

SUPPLEMENTARY INFORMATION

Kinetic Modeling of Microwave-Assisted Esterification for Biofuel Additive Production: Conversion of Levulinic Acid with Pentanol Using Dowex® 50WX8 Catalyst

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I. Power in microwave-assisted reactor

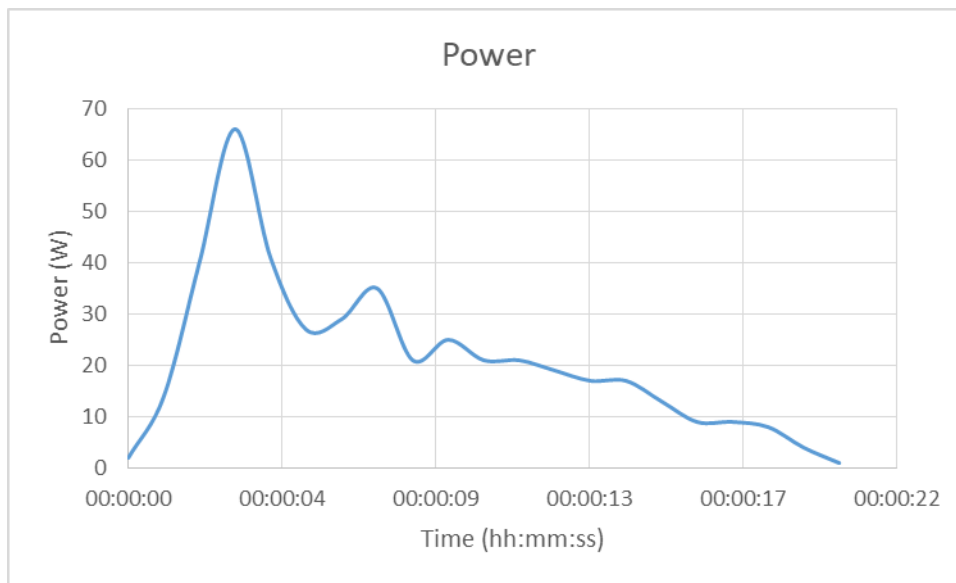
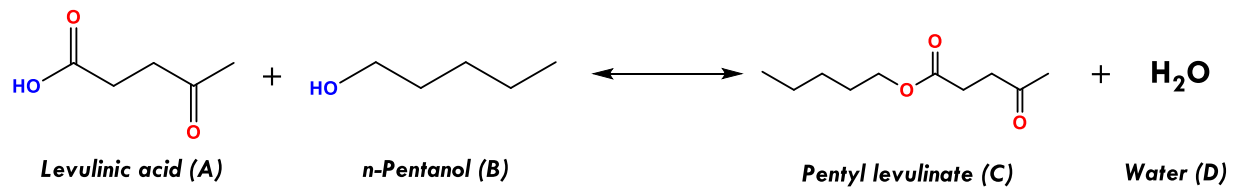


Fig. S1. Power as a function of the time in the microwave-assisted reactor.

2. Heterogeneous kinetic models

The esterification reaction is described by Scheme I.



Scheme I. Esterification reaction of levulinic acid with n-pentanol.

The terminology used is the following:

S: Surface site on catalyst

C_i : Concentration of species i in the bulk of the solution

C_v : Concentration of available surface site on the catalyst

C_{is} : Concentration of species i bounded at the surface site

C_t : Total number of sites available on the catalyst surface.

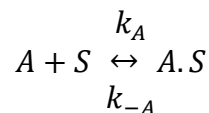
k_f : Constant of the direct reaction

k_r : Constant of the reverse reaction

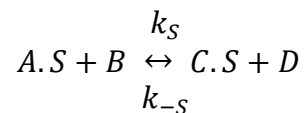
2.1. Eley-Rideal Models

2.1.1. Levulinic acid adsorption and pentyl levulinate desorption

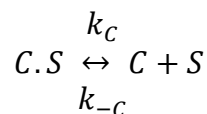
Step 1: Levulinic acid adsorption (r_{ADA})



Step 2: Surface reaction (r_s)



Step 3: Pentyl levulinate desorption (r_{DC})



The expressions for the reaction rate of each step are described below, considering elemental reactions in both directions of each step.

$$r_{ADA} = k_A C_A C_V - k_{-A} C_{AS} \rightarrow \frac{r_{ADA}}{k_A} = C_A C_V - \frac{C_{AS}}{K_A} \quad (S1)$$

$$r_S = k_S C_{AS} C_B - k_{-S} C_{CS} C_D \rightarrow \frac{r_S}{k_S} = C_{AS} C_B - \frac{C_{CS} C_D}{K_S} \quad (S2)$$

$$r_{DC} = k_C C_{CS} - k_{-C} C_C C_V \rightarrow \frac{r_{DC}}{k_C} = C_{CS} - \frac{C_C C_V}{K_C} \quad (S3)$$

Where K_i is the equilibrium constant for step i and it is defined by Eq. S4:

$$K_i = \frac{k_i}{k_{-i}} \quad (S4)$$

Model ERI: Surface reaction on the catalyst is the rate limiting step

Solving Eqs. S1 and S3 equal to zero, the following is obtained:

$$\frac{r_{ADA}}{k_A} = C_A C_V - \frac{C_{AS}}{K_A} = 0 \rightarrow C_{AS} = K_A C_A C_V \quad (S5)$$

$$\frac{r_{DC}}{k_C} = C_{CS} - \frac{C_C C_V}{K_C} = 0 \rightarrow C_{CS} = \frac{C_C C_V}{K_C} \quad (S6)$$

The site balance is defined by Eq. S7:

$$C_t = C_V + C_{AS} + C_{CS} \quad (S7)$$

By replacing Eqs. S5 and S6 in Eq. S7 and simplifying, Eq. S8 is obtained:

$$C_t = C_V + K_A C_A C_V + \frac{C_C C_V}{K_C}$$

$$C_V = \frac{C_t}{1 + K_A C_A + \frac{C_C}{K_C}} \quad (S8)$$

By replacing Eqs. S5 and S6 in Eq. S2:

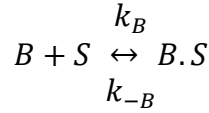
$$\frac{r_S}{k_S} = K_A C_A C_V C_B - \frac{C_C C_V}{K_C} C_D = C_V \left(K_A C_A C_B - \frac{C_C C_D}{K_S K_C} \right) \quad (S9)$$

Defining the constant $k = k_S C_t$ and replacing Eq. S8 in Eq. S9, the final expression for the reaction rate of the limiting step is obtained:

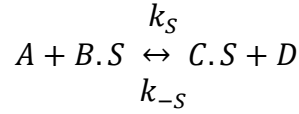
$$r_S = \frac{k \left[K_A C_A C_B - \frac{C_C C_D}{K_S K_C} \right]}{\left[1 + K_A C_A + \frac{C_C}{K_C} \right]} \quad (S10)$$

2.1.2. Pentanol adsorption and pentyl levulinate desorption

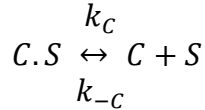
Step I: Pentanol adsorption (r_{ADB})



Step 2: Surface reaction (r_s)



Step 3: Pentyl levulinate desorption (r_{DC})



The expressions for reaction rate of each step are described below, considering elemental reactions in both directions of each step.

$$r_{ADB} = k_B C_B C_V - k_{-B} C_{BS} \rightarrow \frac{r_{ADB}}{k_B} = C_B C_V - \frac{C_{BS}}{K_B} \quad (S11)$$

$$r_S = k_S C_A C_{BS} - k_{-S} C_{CS} C_D \rightarrow \frac{r_S}{k_S} = C_A C_{BS} - \frac{C_{CS} C_D}{K_S} \quad (S12)$$

$$r_{DC} = k_C C_{CS} - k_{-C} C_C C_V \rightarrow \frac{r_{DC}}{k_C} = C_{CS} - \frac{C_C C_V}{K_C} \quad (S13)$$

Where K_i is the equilibrium constant for step i and it is defined by Eq. S14:

$$K_i = \frac{k_i}{k_{-i}} \quad (S14)$$

Model ER2: Ethyl laurate desorption on catalyst is the rate limiting step

Solving Eqs. S11 and S12 equal to zero, the following is obtained:

$$\frac{r_{ADB}}{k_B} = C_B C_V - \frac{C_{BS}}{K_B} = 0 \rightarrow C_{BS} = K_B C_B C_V \quad (S15)$$

$$\frac{r_S}{k_S} = C_A C_{BS} - \frac{C_{CS} C_D}{K_S} = 0 \rightarrow C_{CS} = \frac{K_S C_A C_{BS}}{C_D} \quad (S16)$$

By replacing Eq. S15 in Eq. S16, Eq. S17 is obtained:

$$C_{CS} = \frac{K_S C_A K_B C_B C_V}{C_D} \rightarrow C_{CS} = \frac{K_S K_B C_A C_B C_V}{C_D} \quad (S17)$$

The site balance is defined by Eq. S18:

$$C_t = C_V + C_{BS} + C_{CS} \quad (S18)$$

By replacing Eqs. S15 and S17 in Eq. S18 and simplifying, Eq. S19 is obtained:

$$C_t = C_V + K_B C_B C_V + \frac{K_S K_B C_A C_B C_V}{C_D}$$

$$C_V = \frac{C_t}{1 + K_B C_B + \frac{K_S K_B C_A C_B}{C_D}} \quad (S19)$$

By replacing Eq. S17 in Eq. S13:

$$\frac{r_{DC}}{k_C} = \frac{K_S K_B C_A C_B C_V}{C_D} - \frac{C_C C_V}{K_C} = C_V \left(\frac{K_S K_B C_A C_B}{C_D} - \frac{C_C}{K_C} \right) \quad (S20)$$

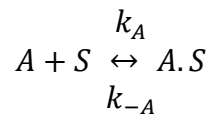
Defining the constant $k = k_C C_t$ and replacing Eq. S19 in Eq. S20, the final expression for the reaction rate of the limiting step is obtained:

$$r_{DC} = \frac{k \left[\frac{K_S K_B C_A C_B}{C_D} - \frac{C_C}{K_C} \right]}{\left[1 + K_B C_B + \frac{K_S K_B C_A C_B}{C_D} \right]} \quad (S21)$$

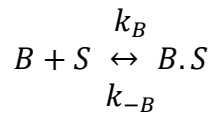
2.2. Langmuir-Hinshelwood-Hougen-Watson (LHHW) Models

The five steps of the LHHW Model are described below.

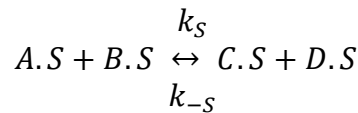
Step 1: Levulinic acid adsorption (r_{ADA})



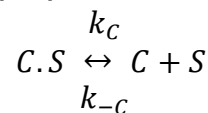
Step 2: Pentanol adsorption (r_{ADB})



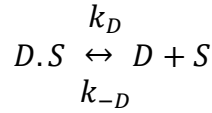
Step 3: Surface reaction (r_s)



Step 4: Levulinate desorption (r_{DC})



Step 5: Water desorption (r_{DD})



The expressions for the reaction rate of each step are described below, considering elemental reactions in both directions of each step.

$$r_{ADA} = k_A C_A C_V - k_{-A} C_{AS} \rightarrow \frac{r_{ADA}}{k_A} = C_A C_V - \frac{C_{AS}}{K_A} \quad (S22)$$

$$r_{ADB} = k_B C_B C_V - k_{-B} C_{BS} \rightarrow \frac{r_{ADB}}{k_B} = C_B C_V - \frac{C_{BS}}{K_B} \quad (S23)$$

$$r_S = k_S C_{AS} C_{BS} - k_{-S} C_{CS} C_{DS} \rightarrow \frac{r_S}{k_S} = C_{AS} C_{BS} - \frac{C_{CS} C_{DS}}{K_S} \quad (S24)$$

$$r_{DC} = k_C C_{CS} - k_{-C} C_C C_V \rightarrow \frac{r_{DC}}{k_C} = C_{CS} - \frac{C_C C_V}{K_C} \quad (S25)$$

$$r_{DD} = k_D C_{DS} - k_{-D} C_D C_V \rightarrow \frac{r_{DD}}{k_D} = C_{DS} - \frac{C_D C_V}{K_D} \quad (S26)$$

Where K_i is the equilibrium constant for step i and it is defined by Eq. S27:

$$K_i = \frac{k_i}{k_{-i}} \quad (S27)$$

Model LHI: Surface reaction on catalyst is the rate limiting step

Solving Eqs. S22-S23, S25-S26 equal to zero, the following is obtained:

$$\frac{r_{ADA}}{k_A} = C_A C_V - \frac{C_{AS}}{K_A} = 0 \rightarrow C_{AS} = K_A C_A C_V \quad (S28)$$

$$\frac{r_{ADB}}{k_B} = C_B C_V - \frac{C_{BS}}{K_B} = 0 \rightarrow C_{BS} = K_B C_B C_V \quad (S29)$$

$$\frac{r_{DC}}{k_C} = C_{CS} - \frac{C_C C_V}{K_C} = 0 \rightarrow C_{CS} = \frac{C_C C_V}{K_C} \quad (S30)$$

$$\frac{r_{DD}}{k_D} = C_{DS} - \frac{C_D C_V}{K_D} = 0 \rightarrow C_{DS} = \frac{C_D C_V}{K_D} \quad (S31)$$

By replacing Eqs. S28-S31 in Eq. S24, Eq. S32 is obtained:

$$\frac{r_S}{k_S} = K_A C_A C_V K_B C_B C_V - \frac{\frac{C_C C_V}{K_C} \frac{C_D C_V}{K_D}}{K_S} = C_V^2 \left(K_A K_B C_A C_B - \frac{C_C C_D}{K_S K_C K_D} \right) \quad (S32)$$

The site balance is defined by Eq. S33:

$$C_t = C_V + C_{AS} + C_{BS} + C_{CS} + C_{DS} \quad (S33)$$

By replacing Eqs. S28-S31 in Eq. S33 and simplifying, Eq. S34 is obtained:

$$C_t = C_V + K_A C_A C_V + K_B C_B C_V + \frac{C_C C_V}{K_C} + \frac{C_D C_V}{K_D}$$

$$C_V = \frac{C_t}{1 + K_A C_A + K_B C_B + \frac{C_C}{K_C} + \frac{C_D}{K_D}} \quad (S34)$$

Defining the constant $k = k_s C_t^2$ and replacing Eq. S34 in Eq. S32, the final expression for the reaction rate of the limiting step is obtained:

$$r_S = \frac{k \left[K_A K_B C_A C_B - \frac{C_C C_D}{K_S K_C K_D} \right]}{\left[1 + K_A C_A + K_B C_B + \frac{C_C}{K_C} + \frac{C_D}{K_D} \right]^2} \quad (S35)$$

3. Experimental concentrations vs. Modeled concentrations

Figs. S2-S5 show the profiles of the fitting of the molar concentrations using the pseudo-homogeneous and the heterogeneous models LHI, ERI and ER2.

