Kinetic modelling

A model FAME production system, with 6 species, triglyceride (tributyrin), diglyceride (dibutyrin), monoglyceride (monobutyrin), methanol, glycerol and fatty acid methyl ester (FAME) (methyl butyrate), denoted by species *i* = 1-6, respectively, is considered.

The 6 groups, CH_3, CH_2, CH, CH=CH, COO and OH, present are denoted by their secondary group number, p = 1, 2, 3, 6, 77 and 14, respectively[1].

There are 14 Tables constructed to demonstrate the UNIQUAC calculations for an estimation of activities of species in a biodiesel reaction system. Figure 1 illustrates the way the UNIQUAC calculation proceeds. The calculation involves evaluation of parameters using algebraic expressions and can be performed in spreadsheet.

Tables 1-4 present the input parameters. In addition, the operating temperature (in this case 343K) must be specified as an input. Tables 5 and 7-13 provide the calculation of dependent variables. Output results in terms of the activity coefficients are provided in Tables 6 and 14-15.

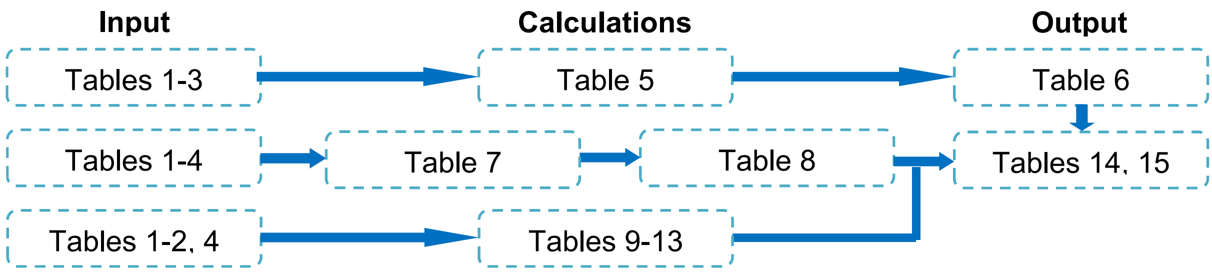

Figure 1. The UNIQUAC calculation sequence.

UNIQUACK calculation background

To account for the non-ideality of a mixture, the correlation between the activity of specie ([*i*]) and its concentration C_i is applied. The UNIQUAC contribution method outlined is used to calculate the activity coefficient γ_i of a specie *i*.

$$[i] = C_i \gamma_i \qquad \forall i \in nspc \qquad \text{equation 1}$$

The molecular activity coefficient (γ_i) of a specie *i* comprises of two parts, one part known as combinatorial part (γ_i^C) is contributed due to the effect of molecular size and shape predicted from constituent group sizes and shapes and the other part known as residual part (γ_i^R) reflects the effect of molecular interactions (equation 2). The total number of species is presented by *nspc*.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \forall i \in nspc \qquad \text{equation 2}$$

Using the mole fraction x_i, area fraction θ_i and volume or segment fraction Φ_i of specie *i*, γ_i^C is evaluated (equation 3).

The molecular van der Waals area and volume parameters, q_i and s_i are calculated as the sum of the group (p) van der Waals surface area and volume, Q_p and S_p, experimentally determined, respectively (equations 4-5).

$v_p^{(i)}$ is the number of p group present in molecule i and is always an integer. Equation 6 presents a group of parameters l_i used in equation 3.

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{x_i} + 5q_i\ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum_{i'}^{nspc} x_{i'}l_{i'} \qquad \forall i \in nspc$$

equation 3

$$\theta_i = \frac{x_i q_i}{\sum_{i'}^{nspc} x_{i'}q_{i'}} \qquad \Phi_i = \frac{x_i s_i}{\sum_{i'}^{nspc} x_{i'}s_{i'}} \qquad \forall i \in nspc$$

equation 4

$$q_i = \sum_p^g v_p^{(i)} Q_p \qquad s_i = \sum_p^g v_p^{(i)} S_p \qquad \forall i \in nspc$$

equation 5

$$l_i = 5(s_i - q_i) - (s_i - 1) \qquad \forall i \in nspc$$

equation 6

Equation 7 for the estimation of γ_i^R also requires a group residual activity coefficient Γ_p and another similar type in a reference solution containing only molecules of type i, $\Gamma_p^{(i)}$.

