TC (HR3, BR43, HT4, HT38) | TC, E (HR1, HR3, BR43, HT1, HT4, HT38) | TC, E (HR1, HR3, BR43, HT1, HT4, HT38) | TC, E (HR1, HR3, BR43, HT1, HT4, HT38) | E (HR2, HR3, HT2, HT3, HT4) |            |
| **furans** |              |             |             |             |             |            |
| 2-MF     | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) |
| DMF      | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) | BC, E (BR1, BR5, BR8, BR11, BR12, BR58, BT3, BT4, BT5, BT57, BT58, VRC49) |
Table S15: Active reaction fluxes in PNFA for all points of the Pareto fronts of esters, ketones, and ethers. Cost \((\text{Cost}_{PNFA})\) and carbon loss (CL) are optimized.

| Fuel          | min Cost (1) | 2 | 3 | 4 | 5 | min CL (6) |
|---------------|--------------|---|---|---|---|------------|
| esters        |              |   |   |   |   |            |
| ethyl levulinate | BC (BR1, BR5, BR6, BR8, BR26, BT2, BT5, BT14) | BC (BR1, BR4, BR5, BR7, BR8, BR26, BT2, BT5, BT14) | BC, E (HR8, HR9, BR1, BR4, BR5, BR6, BR7, BR8, BR26, BT2, BT5, BT14, HT12, HT13, HT14) | BC, E (HR8, HR9, BR1, BR4, BR5, BR6, BR8, BR15, BR16, BR25, BR26, BT2, BT5, BT14, HT12, HT13, HT14) | BC, E (HR8, HR9, BR1, BR4, BR5, BR6, BR7, BR11, BR12, BR26, BT2, BT3, BT4, BT14, VRC49, HT12, HT13, HT14) |
| γ-valerolactone | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR8, BR9, BR29, BT6, BT33) | BC (BR1, BR5, BR8, BR9, BR29, BT6, BT33) | BC (BR1, BR5, BR11, BR29, BR30, BT33, VRC22, VRC50) | BC (BR1, BR5, BR11, BR29, BR30, BT33, VRC22, VRC50) |
| FAME          | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) |
| uFAME         | V, E, BC (HR4, HR11, BR1, BR5, BR6, BHR2b, BHR3, BHT6, BHT7, BT2, BT6, HT7, HT23, HT24) | V, E, BC (HR4, HR11, BR1, BR4, BR5, BR6, BHR2b, BHR3, BHT6, BHT7, BT2, BT6, HT7, HT23, HT24) | V, E, BC (HR4, HR11, BR1, BR5, BR8, BR9, BR29, BT6, HT7) | V, E, BC (HR4, HR11, BR1, BR5, BR8, BR9, BR29, HT6, HT7) | V, E, BC (HR4, HR11, BR1, BR5, BR8, BR9, BR29, HT6, HT7) |
| ketones       |              |   |   |   |   |            |
| 2-butanone    | BC (BR1, BR5, BR35, BR41, BT44, BT48) | BC (BR1, BR5, BR35, BR41, BT44, BT48) | BC (BR1, BR5, BR35, BR41, BT44, BT48) | BC (BR1, BR5, BR35, BR41, BT44, BT48) | BC (BR1, BR5, BR35, BR41, BT44, BT48) |
| ethers        |              |   |   |   |   |            |
| DME           | TC (HR5, HR15, BR43, HT8, HT17, HT38) | TC, E (HR16, HR17, BR43, HT18, HT19, HT20, HT38, HT44) | TC, E (HR16, HR17, BR43, HT18, HT19, HT20, HT38, HT44) | TC, E (HR16, HT18, HT19, HT20, HT38, HT44) | E (HR16, HT18, HT19) |
| DEM           | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR4, BR5, BR6, BR7, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (HR2, HR7, BR1, BR4, BR5, BR6, BR7, BHR1, BHT1, BHT2, VRCBHT1, VRCBHT2, VRCBHT3, HT2, HT3, HT11) | E (HR2, HR8, HR9, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, HT2, HT3, HT12, HT13, HT14) | E (HR2, HR8, HR9, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, HT2, HT3, HT12, HT13, HT14) |
Table S16: Active reaction fluxes in the PNFA for all points of the Pareto fronts of alcohols, alkanes, furans, and ketones. Cost ($\text{Cost}_{\text{PNFA}}$) and global warming potential (GWP) are optimized. *: biomass is fractionated but no subsequent hydrolysis or fermentation occurs; for simplicity, it is still counted to the BC-route, even though no biochemical reaction occurs.