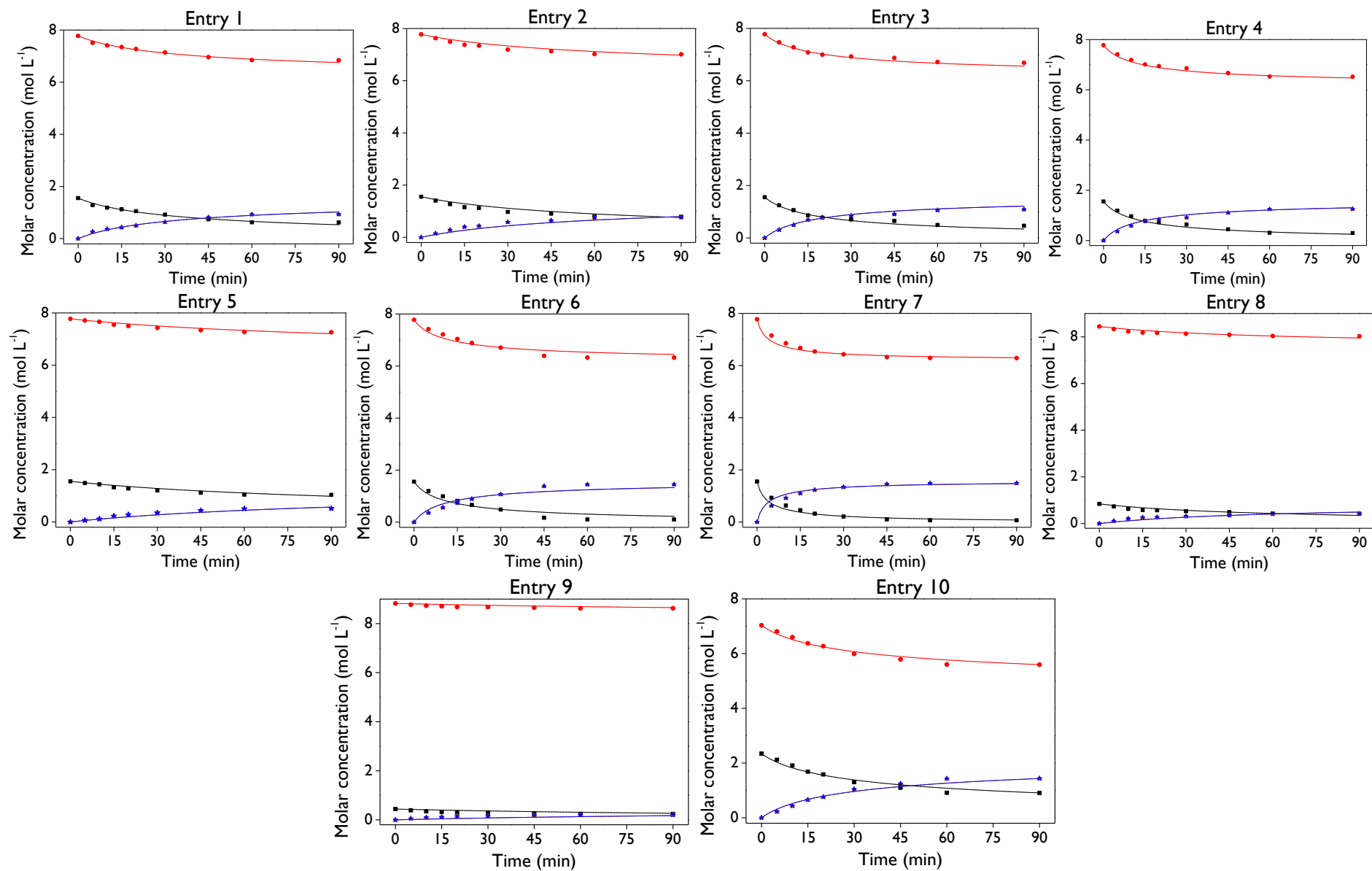


Fig. S2. Concentrations profiles of the species (C_A (—, ■), C_B (—, ●), C_C (—, ▲), C_D (—, ★) involved in the esterification of levulinic acid over 50WX8, with experimental values (symbols) and modeled values (solid lines) with the pseudo-homogeneous reversible model. Reaction conditions were described for each entry in Table I.

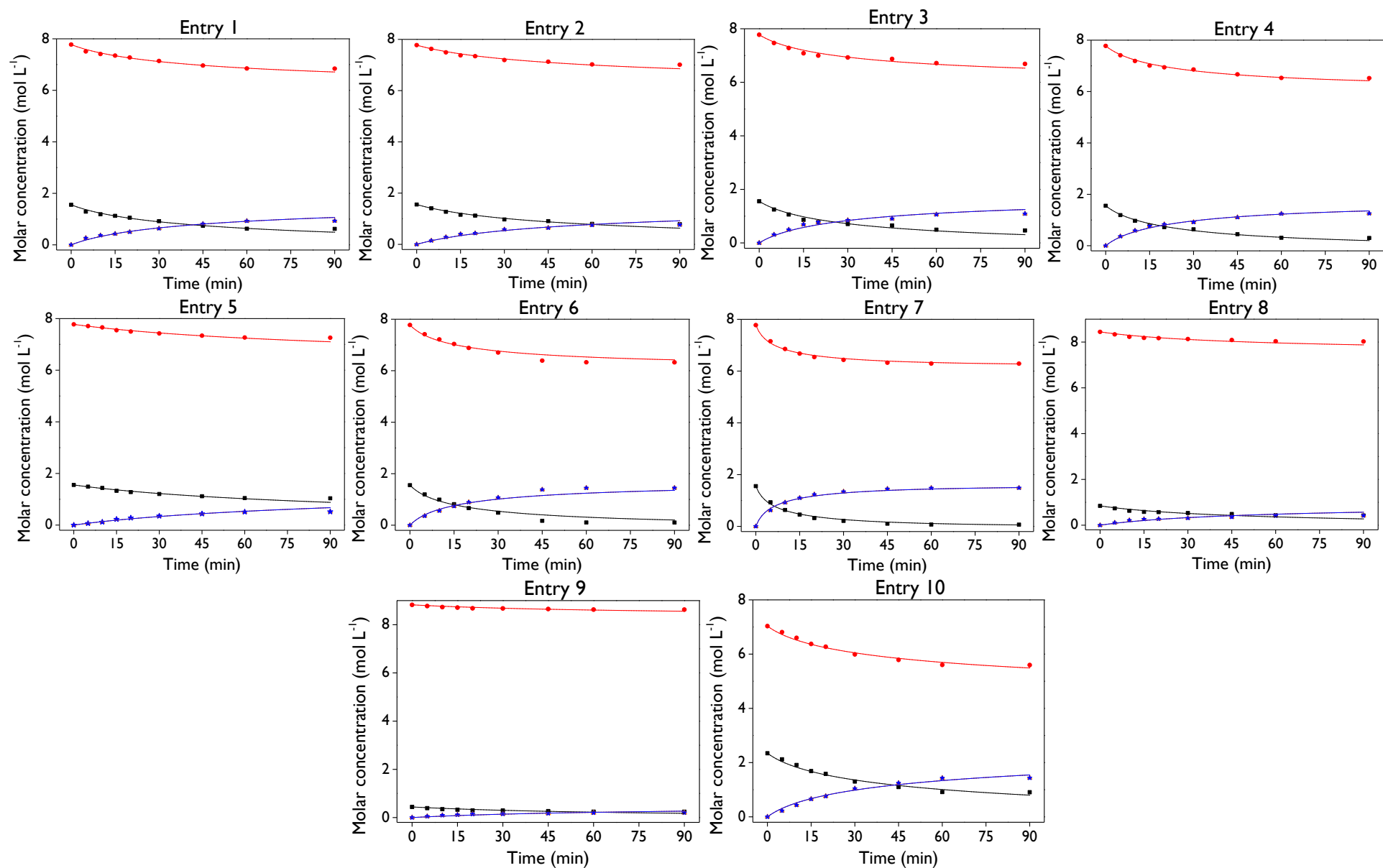


Fig. S3. Concentrations profiles of the species (C_A (—, ■), C_B (—, ●), C_C (—, ▲), C_D (—, ★) involved in the esterification of levulinic acid over 50WX8, with experimental values (symbols) and modeled values (solid lines) with the heterogeneous model LHI. Reaction conditions were described for each entry in Table I.

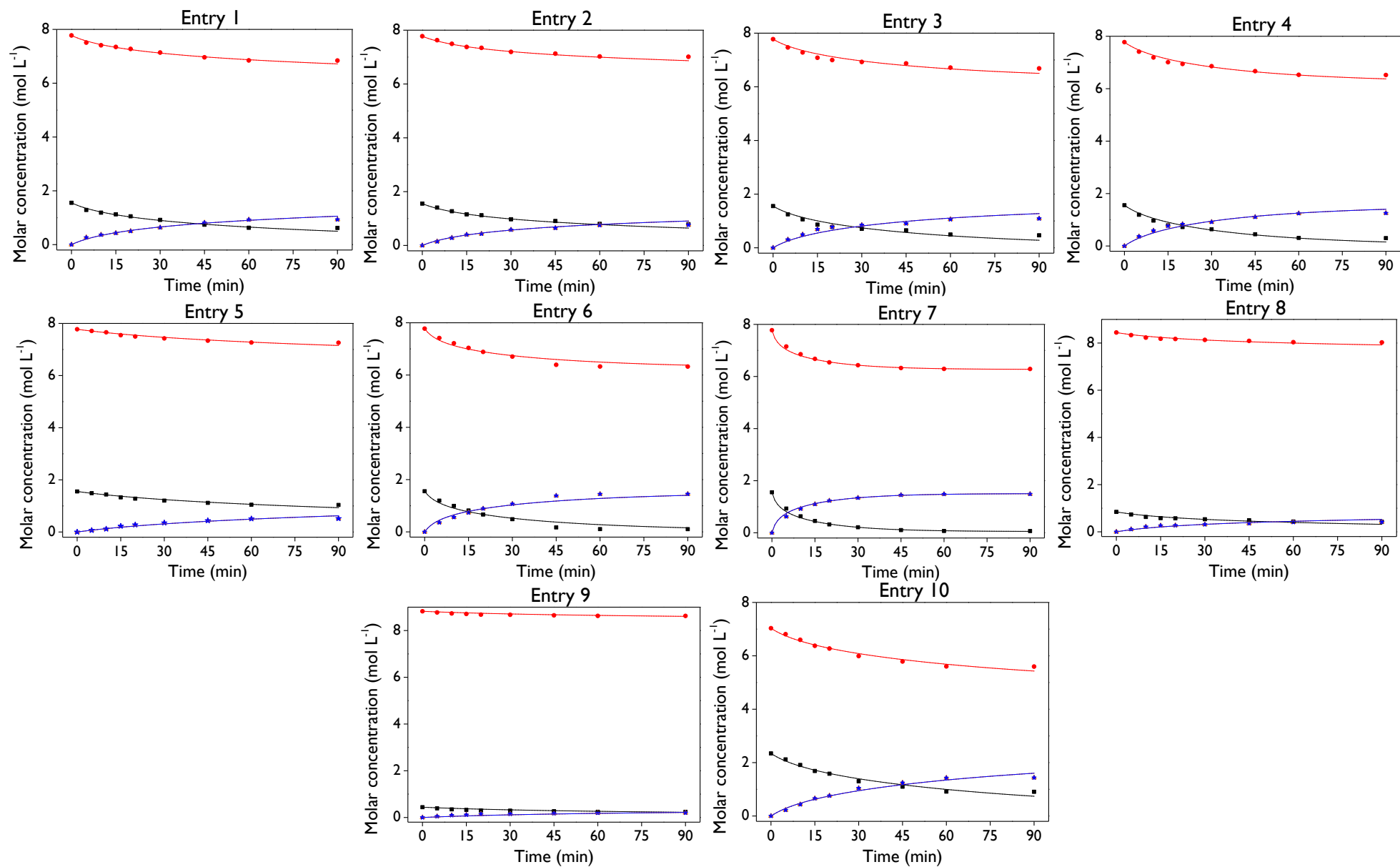


Fig. S4. Concentrations profiles of the species (C_A (—, ■), C_B (—, ●), C_C (—, ▲), C_D (—, ★) involved in the esterification of levulinic acid over 50WX8, with experimental values (symbols) and modeled values (solid lines) with the heterogeneous model ERI. Reaction conditions were described for each entry in Table I.