Γ_p and $\Gamma_p^{(i)}$ are related to the corresponding area parameters in equations 8-11.

$$\ln\gamma_i^R = \sum_p^g v_p^{(i)}\left(\ln\Gamma_p - \ln\Gamma_p^{(i)}\right) \qquad \forall i \in nspc$$

equation 7

$$\ln\Gamma_p = Q_p\left\{1 - \ln\left(\sum_m^g \theta_m \Psi_{m,p}\right) - \sum_m^g \frac{\theta_m \Psi_{p,m}}{\sum_n^g \theta_n \Psi_{n,m}}\right\} \qquad \forall m,n,p \in g$$

equation 8

$$\theta_p = \frac{Q_p \times X_p}{\sum_p Q_p \times X_p}$$

equation 9

$$X_p = \frac{\sum_i v_p^{(i)} x_i}{\sum_i x_i \sum_p v_p^{(i)}}$$

equation 10

$$\ln\Gamma_p^{(i)} = Q_p\left\{1 - \ln\left(\sum_m^g \theta_m^{(i)} \Psi_{m,p}\right) - \sum_m^g \frac{\theta_m^{(i)} \Psi_{p,m}}{\sum_n^g \theta_n^{(i)} \Psi_{n,m}}\right\} \qquad \forall m,n,p \in g \quad and \quad \forall i \in nspc$$

equation 11

θ_p is the area fraction relating to a particular group *p* over the sum of all different groups in a given specie (equation 12).

It is calculated in the same manner as $\theta_p^{(i)}$, except that $X_p^{(i)}$ is the fraction of a group *p* amongst all groups within a specie *i.*

$$\theta_p^{(i)} = \frac{Q_p \times X_p^{(i)}}{\sum_p Q_p \times X_p^{(i)}} \qquad \text{equation 12}$$

The group interaction parameter $\Psi_{m,n}$ in a specie *i* is related to $a_{m,n}$ indicative of the energy of interaction between main groups *m* and *n* and the temperature of the mixture, *Te* (equation 13).

An extensive set of experimentally determined values of $a_{m,n}$ is provided in[1].

$$\Psi_{m,n} = \exp\left(-\frac{a_{m,n}}{Te}\right) \qquad \text{equation 13}$$

Table 1 presents the matrix of $v_p^{(i)}$ with the number of *p* group present in specie *i*. There is a total of *g* number of groups present in a total of *nspc* number of species. Thus, the $v_p^{(i)}$ matrix is a *g* × *nspc* matrix (6 × 6 matrix for the given biodiesel case).

Table 1. $v_p^{(i)}$ matrix of *p* group present in specie *i*

Specie	**1**	**2**	**3**	**4**	**5**	**6**
Group: 1	3	2	1	1	0	2
2	8	6	4	0	2	2
3	1	1	1	0	1	0
6	0	0	0	0	0	0
77	3	2	1	0	0	1
14	0	1	2	1	3	0

The group (*p*) van der Waals surface area and the volume parameters, Q_p and S_p, are shown in Table 2[1]. Table 3 shows a set of mole fractions of the species.

Table 2. Group (*p*) van der Waals surface area and volume parameters Q_p and S_p

Group	1	2	3	6	77	14
Q_p	0.848	0.54	0.228	0.867	1.2	1.2
S_p	0.9011	0.6744	0.4469	1.1167	1.38	1

Table 3. mole fraction x_i of specie *i*

Specie	1	2	3	4	5	6
x_i	0.0063	0.0106	0.0087	0.9226	0.0124	0.0394

Table 4 provides the binary energy of interaction $a_{m,n}$ between any two groups to be used as input for the calculation of the residual activity coefficient. The secondary groups, p = 1, 2, 3, 6, 77 and 14, corresponding to CH_3, CH_2, CH, CH=CH, COO and OH, respectively, are categorised into the main groups[1].

Table 4. Binary energy of interaction between two groups

Secondary group	1	2	3	6	77	14
1	0	0	0	86.02	387.1	986.5
2	0	0	0	86.02	387.1	986.5
3	0	0	0	86.02	387.1	986.5
6	-35.36	-35.36	-35.36	0	48.33	524.1
77	529	529	529	1397	0	88.63
14	156.4	156.4	156.4	457	190.3	0

The specie (*i*) van der Waals area, volume and group parameters, q_i, s_i and l_i, are calculated using equations 5-6, in Table 5. Sample calculations for q_i, s_i and l_i for specie 1 are shown in equations 14 – 16.