| Fuel     | min Cost (1) | 2                  | 3                  | 4                  | 5                  | min GWP (6) |
|----------|--------------|--------------------|--------------------|--------------------|--------------------|-------------|
| **alcohols** |              |                    |                    |                    |                    |             |
| methanol | TC (BR43, HR5, HT8, HT38) | TC, E (BR43, HR1, HR5, HR6, HT1, HT8, HT9, HT38, HT44) | TC, E (BR43, HR1, HR5, HR6, HT1, HT8, HT9, HT38) | TC, E (BR43, HR1, HR5, HR6, HT1, HT8, HT9, HT38) | E (HR1, HR4, HR6, HT1, HT6, HT7, HT9) | E (HR1, HR6, HT1, HT9) |
| ethanol  | BC (BR1, BR5, BR6, VRC2) | BC (BR1, BR5, BR6, VRC2) | BC (BR1, BR5, BR6, VRC2) | BC (BR1, BR5, BR6, VRC2) | BC (BR1, BR5, BR6, VRC2) | BC (BR1, BR5, BR6, VRC2) |
| iso-butanol | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) | BC (BR1, BR5, BR38, BT39) |
| **alkanes** |              |                    |                    |                    |                    |             |
| methane  | TC (BR43, HR3, HT4, HT38) | TC, E (BR43, HR1, HR3, HT1, HT4, HT38) | TC, E (BR43, HR1, HR3, HT1, HT4, HT38) | TC, E (BR43, HR1, HR3, HT1, HT4, HT38) | TC, E (BR43, HR1, HR3, HT1, HT4, HT38) | E (HR1, HT1) |
| **furans** |              |                    |                    |                    |                    |             |
| 2-MF     | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) | BC* (BR1, BR90, BR91, BT69, BT70, BT71) |
| DMF      | BC, E (BR1, BR5, BR8, BR58, BT5, BT57, BT58, VRC5) | BC, E (BR1, BR5, BR8, BR58, BT57, BT58, VRC5) | BC, E (BR1, BR5, BR8, BR58, BT57, BT58, VRC5) | BC, E (BR1, BR5, BR8, BR58, BT57, BT58, VRC5) | BC, E (BR1, BR5, BR8, BR58, BT57, BT58, VRC5) | BC, E (BR1, BR5, BR8, BR58, BT57, BT58, VRC5) |
| **ketones** |              |                    |                    |                    |                    |             |
| 2-butane | BC (BR1, BR5, BR35, BR41, BT44, VRC47) | BC (BR1, BR5, BR35, BR41, BT44, VRC47) | BC (BR1, BR5, BR35, BR41, BT44, VRC47) | BC (BR1, BR5, BR35, BR41, BT44, VRC47) | BC (BR1, BR5, BR35, BR41, BT44, VRC47) | BC (BR1, BR5, BR35, BR41, BT44, VRC47) |
Table S17: Active reaction fluxes in the PNFA for all points of the Pareto curve of esters and ethers. Cost ($Cost_{PNFA}$) and global warming potential (GWP) are optimized.

| Fuel    | min Cost (1) | 2     | 3     | 4     | 5     | min CL (6) |
|---------|--------------|-------|-------|-------|-------|------------|
| ester   |              |       |       |       |       |            |
| ethyl levulinate | BC (BR1, BR5, BR6, BR8, BR26, BT2, BT5, BT14) | BC (BR1, BR5, BR6, BR8, BR26, BT5, BT14, VRC2) | BC (BR1, BR5, BR6, BR8, BR26, BT5, BT14, VRC2) | BC (BR1, BR5, BR6, BR8, BR26, BT5, BT14, VRC2) | BC (BR1, BR5, BR6, BR8, BR26, VRC2, VRC5, VRC14) | BC (BR1, BR5, BR6, BR8, BR9, BR10, BT10, BT18, VRC2, VRC6, VRC11) |
| γ-valerolactone | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR33, VRC35, VRC36) | BC (BR1, BR5, BR33, VRC35, VRC36) |
| FAME    | V, E (HR4, BHR2b, BHT6, BHT7, HT6, HT7) | V, E (HR1, HR6, BHR2b, BHT6, BHT7, HT1, HT9) | V, E (HR1, HR6, BHR2b, BHT6, BHT7, HT1, HT9) | V, E (HR1, HR6, BHR2b, BHT6, BHT7, HT1, HT9) | V, E (HR1, HR6, BHR2b, BHT6, BHT7, HT1, HT9) | V, E (HR1, HR6, BHR2b, BHT6, BHT7, HT1, HT9) |
| uFAME   | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, BT2, HT6, HT7, HT23, HT24) | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, VRC2, HT6, HT7, HT23, HT24) | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, VRC2, HT6, HT7, HT23, HT24) | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, VRC2, HT6, HT7, HT23, HT24) | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, VRC2, HT6, HT7, HT23, HT24) | V, E, BC (BR1, BR5, BR6, HR4, HR11, BHR2b, BHR3, BHT6, BHT7, VRC2, HT6, HT7, HT23, HT24) |
| ether   |              |       |       |       |       |            |
| DME     | TC (BR43, HR5, HR15, HT8, HT17, HT38) | TC, E (BR43, HR16, HR17, HT18, HT19, HT20, HT38, HT44) | TC, E (BR43, HR16, HR17, HT18, HT19, HT20, HT38, HT44) | E (HR16, HT18, HT19) | E (HR1, HR6, HR15, HT16, HT1, HT9, HT17, HT18, HT19) | E (HR1, HR6, HR15, HT1, HT9, HT17) |
| DEM     | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) | BC, E (BR1, BR5, BR6, BHR1, VRCBHT1, VRCBHT2, VRCBHT3, VRC2) |
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