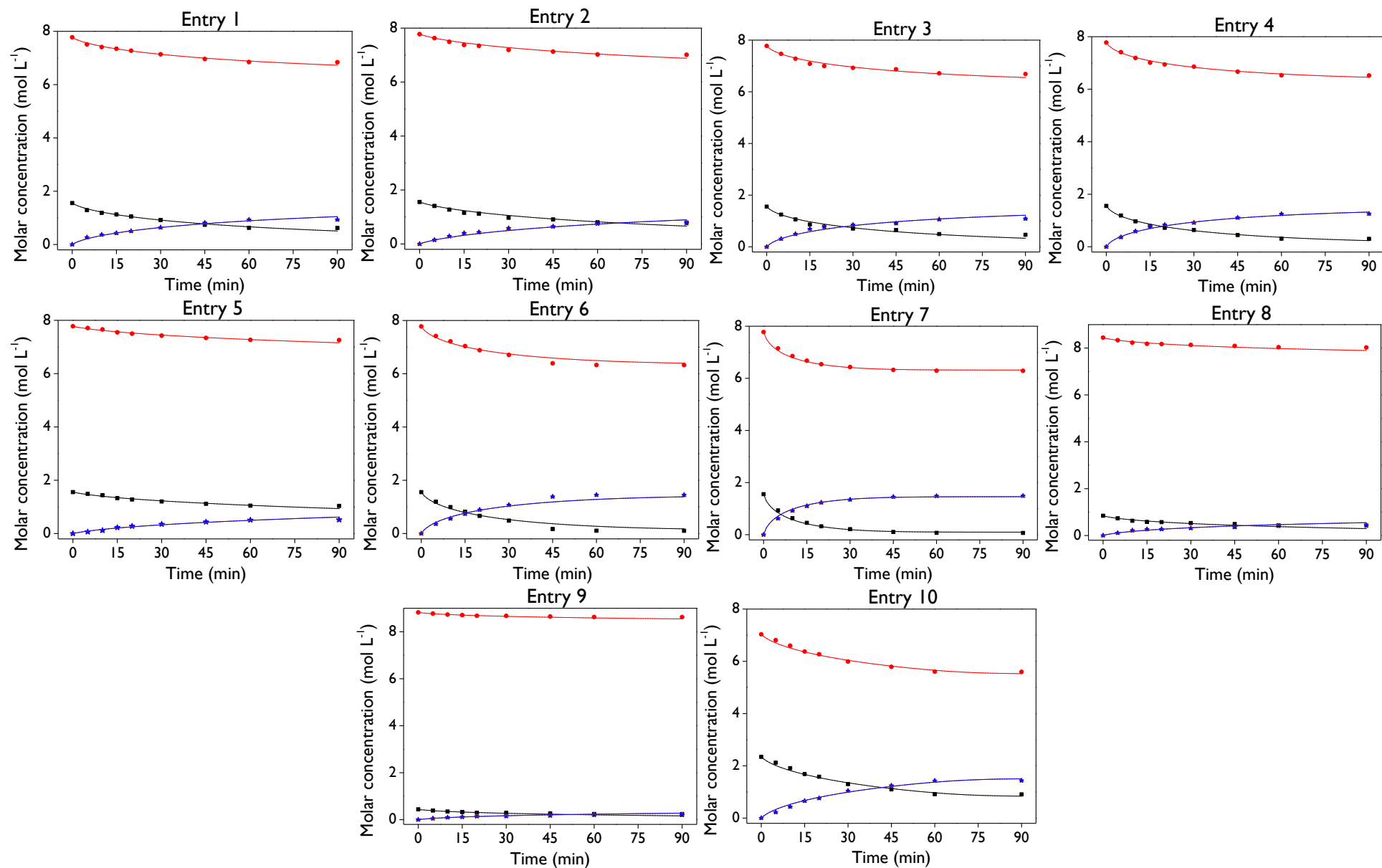


Fig. S5. Concentrations profiles of the species (C_A (—, ■), C_B (—, ●), C_C (—, ▲), C_D (—, ★) involved in the esterification of levulinic acid over 50WX8, with experimental values (symbols) and modeled values (solid lines) with the heterogeneous model ER2. Reaction conditions were described for each entry in Table I.

4. Markov Chain Monte Carlo (MCMC) results

4.1. Pseudo-homogeneous reversible model

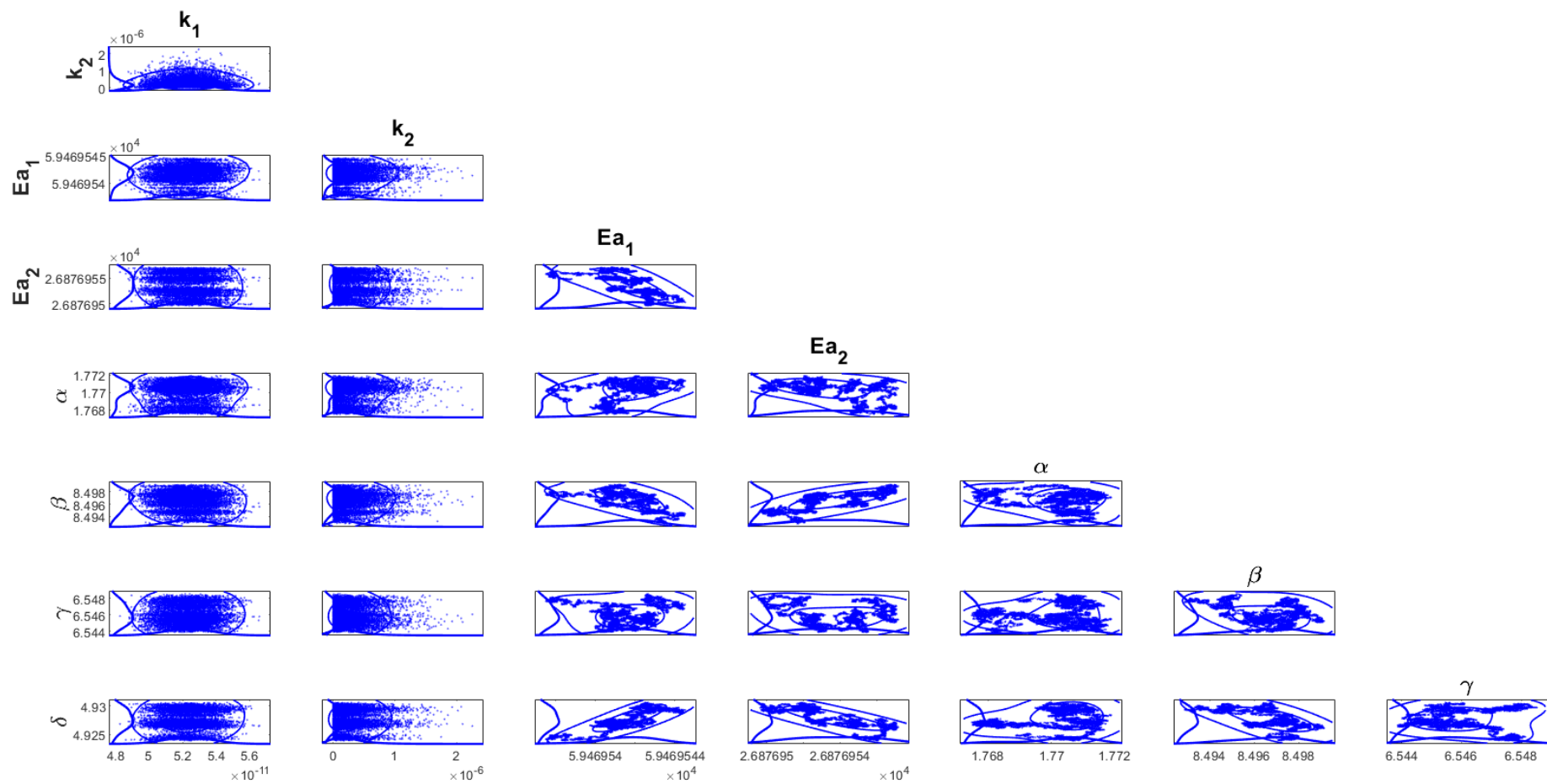


Fig. S6. Contour plots for the eight parameter combinations of the pseudo-homogeneous reversible model.