$$q_1 = (3 \times 0.848) + (8 \times 0.54) + (1 \times 0.228) + (0 \times 0.867) + (3 \times 1.2) + (0 \times 1.2) = 10.69$$
equation 14

$$s_1 = (3 \times 0.9011) + (8 \times 0.6744) + (1 \times 0.4469) + (0 \times 1.1167) + (3 \times 1.38) + (0 \times 1) = 12.69$$
equation 15

$$l_1 = 5 \times (12.6854 - 10.692) - (12.6854 - 1) = -1.72$$
equation 16

Table 5. Molecular van der Waals area, volume and group parameters, q_i, s_i and l_i

Specie	**1**	**2**	**3**	**4**	**5**	**6**
q_i	10.69	8.76	6.84	2.05	4.91	3.98
s_i	12.69	10.06	7.43	1.9	4.79	4.53
l_i	-1.72	-2.59	-3.48	-1.64	-4.36	-0.76

For a given mole fraction x_i of specie *i* in Table 3, the area fraction θ_i, volume or segment fraction Φ_i and the combinatorial activity coefficient γ_i^C of the specie *i* are evaluated using equations 3-4, in Table 6. Equations 17 – 19 show the calculations of Φ_i, θ_i and γ_i^C for specie 1.

$$\Phi_1 = \frac{0.00634 \times 12.685}{0.00634 \times 12.685 + 0.01057 \times 10.056 + 0.00873 \times 7.426 + 0.92262 \times 1.901 + 0.01238 \times 4.796 + 0.03936 \times 4.531} = 0.0359$$
equation 17

$$\theta_1 = \frac{0.00634 \times 10.692}{0.00634 \times 10.692 + 0.01057 \times 8.764 + 0.00873 \times 6.836 + 0.92262 \times 2.048 + 0.01238 \times 4.908 + 0.03936 \times 3.976} = 0.0291$$
equation 18

$$ln\gamma_1^c = ln\frac{0.0359}{0.00634} + 5 \times 10.692 \times ln\frac{0.0291}{0.0359} + (-1.7184) - \frac{0.0359}{0.0634} \times (0.00634 \times (-1.718) + 0.01057 \times (-2.598) + 0.00873 \times (-3.478) + 0.92262 \times (-1.636) + 0.01238 \times (-4.357) + 0.03936 \times (-0.756)) = -1.6868$$
equation 19

Table 6. Volume or segment fraction Φ_i, area fraction θ_i and combinatorial activity coefficient γ_i^C for a given mole fraction x_i of specie *i* in Table 3

Specie	**1**	**2**	**3**	**4**	**5**	**6**
Φ_i	0.0359	0.0474	0.0289	0.7819	0.0265	0.0795

θ_i	0.0291	0.0398	0.0256	0.8120	0.0261	0.0673
ln γ_i^C	-1.6868	-1.2782	-0.8598	-0.0057	-0.3758	-0.0225

For an operating temperature of 343K, Table 7 with group interaction parameter $\Psi_{m,n}$ in terms of $a_{m,n}$ in Table 4 using equation 13 is generated. Sample calculations for secondary group interaction parameters of group 1 interacting with group 6 ($\Psi_{1,6}$), and group 6 interacting with group 1 ($\Psi_{6,1}$) are shown in equations 20 – 21.

$$\Psi_{1,6} = \exp\left(-\frac{86.02}{343.15}\right) = 0.7783 \qquad \text{equation 20}$$

$$\Psi_{6,1} = \exp\left(-\frac{-35.36}{343.15}\right) = 1.1085 \qquad \text{equation 21}$$

Table 7. Secondary group interaction parameter $\Psi_{m,n}$

Secondary group	**1**	**2**	**3**	**6**	**77**	**14**
1	1.0000	1.0000	1.0000	0.7783	0.3237	0.0564
2	1.0000	1.0000	1.0000	0.7783	0.3237	0.0564
3	1.0000	1.0000	1.0000	0.7783	0.3237	0.0564
6	1.1085	1.1085	1.1085	1.0000	0.8686	0.2171
77	0.2140	0.2140	0.2140	0.0171	1.0000	0.7724
14	0.6340	0.6340	0.6340	0.2640	0.5743	1.0000

The steps for calculating the group residual activity coefficient Γ_p using equations 8-9 are shown in Table 8. Sample calculations for group 1 are shown in equations 22 – 26.