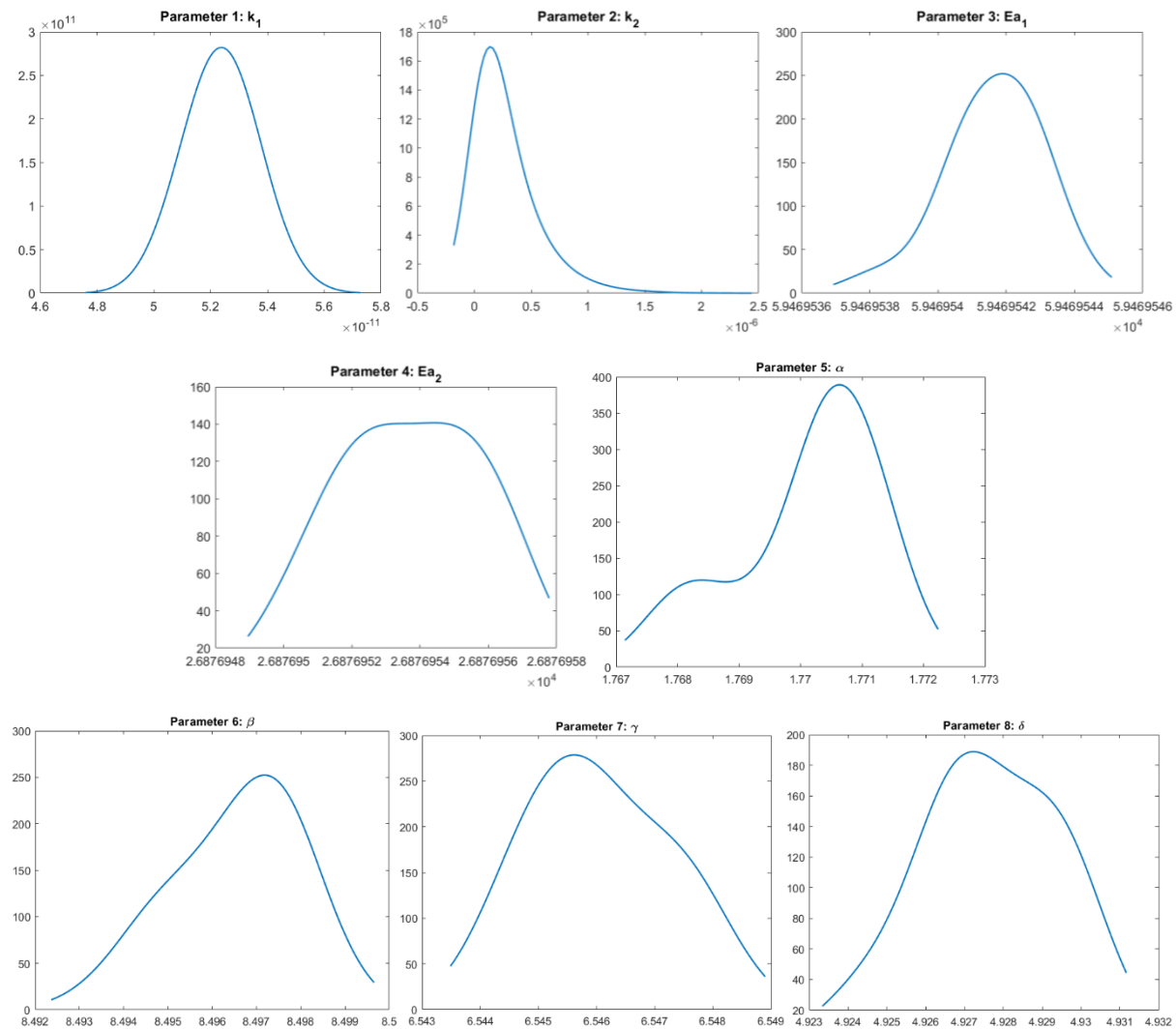
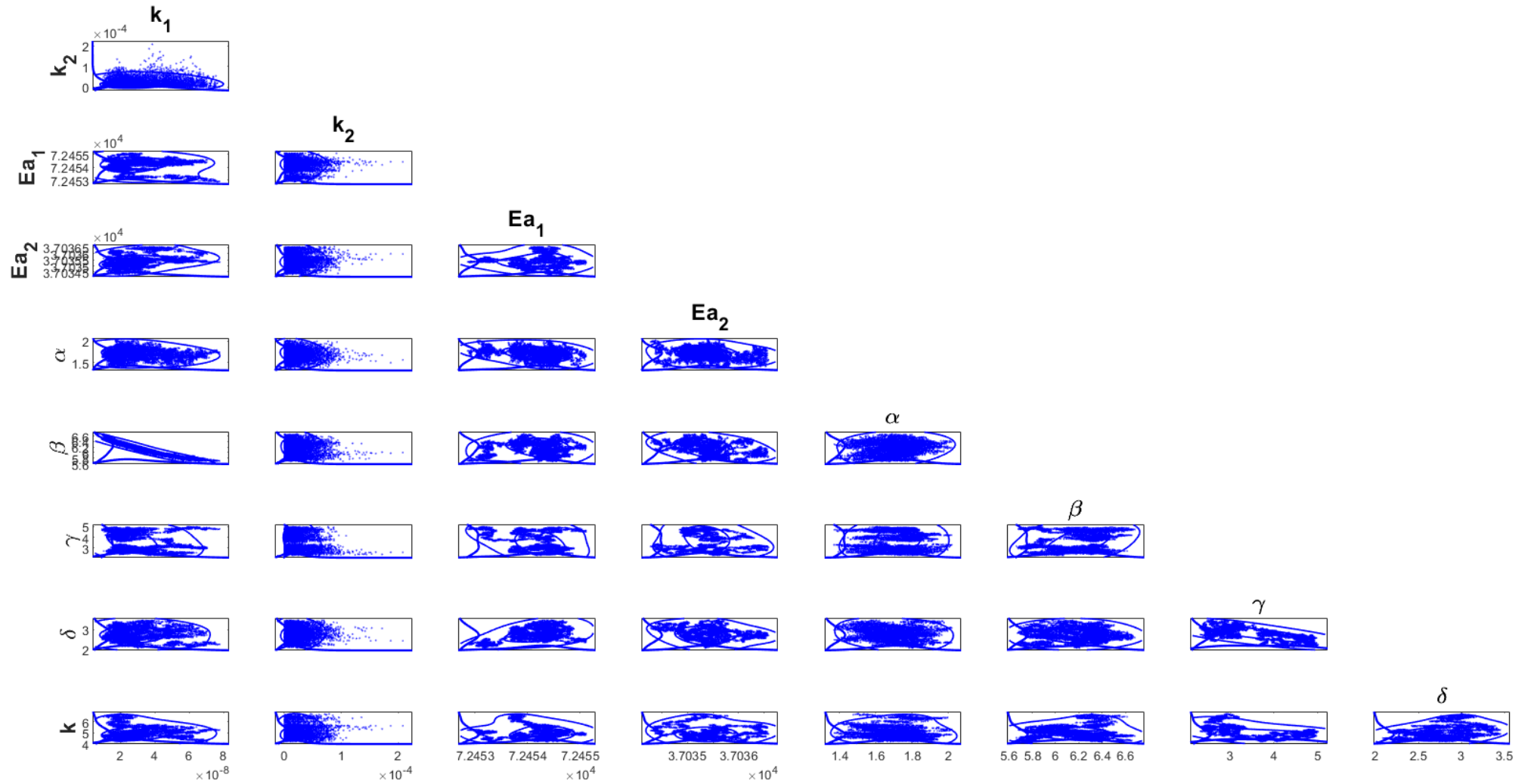
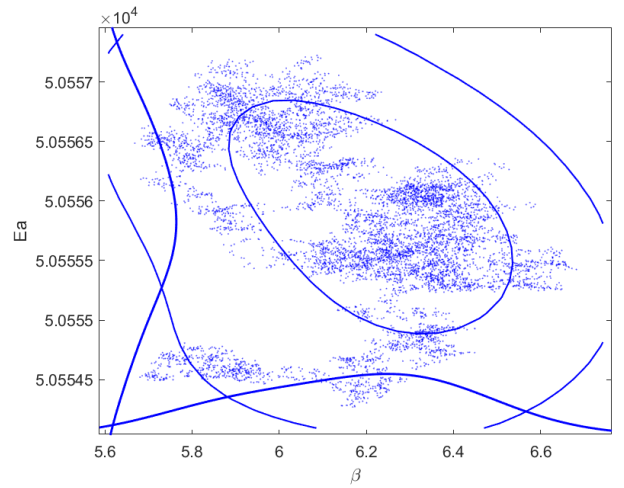
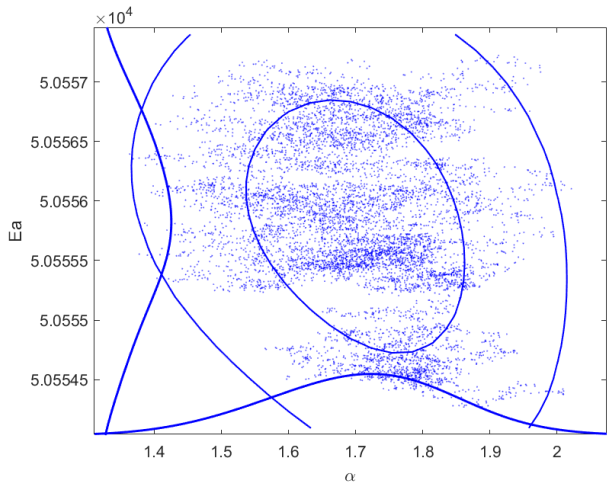
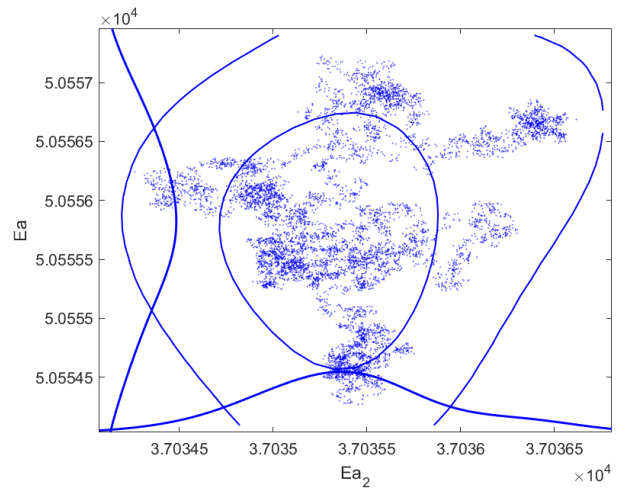
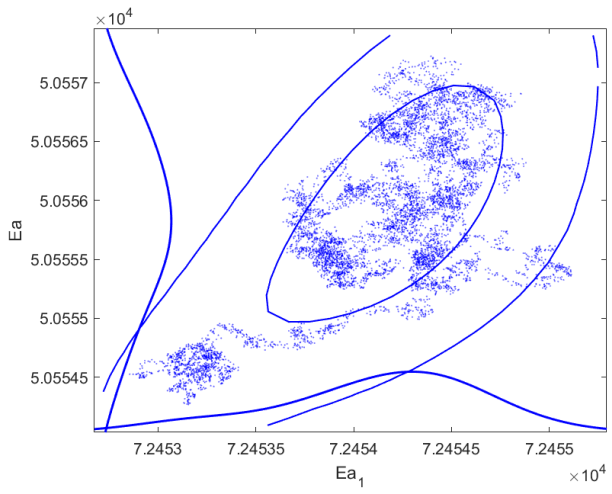
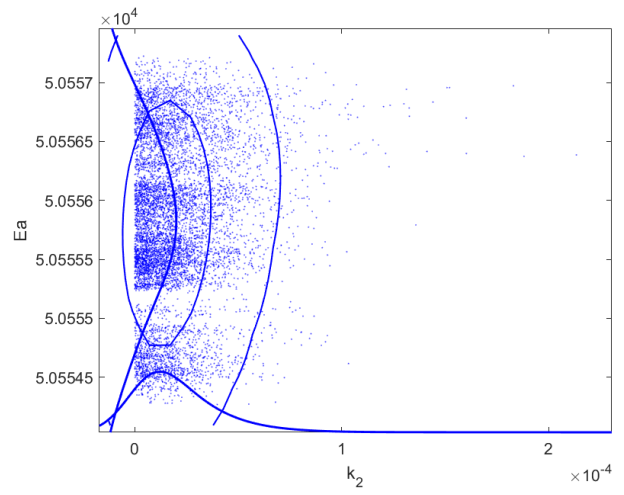
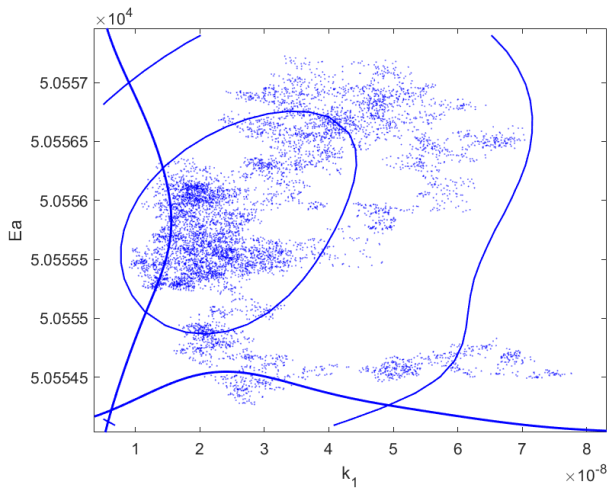
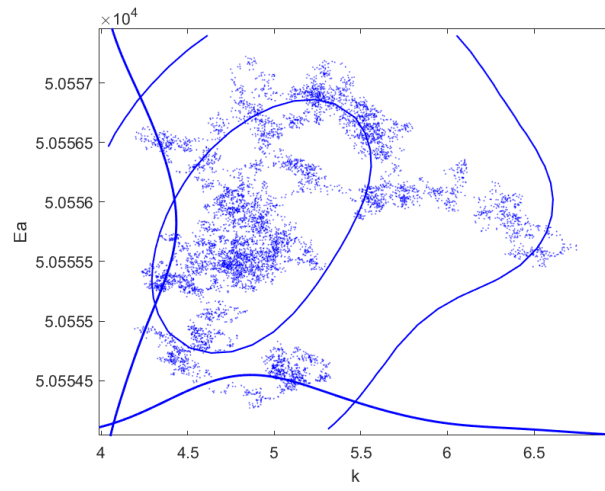
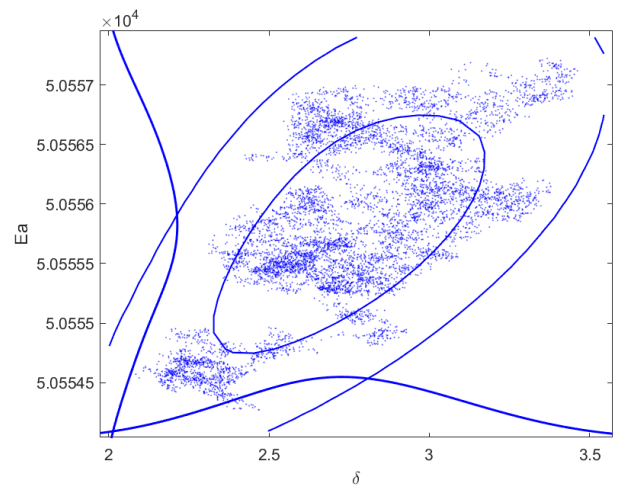
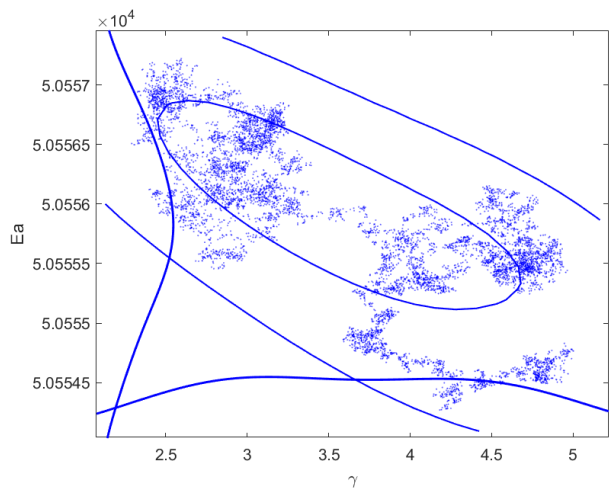


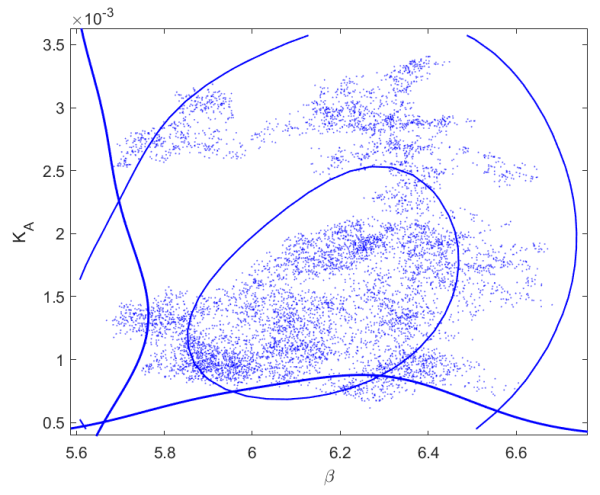
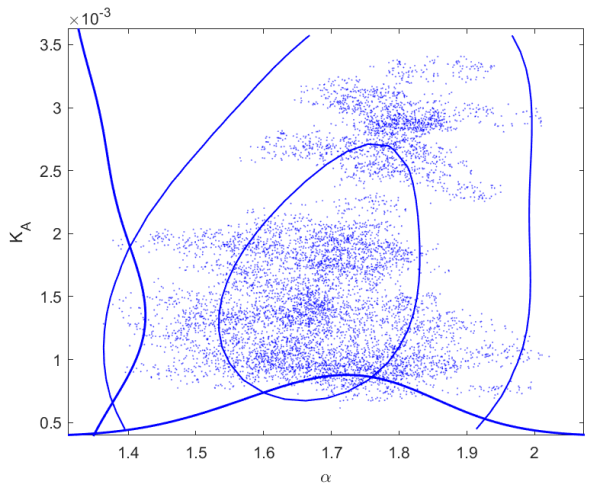
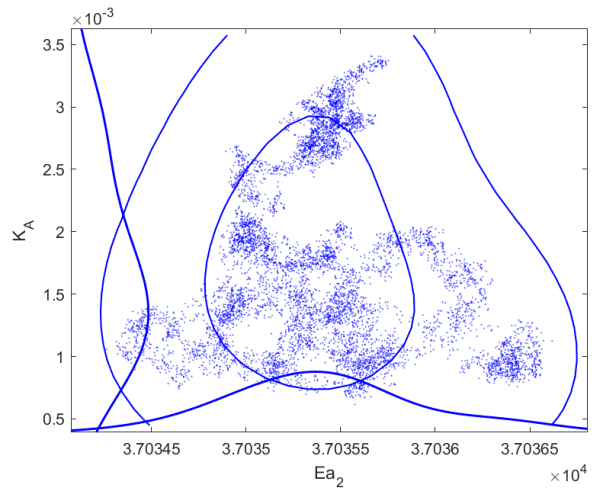
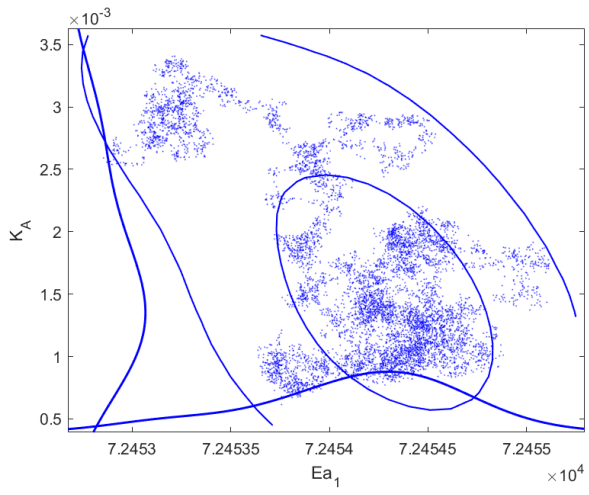
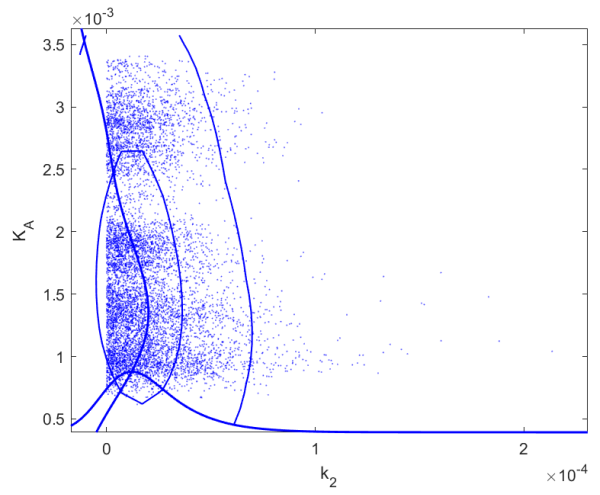
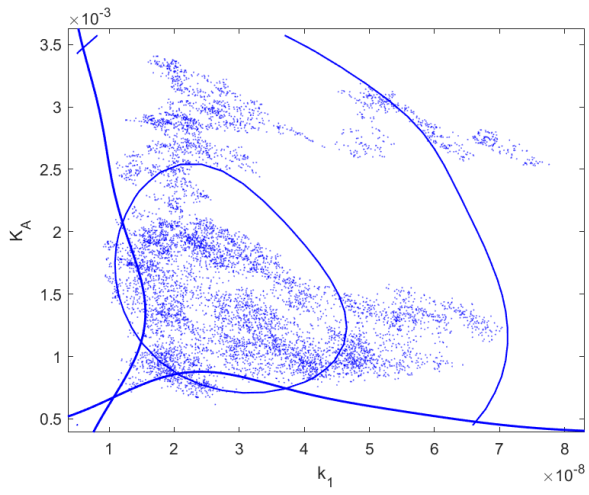
Fig. S7. MCMC analysis of parameters determined through nonlinear regression for the pseudo-homogeneous reversible model. The Y-axes represent posterior distributions for the parameters, reflecting their probabilities, while the corresponding parameter values are displayed on the X-axes. The most probable values for the parameters are located at the maxima of the distributions.

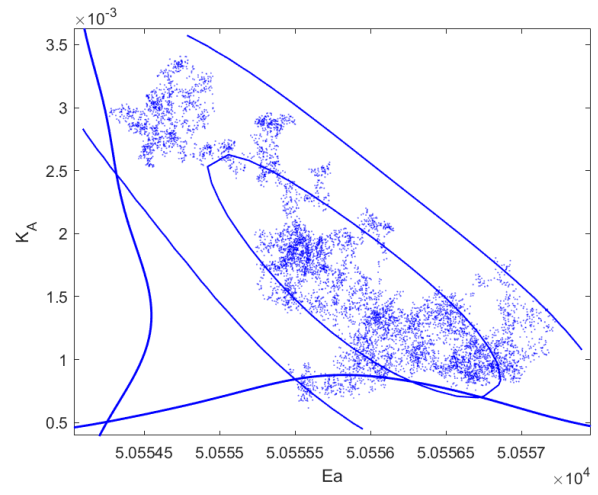
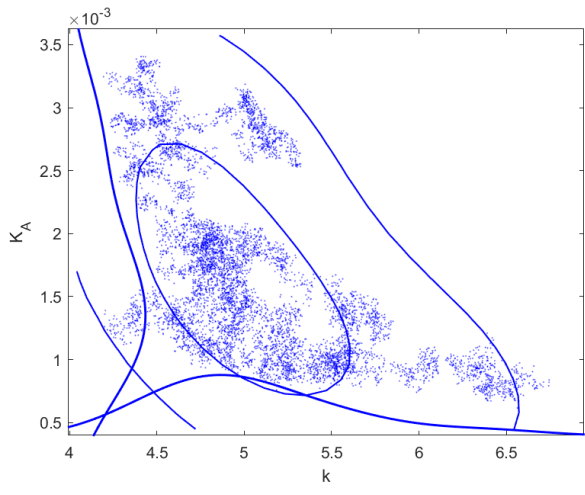
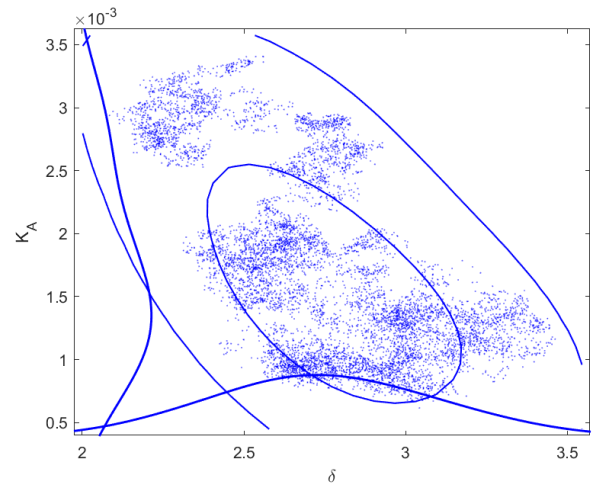
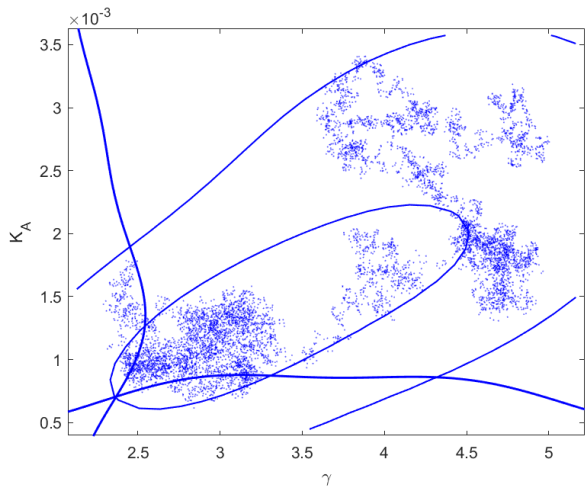
4.2. Contour plots from the MCMC Analysis for the LHI model

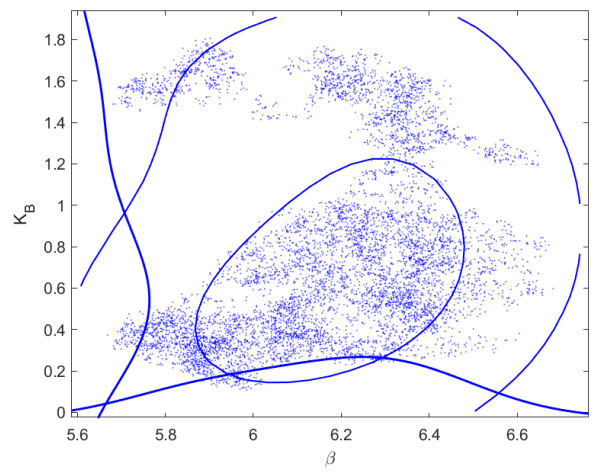
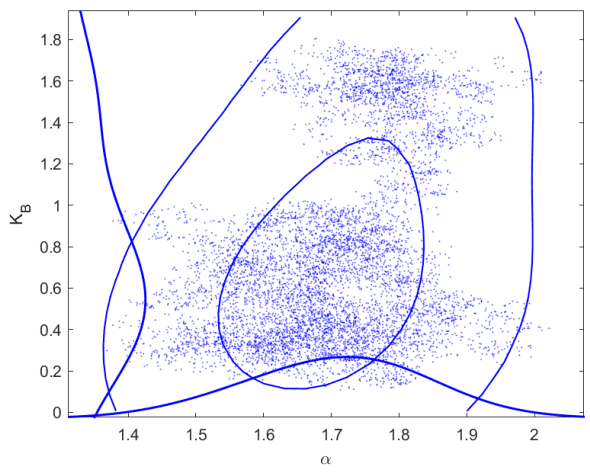
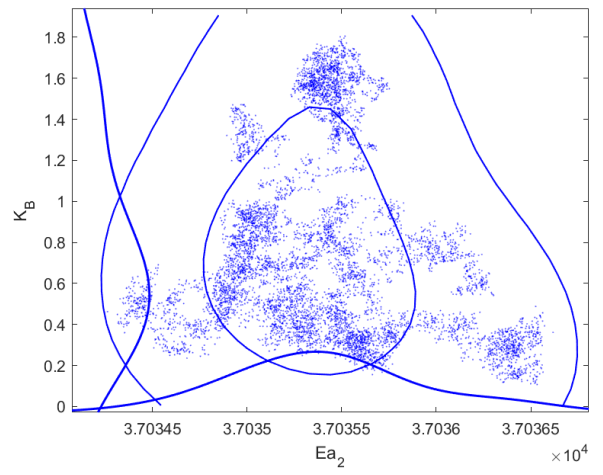
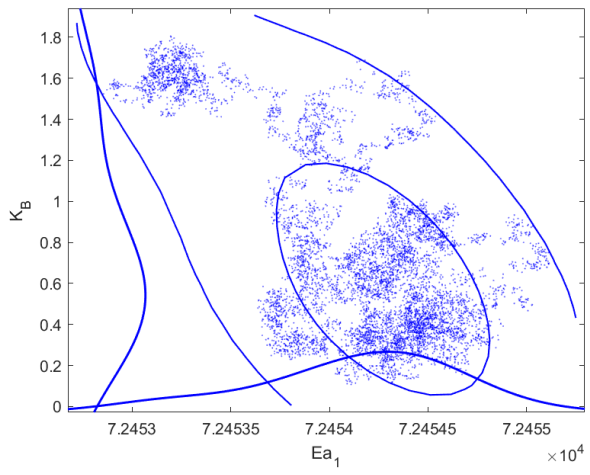
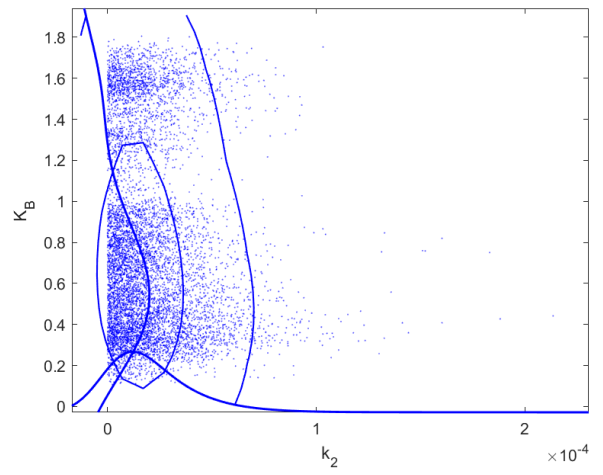
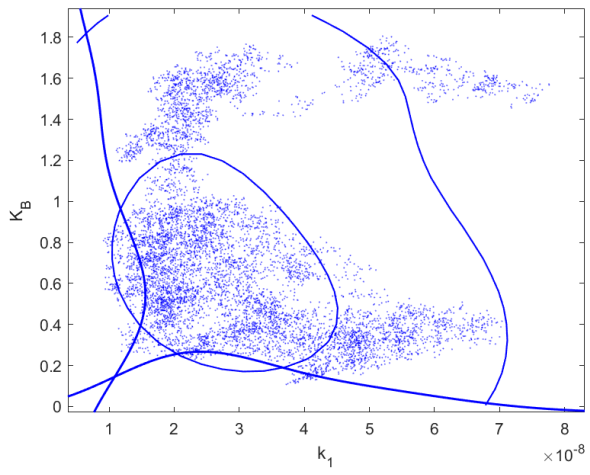