$$X_1 = \frac{0.0063\times3+0.0106\times2+0.0087\times1+0.9226\times1+0.0124\times0+0.0394\times2}{0.0063\times15+0.0106\times12+0.0087\times9+0.9226\times2+0.0124\times6+0.0394\times5} = 0.4341 \qquad \text{equation 22}$$

$$\theta_1 = \frac{0.848\times0.4341}{0.848\times0.4341+0.1044\times0.54+0.0157\times0.228+0\times0.867+0.0365\times1.2+0.4083\times1.2} = 0.3827 \text{ equation 23}$$

$$\sum_m^g \frac{\theta_m\Psi_{1,m}}{\sum_{n=1}^{g=last\ group}\theta_n\Psi_{n,m}} = \frac{0.3827}{0.7778}+\frac{0.0586}{0.7778}+\frac{0.0037}{0.7778}+\frac{0.0037}{0.7778}+\frac{0}{0.4817}+\frac{0.0147}{0.4821} = 0.6533 \text{ equation 24}$$

$\sum_m^g \theta_m \Psi_{m,1} = 0.3827 \times 1 + 0.0586 \times 1 + 0.037 \times 1 + 0 \times 1.1085 + 0.0455 \times 0.2140 + 0.5094 \times 0.6340 = 0.7778$ equation 25

$ln\Gamma_1 = 0.848 \times (1 - \ln(0.7778) - 0.6533) = 0.5072$ equation 26

Table 8. Constitution of group residual activity coefficient Γ_p

Group	**1**	**2**	**3**	**6**	**77**	**14**
X_p	0.4341	0.1044	0.0157	0.0000	0.0365	0.4083
θ_m	0.3827	0.0586	0.0037	0.0000	0.0455	0.5094
$\sum_m^g \frac{\theta_m \Psi_{p,m}}{\sum_n^g \theta_n \Psi_{n,m}}$	0.6533	0.6533	0.6533	0.9105	0.9075	1.3112
$\sum_m^g \theta_m \Psi_{m,p}$	0.7778	0.7778	0.7778	0.4817	0.4821	0.5697
$\ln \Gamma_p$	0.5072	0.3230	0.1364	0.7110	0.9864	0.3018

The van der Waals surface area parameter for a group p, Q_p, and the mole fraction of the group p amongst all groups within specie, $X_p^{(i)}$, are multiplied and the ratio of ($Q_p\ X_p^{(i)}$) for the group p to the sum of ($Q_p\ X_p^{(i)}$) over all groups within individual species is generated in Tables 9-10. This ratio provides the area fraction relating to a particular group p, $\theta_p^{(i)}$, within individual species to incorporate in equation 11.

Sample calculations for $X_p^{(i)}$ and $\theta_p^{(i)}$ for group 1 and specie 1 are shown in equations 27 – 28.

$X_1^{(1)} = \frac{3}{3+8+1+0+3+0} = 0.2$ equation 27

$\theta_1^{(1)} = \frac{0.848 \times 0.2}{0.848 \times 0.2 + 0.54 \times 0.5333 + 0.228 \times 0.067 + 0.867 \times 0 + 1.2 \times 0.3367 + 1.2 \times 0} = 0.2379$ equation 28

Table 9. Mole fraction of group p amongst all groups within each type of specie, $X_p^{(i)}$

Specie	**1**	**2**	**3**	**4**	**5**	**6**

Group: 1	0.2	0.1667	0.1111	0.5	0	0.4
2	0.5333	0.5	0.4444	0	0.3333	0.4
3	0.0667	0.0833	0.1111	0	0.1667	0
6	0	0	0	0	0	0
77	0.2	0.1667	0.1111	0	0	0.2
14	0	0.0833	0.2222	0.5	0.5	0

Table 10. Matrix of area fraction relating to a particular group *p* over the sum of all different groups in given specie, $\theta_p^{(i)}$

Specie	**1**	**2**	**3**	**4**	**5**	**6**
Group: 1	0.2379	0.1935	0.1240	0.4141	0	0.4266
2	0.4040	0.3697	0.3160	0	0.2200	0.2716
3	0.0213	0.0260	0.0334	0	0.0465	0
6	0	0	0	0	0	0
77	0.3367	0.2738	0.1755	0	0	0.3018
14	0	0.1369	0.3511	0.5859	0.7335	0

Table 11 presents individual values of $\sum_{m}^{g} \theta_m^{(i)} \Psi_{m,p}$ in equation 11 in a matrix form. Table 14 provides the group residual activity coefficient in a reference solution containing only molecules of type *i*, ln $\Gamma_p^{(i)}$, using the calculation steps given in Tables 11-13 and given Q_p in Table 2.