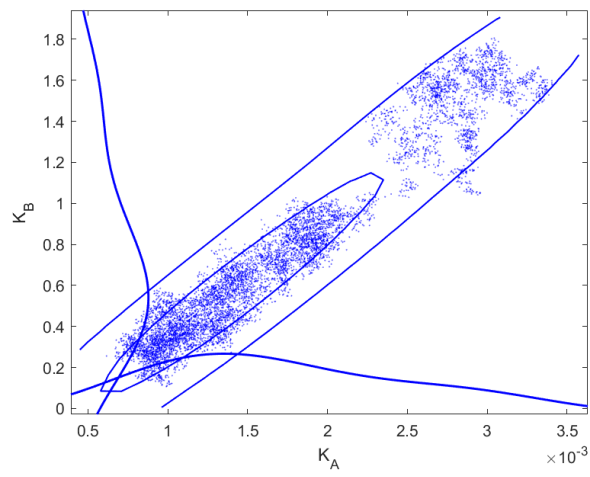
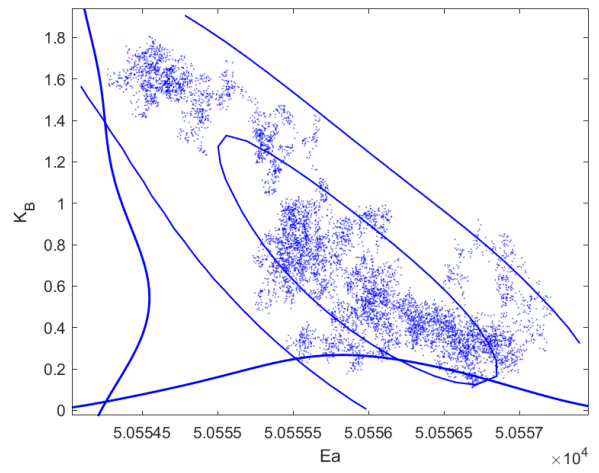
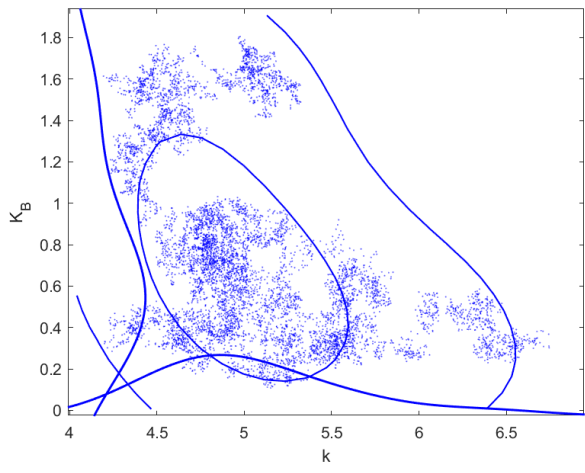
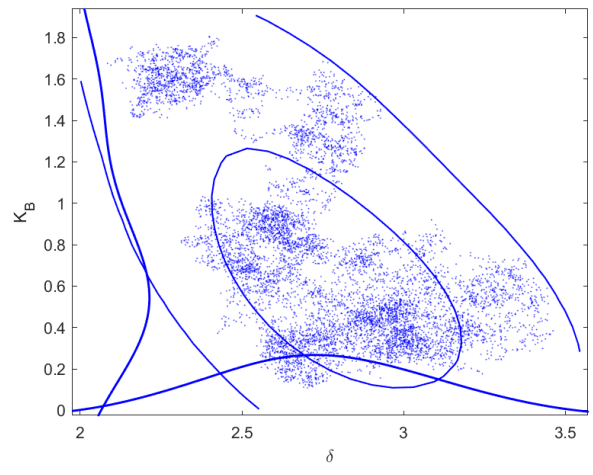
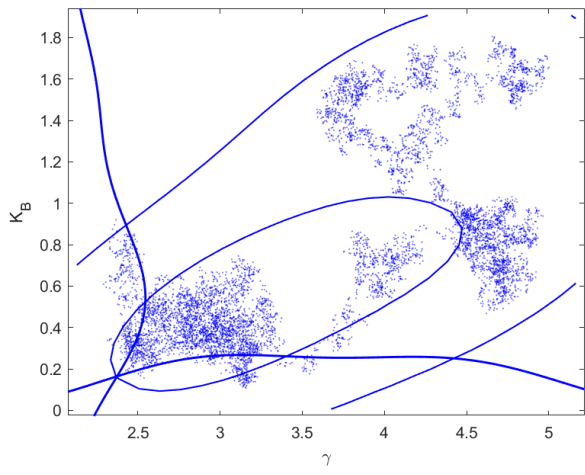


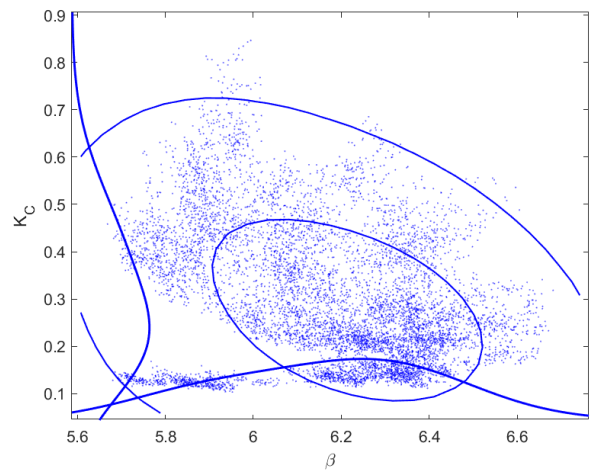
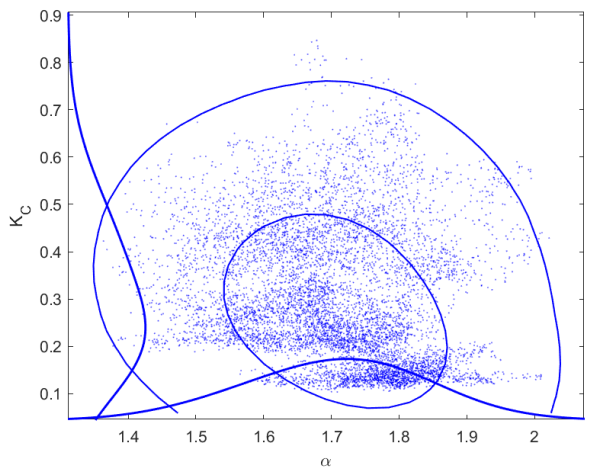
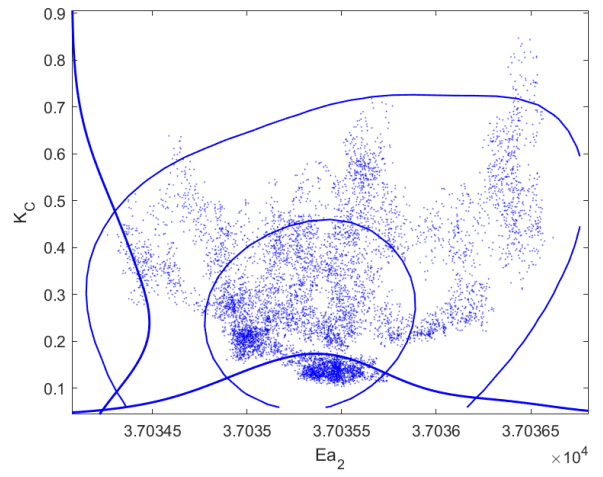
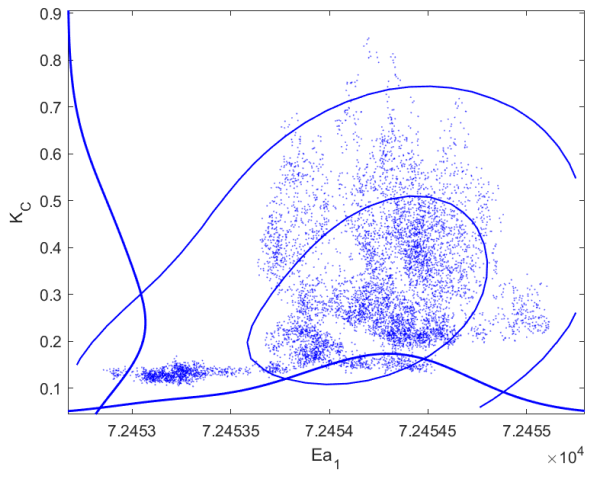
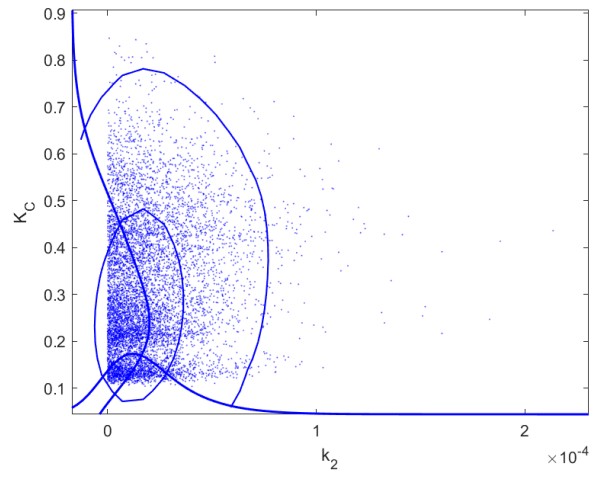
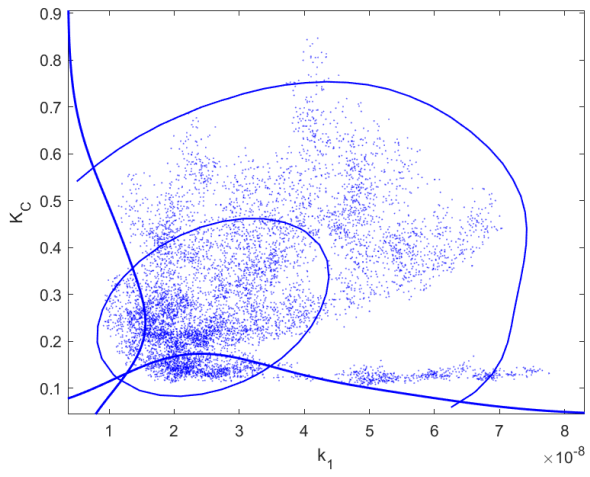


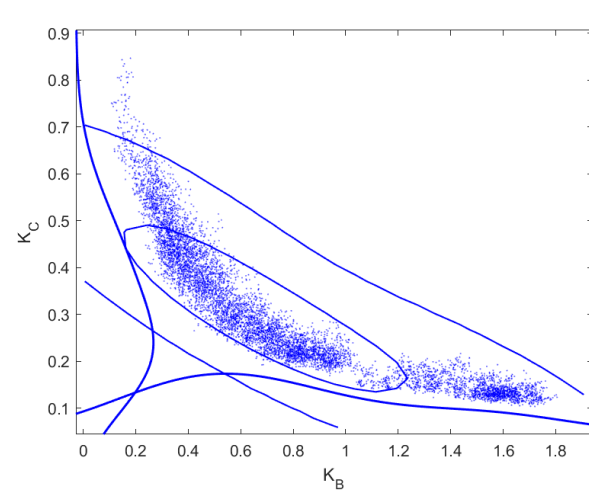
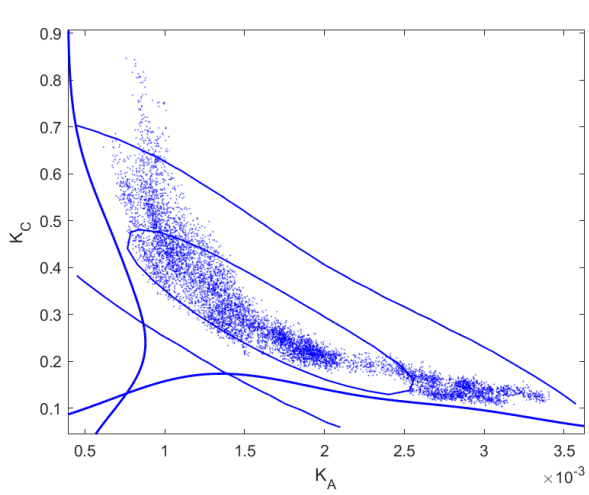
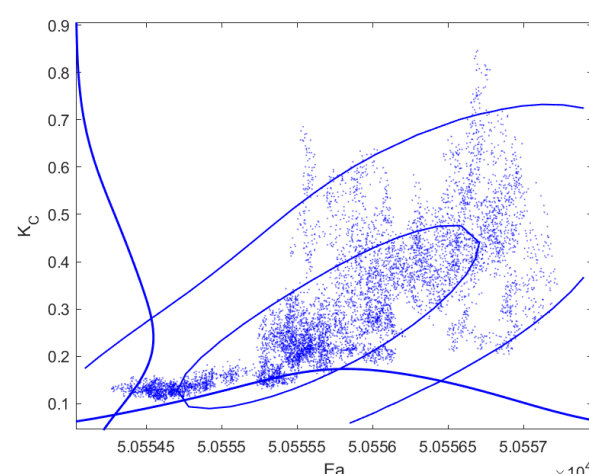
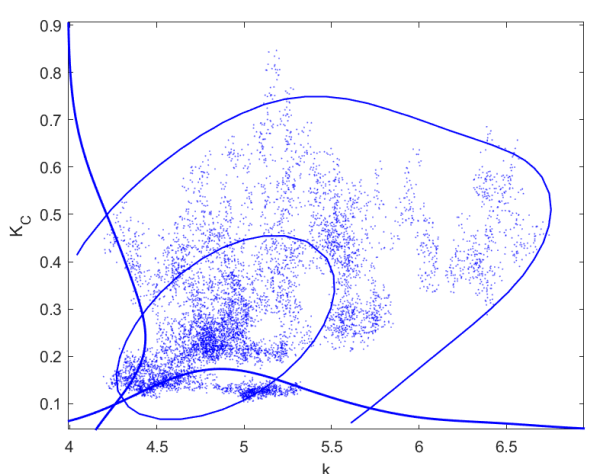
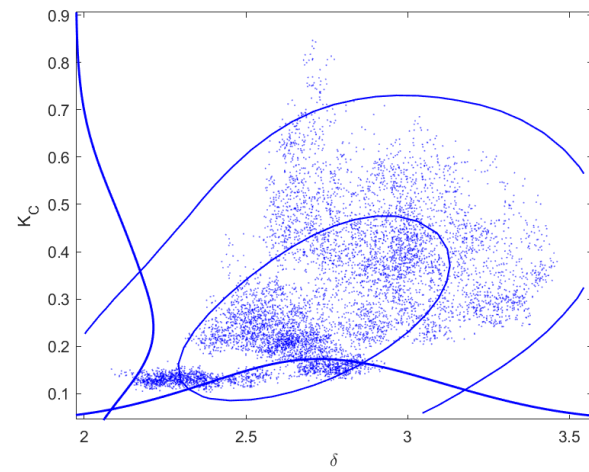
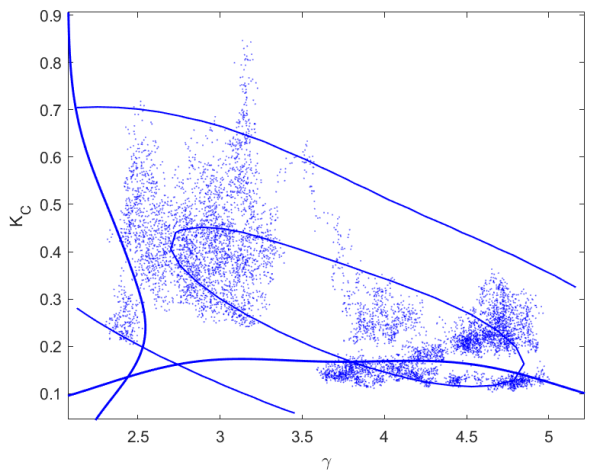


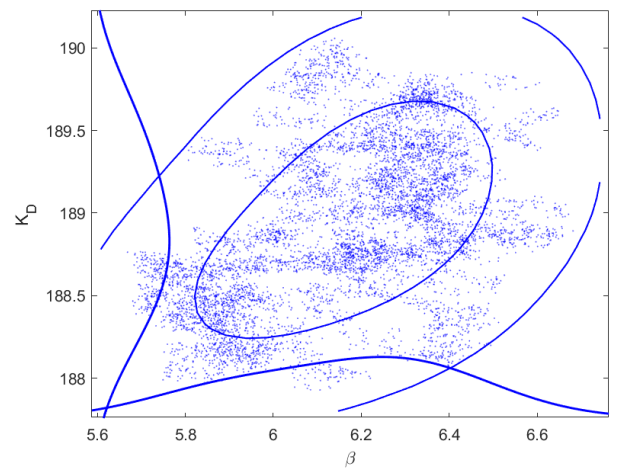
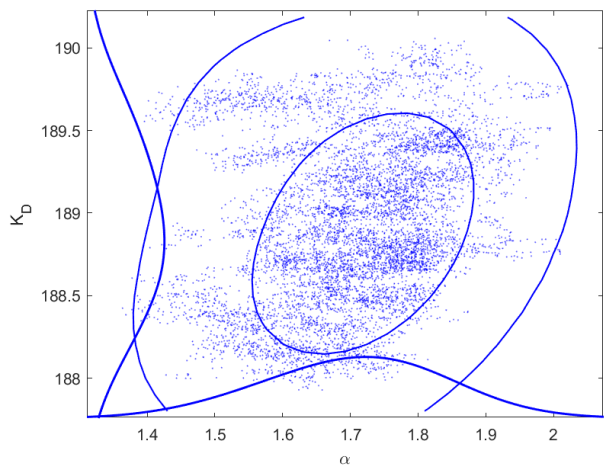
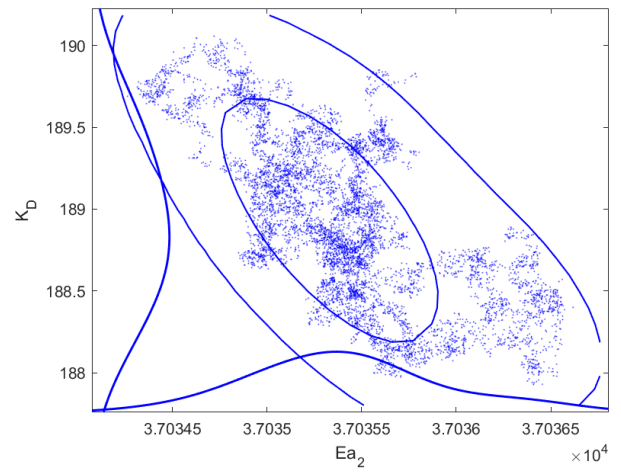
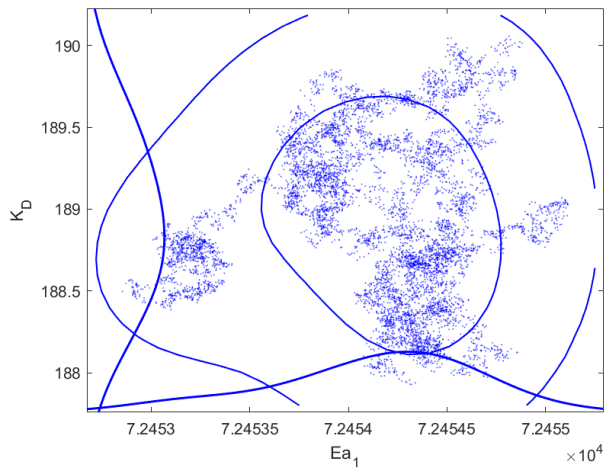
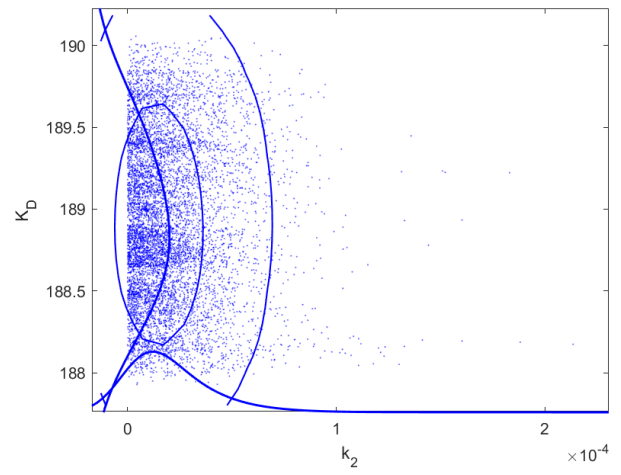
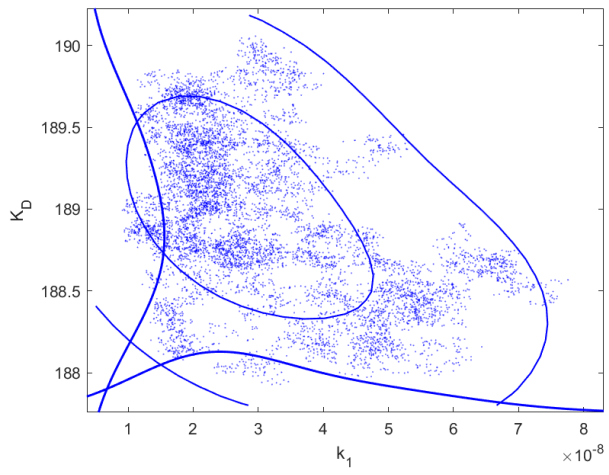


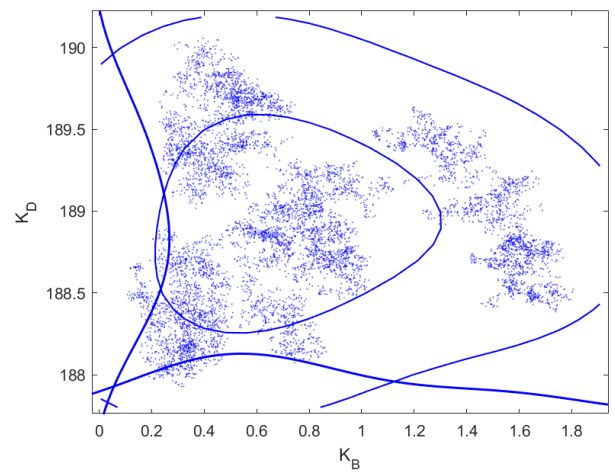
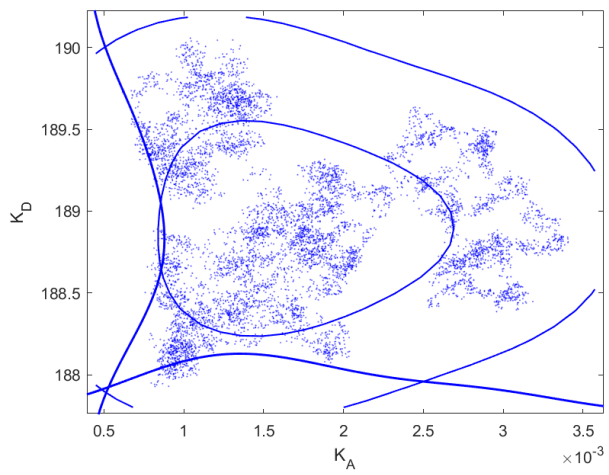
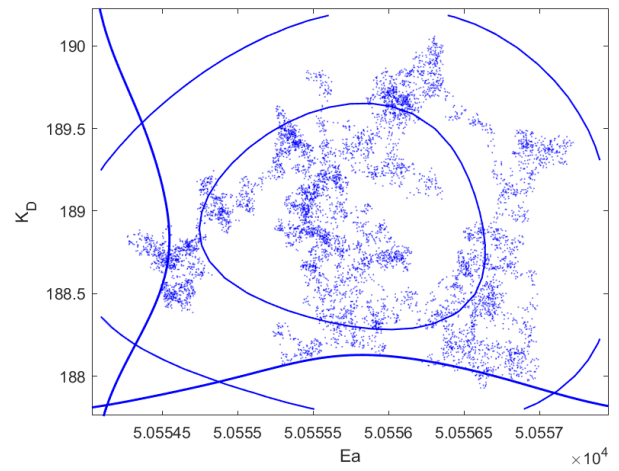
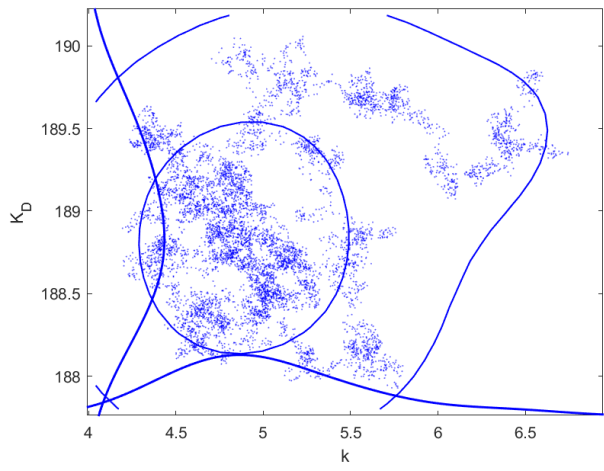
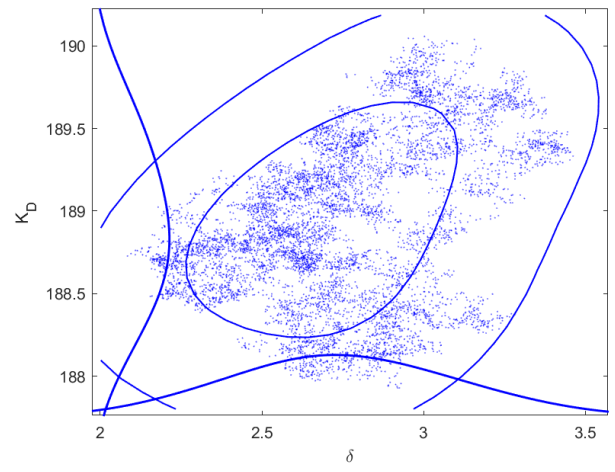
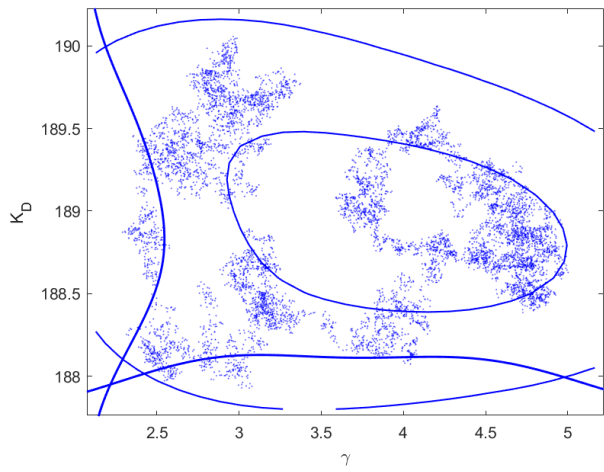