Sample calculations of $\theta_m^{(i)} \times \Psi_{p,m}$ for specie *i* = 1 are shown in equations 29 – 30 for groups *m* = 1, *p* = 2 and *m* = 2, *p* = 1. Also the calculations of $\sum_m^g \theta_m^{(i)} \Psi_{m,p}$ and $\sum_m^g \frac{\theta_m^{(i)} \Psi_{p,m}}{\sum_n^g \theta_n^{(i)} \Psi_{n,m}}$ for group 1 and specie 1 are shown in equations 31 – 32. A calculation of ln $\Gamma_{p=2}^{(i=1)}$ is shown in equation 33.

$$\theta_1^{(1)} \times \Psi_{2,1} = 0.2379 \times 1 = 0.2379 \qquad \text{equation 29}$$

$$\theta_2^{(1)} \times \Psi_{1,2} = 0.4040 \times 1 = 0.4040 \qquad \text{equation 30}$$

$$\sum_m^g \theta_m^{(1)} \Psi_{m,1} = 0.2379 \times 1 + 0.4040 \times 1 + 0.0213 \times 1 + 0 \times 1.1085 + 0.3367 \times 0.2140 + 0 \times 0.6340 = 0.7354 \qquad \text{equation 31}$$

$$\sum_m^g \frac{\theta_m^{(1)} \Psi_{1,m}}{\sum_{n=1}^{g=last\ group} \theta_n^{(1)} \Psi_{n,m}} = \frac{0.2379}{0.7354} + \frac{0.4040}{0.7354} + \frac{0.0213}{0.7354} + \frac{0.0000}{0.5220} + \frac{0.1090}{0.5514} + \frac{0.0000}{0.2975} = 1.0966 \qquad \text{equation 32}$$

ln $\Gamma_{p=2}^{(i=1)}$ = 0.54 (1 – ln(0.7354) -1.0996) = 0.1122 equation 33

Table 11. $\theta_m^{(i)} \times \Psi_{p,m}$ matrix for specie *i* = 1

Group p	**1**	**2**	**3**	**4**	**5**	**6**
Group m: 1	0.2379	0.2379	0.2379	0.2638	0.0509	0.1508
2	0.4040	0.4040	0.4040	0.4479	0.0865	0.2561
3	0.0213	0.0213	0.0213	0.0236	0.0046	0.0135
6	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
77	0.1090	0.1090	0.1090	0.2925	0.3367	0.1934
14	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 12. Calculation of $\sum_m^g \theta_m^{(i)} \Psi_{m,p}$

Group	**1**	**2**	**3**	**6**	**77**	**14**
Specie: 1	0.7354	0.7354	0.7354	0.5220	0.5514	0.2975
2	0.7346	0.7346	0.7346	0.4994	0.5432	0.3817
3	0.7335	0.7335	0.7335	0.4641	0.5304	0.5134
4	0.7855	0.7855	0.7855	0.4769	0.4705	0.6093
5	0.7315	0.7315	0.7315	0.4011	0.5075	0.7485
6	0.7628	0.7628	0.7628	0.5485	0.5278	0.2725

Table 13. Calculation of $\sum_{m}^{g} \frac{\theta_m^{(i)} \Psi_{p,m}}{\sum_{n}^{g} \theta_n^{(i)} \Psi_{n,m}}$

Groups	**1**	**2**	**3**	**6**	**77**	**14**
Specie: 1	1.0996	1.0996	1.0996	1.5303	0.8037	0.9225
2	0.9855	0.9855	0.9855	1.4049	0.9529	1.1567
3	0.7911	0.7911	0.7911	1.1514	0.9973	1.2831
4	0.5814	0.5814	0.5814	0.7931	0.8556	1.2958
5	0.4196	0.4196	0.4196	0.6166	0.8348	1.2109
6	1.1004	1.1004	1.1004	1.5114	0.7678	0.9087

Table 14. Group residual activity coefficient in a reference solution containing only molecules of type *i*, ln $\Gamma_p^{(i)}$

Groups	**1**	**2**	**3**	**6**	**77**	**14**
Specie: **1**	0.1762	0.1122	0.0474	0.1039	0.9499	1.5478
2	0.2738	0.1744	0.0736	0.2509	0.7889	0.9677
3	0.4400	0.2802	0.1183	0.5343	0.7642	0.4604
4	0.5597	0.3564	0.1505	0.8212	1.0780	0.2395
5	0.7573	0.4822	0.2036	1.1245	1.0121	0.0945
6	0.1445	0.0920	0.0388	0.0773	1.0456	1.6697

The activity coefficients of species for their given mole fractions in Table 3 are calculated in Table 15. Equations 34 – 35 show the calculations of lnγ_i^R and γ_i for specie 1.

$$ln\gamma_1^R = 3 \times (0.5072 - 0.1762) + 8 \times (0.3230 - 0.1122) + 1 \times (0.1364 - 0.0474) + 0 \times (0.7110 - 0.1039) + 3 \times (0.9864 - 0.9499) + 0 \times (0.3018 - 1.5478) = 2.8776 \quad \text{equation 34}$$

$$\gamma_1 = \exp(-1.6868 + 2.8776) = 3.2896 \quad \text{equation 35}$$

Table 15. Residual activity coefficient γ_i^R and the activity coefficient for a given mole fraction x_i of specie *i* in Table 11

Specie	**1**	**2**	**3**	**4**	**5**	**6**
ln γ_i^C	-1.6868	-1.2782	-0.8598	-0.0057	-0.3758	-0.0225
ln γ_i^R	2.8776	1.1501	0.1613	0.0097	0.2359	1.1281
γ_i	3.2896	0.8798	0.4973	1.0040	0.8695	3.0210

The intrinsic kinetic modelling is performed to decide a kinetic mechanism associated with rational assumptions, to best represent experimental data set on a reaction system. The UNIQUAC calculations are used to correlate the activities used in the rate equations with the concentration of species. Analytical integration of the concentration to time derivatives is undertaken as follows.

Start the computation at (t0, C0) and proceed with time (Figure 2). The calculation for the point 2 is shown in equation 36a-b. The activity coefficient at (t1, C1) is estimated using the UNIQUAC method, discussed above. The value of the rate of reaction of the given component at t = t2 is then calculated from the activity coefficient at t = t2 and the initial guesses of the kinetic parameters. Using the backward derivative method C2 at t2 is predicted in equation 36a. The forward derivative method is shown in equation 36b.

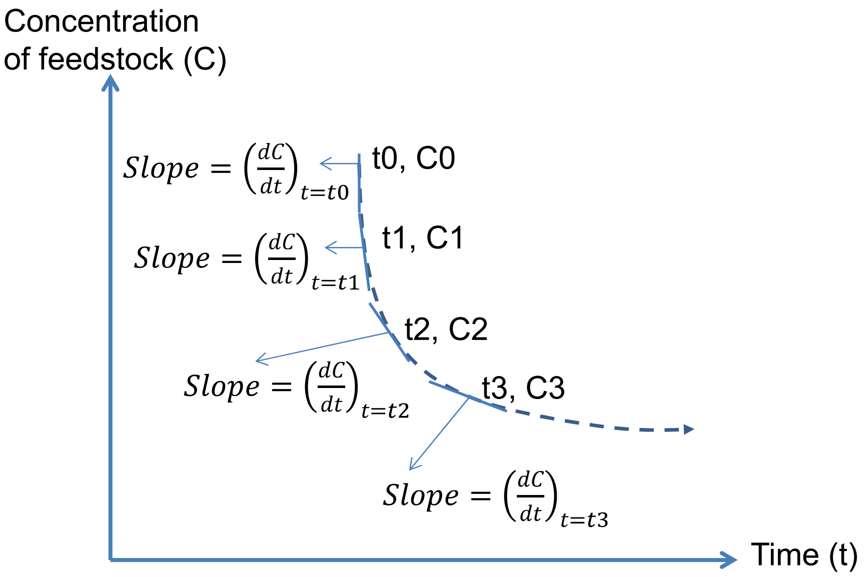

Figure 2. A generic reactant concentration vs. time profile.

$$C2 = C1 + (t2-t1)\left(\frac{dC}{dt}\right)_{t=t2} = C1 + (t2-t1)\times r_{t=t2} \qquad \text{equation 36a}$$

$r_{t=t2}$ = f(activity coefficient at t2 estimated from C2; initial guesses of kinetic parameters)

$$C2 = C1 + (t2-t1)\left(\frac{dC}{dt}\right)_{t=t1} = C1 + (t2-t1)\times r_{t=t1} \qquad \text{equation 36b}$$

$r_{t=t1}$ = f(activity coefficient at t1 estimated from C1; initial guesses of kinetic parameters)

Note that the value of the reaction rate *r* of a reactant is negative (as the concentration decreases with the reaction time) and the value of the formation rate *r* of a product is positive (as the concentration increases with the reaction time).

The kinetic rate expression for FAME is a summation of the kinetic rate expressions of Triglyceride, Diglyceride and Monoglyceride shown in equation 37, where the subscripts T, D, and M represent Triglyceride, Diglyceride and Monoglyceride respectively. The species are consumed, thus the negative sign is used to show that FAME is produced.

$$r_{FAME} = -(r_T + r_D + r_M) \qquad \text{equation 37}$$

The backward calculation method shown in equation 36a can be followed to obtain the consequent concentration points, e.g. C3 from C2: C3 = C2 + (t3-t2)× $r_{t=t3}$.

Once, all the concentration – time data points relevant to the experimental profile are predicted using the initial guesses of the kinetic parameters, the residual sum of the squared error (RSSQ) between the experimentally (e.g. $C1_{exp}$) and the computationally derived concentration (e.g. $C1_{calc}$) shown in equation 38, is minimised using an optimisation algorithm to obtain the optimal values of the kinetic parameters.

$$RSSQ = (C1_{exp} - C1_{calc})^2 + (C2_{exp} - C2_{calc})^2 + (C3_{exp} - C3_{calc})^2 + \ldots \qquad \text{equation 38}$$

A kinetic modelling framework shown so far can be implemented in a spreadsheet environment. The minimisation of RSSQ can be done using the EXCEL solver. The spreadsheet solutions for MgO and MgO-500 catalysts and surface reaction and methanol adsorption as rate limiting steps in ER mechanism are available as supplementary information.

Diffusion modelling

First the infinite dilution diffusion coefficients are calculated which represent the diffusion coefficient for 1 molecule of solute in pure solvent. This can be calculated for all binary combinations of components in the system using the Wilke and Chang correlation in equation 39[3].

$$Đ_{12}^{o} = 7.4\times10^{-8}\,\frac{(\phi_2 M_2)^{0.5}\,T}{\mu_2 V_1^{0.6}} \qquad \text{equation 39}$$

Where $Đ_{12}^{o}$ is the infinite dilution diffusion coefficient of solute 1 in solvent 2 ($cm^2\ s^{-1}$), ϕ_2 is an association constant, M_2 is the molecular mass ($g\ mol^{-1}$), T is the temperature (K), μ_2 is the viscosity (mPa s) and V_1 is the molar volume ($m^3\ mol^{-1}$).

Equations 40 – 41 show the calculations for $Đ_{1,2}^{o}$ and $Đ_{2,1}^{o}$. Input data are shown in Table 4 in the main paper.

$$Đ_{1,2}^{o} = 7.4\times10^{-8}\times\frac{(1\times1009\times0.233)^{0.5}\times(343.15)}{2.9466\times(303)^{0.6}} = 4.29\times10^{-6}\ cm^2\ s^{-1} \qquad \text{equation 40}$$

$$Đ_{2,1}^{o} = 7.4\times10^{-8}\times\frac{(1\times997.5\times0.303)^{0.5}\times(343.15)}{3.03\times(233)^{0.6}} = 5.53\times10^{-6}\ cm^2\ s^{-1} \qquad \text{equation 41}$$

The calculation of the diffusion coefficients, $Đ_{1,2}$ and $Đ_{2,1}$, of the biodiesel system for the mole fractions given in Table 6 in the main paper is shown in equations 42 – 44.

Each component's molar volume is converted into molecular volume assuming that the Avogadro's number, 6.023×10^{23} presents the number of molecules in 1 mole of the component. Assuming a hard spherical shape of each molecule, the molecular diameter of each component is estimated.

Size or diameter of tributyrin particulate = $\frac{2}{100}\times\left(\frac{303}{6.023\times10^{23}}\times\frac{3}{4}\times\frac{7}{22}\right)^{\frac{1}{3}}$ = 9.866×10^{-10} m

Size or diameter of dibutyrin particulate = 9.039×10^{-10} m

Assuming 1 nanometer diameter of catalytic pores:

For tributyrin: λ = 1.0136; Absolute($1+\frac{9}{8}\lambda\ln\lambda-1.54\lambda$) = 0.5455

For dibutyrin: λ = 1.1063; Absolute($1+\frac{9}{8}\lambda\ln\lambda-1.54\lambda$) = 0.5779 equation 42

$$\text{Đ}_{1,2} = (4.29\times10^{-6})^{(1+0.03-0.03)/2}\times(5.53\times10^{-7})^{(1+0.03-0.03)/2}\times(0.5455) = 2.66\times10^{-6}$$

equation 43

$$\text{Đ}_{2,1} = (5.53\times10^{-6})^{(1+0.03-0.03)/2}\times(4.29\times10^{-7})^{(1+0.03-0.03)/2}\times0.5779 = 2.82\times10^{-6}$$

equation 44

Equations 45 – 47 show the calculations of the fluxes $B_{1,2}$ for specie 1 diffusing in specie 2, $B_{2,1}$ for vice versa and $B_{1,1}$ for specie 1, respectively. x_i presents the mole fraction of specie *i*.

$$B_{1,2} = \frac{x_1}{\text{Đ}_{1,2}} = \frac{0.03}{2.66\times10^{-6}} = 1.13\times10^{4}\ \text{s cm}^{-2}$$ equation 45

$$B_{2,1} = \frac{x_2}{\text{Đ}_{2,1}} = \frac{0.03}{2.82\times10^{-6}} = 1.07\times10^{4}\ \text{s cm}^{-2}$$ equation 46

$$B_{1,1} = \frac{x_2}{\text{Đ}_{1,2}}+\frac{x_3}{\text{Đ}_{1,3}}+\frac{x_4}{\text{Đ}_{1,4}}+\frac{x_5}{\text{Đ}_{1,5}}+\frac{x_6}{\text{Đ}_{1,6}}$$

$$= \frac{0.03}{2.66\times10^{-6}}+\frac{0.02}{2.70\times10^{-6}}+\frac{0.01}{6.17\times10^{-7}}+\frac{0.82}{9.95\times10^{-6}}+\frac{0.09}{7.79\times10^{-6}} = 1.29\times10^{5}\ \text{s cm}^{-2}$$ equation 47

The *B* matrix thus evaluated is shown in Table 16.

Table 16. Matrix of binary fluxes

	Solvent					
Solute	Tributyrin	Dibutyrin	Monobutyrin	Glycerol	Methanol	Methyl Butanoate
Tributyrin	1.29E+05	1.13E+04	1.11E+04	4.86E+04	3.02E+03	3.85E+03
Dibutyrin	1.07E+04	1.11E+05	1.02E+04	4.46E+04	2.50E+03	3.50E+03
Monobutyrin	6.62E+03	6.43E+03	9.72E+04	2.85E+04	1.31E+03	2.14E+03
Glycerol	1.43E+04	1.40E+04	1.41E+04	1.99E+05	5.96E+02	4.09E+03
Methanol	8.49E+04	7.45E+04	6.21E+04	5.69E+04	1.27E+04	4.25E+04
Methyl Butanoate	1.01E+04	9.71E+03	9.40E+03	3.63E+04	3.96E+03	4.88E+04

Đ_i^{eff} the effective diffusivity of specie *i* for an average mole fraction for a given time interval (t_1 to t_2) can be calculated by the ratio between change in mole fractions in the time interval and summation of *B* elements for the specie for the given average mole fraction, in equation 48.

$$\text{Đ}_i^{eff} = \frac{x_i^{t=t_2} - x_i^{t=t_1}}{\sum_{j=1}^{nspc} B_{ij}}$$

equation 48

For a constant gradient in mole fraction, e.g. 0.001, the following effective diffusion coefficients of species are obtained.

Table 7. Effective diffusion coefficients of species in cm^2 s^{-1} for a constant concentration gradient

Tributyrin	4.84E-09
Dibutyrin	5.48E-09
Monobutyrin	-7.03E-09
Glycerol	-4.07E-09
Methanol	3.00E-09
Methyl Butanoate	-8.46E-09

The negative sign indicates increase in the mole fractions of products. The change in the number of moles of specie *i* due to diffusion, in mol s^{-1}, in terms of the effective diffusion coefficients is shown in equation 49. For an activity of 0.01 mole per gm of catalyst and specific surface area of 0.01 cm^2 per gm of catalyst, the values in Table 7 represent the change in number of moles of species in mol s^{-1}, shown in Table 8 of the main paper.

$$change \quad in \quad N_i \quad due \quad to \quad diffusion = \frac{\text{Đ}_i^{eff} \times activity}{specific\,area} \qquad \text{equation 49}$$