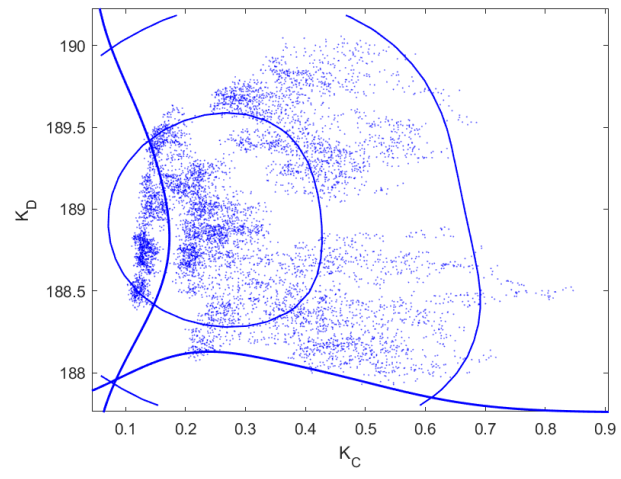


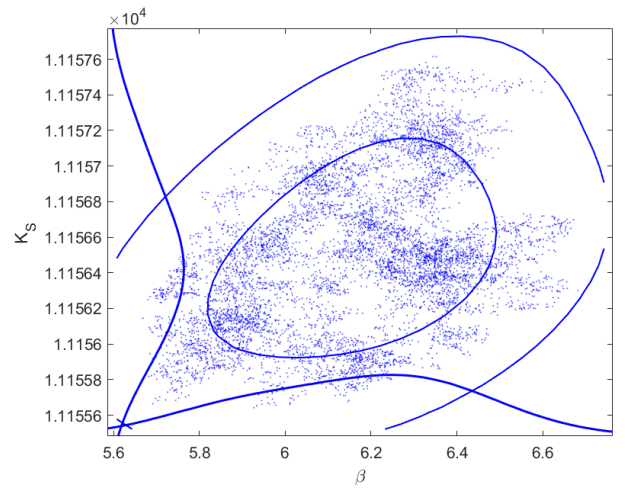
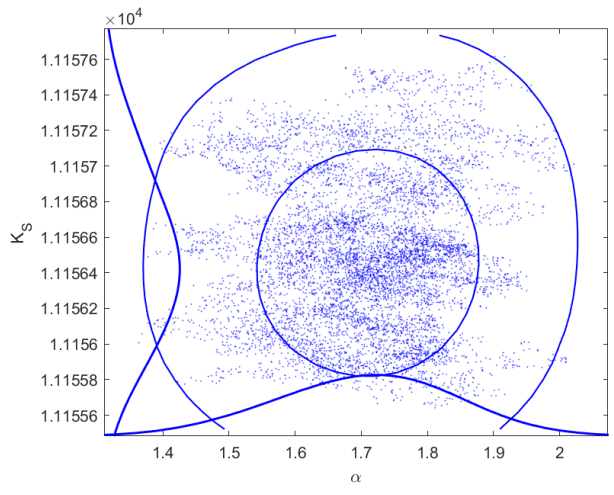
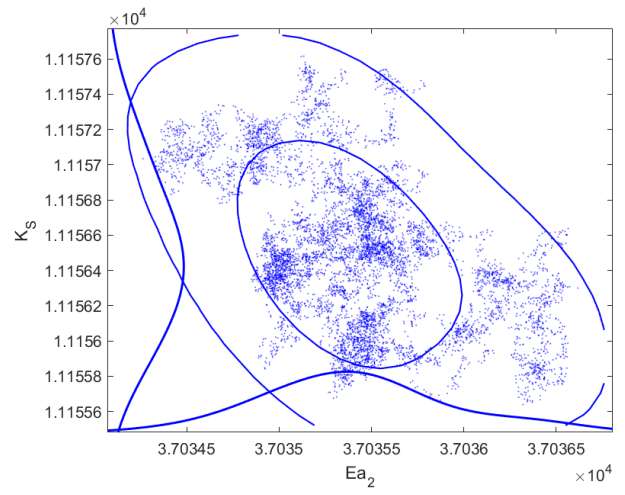
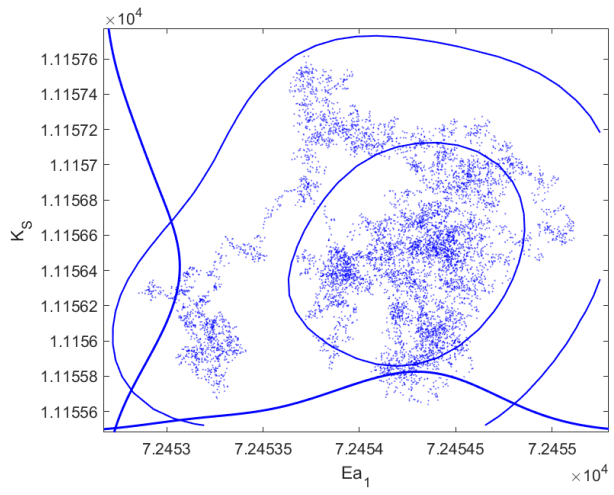
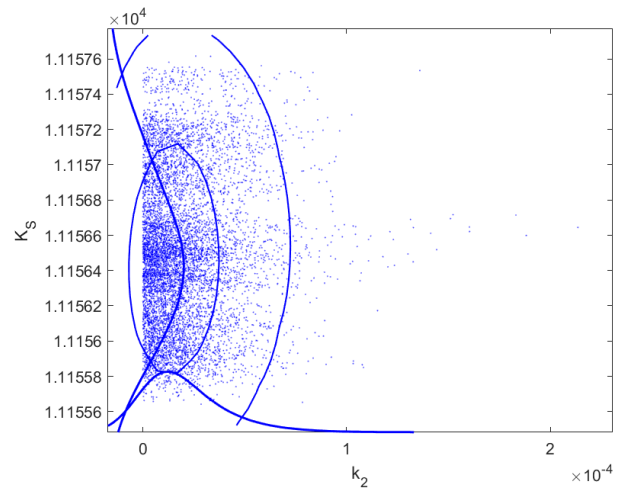
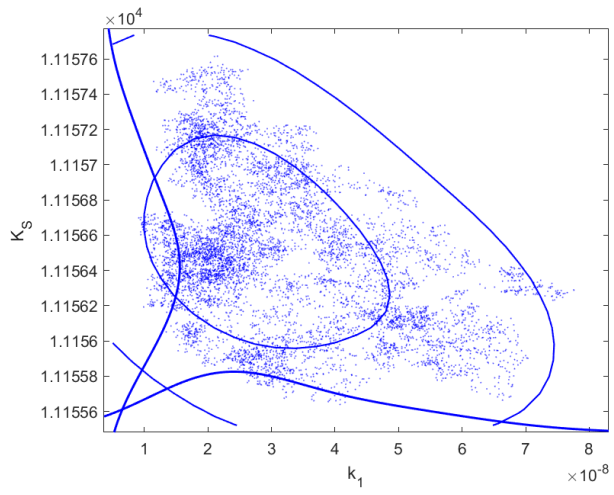


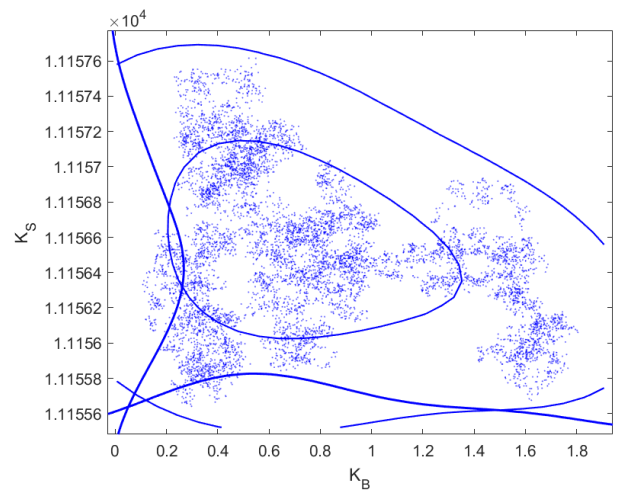
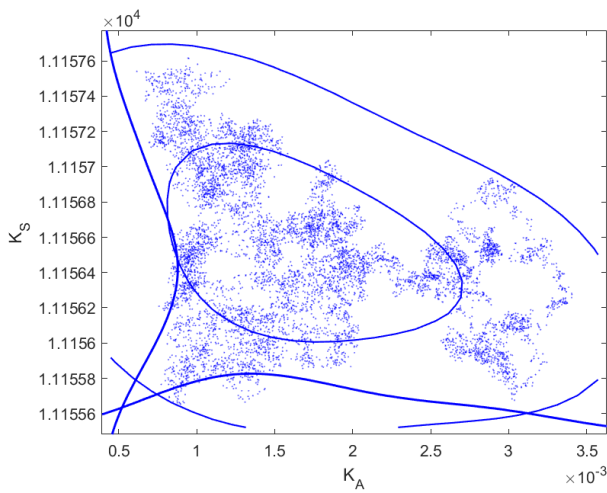
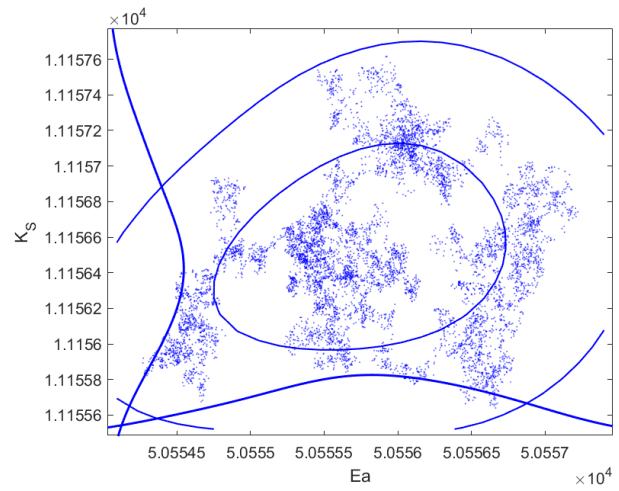
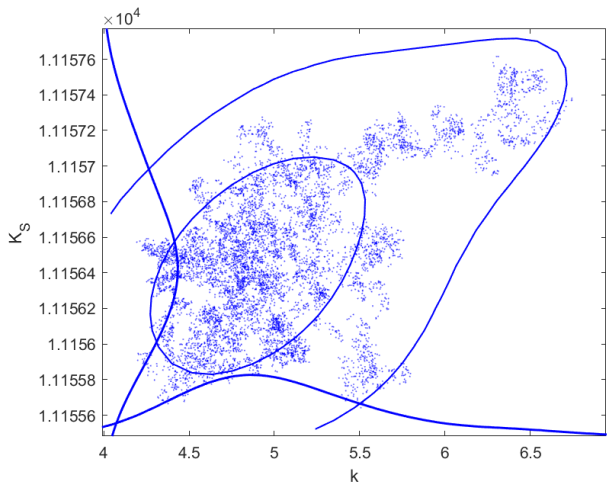
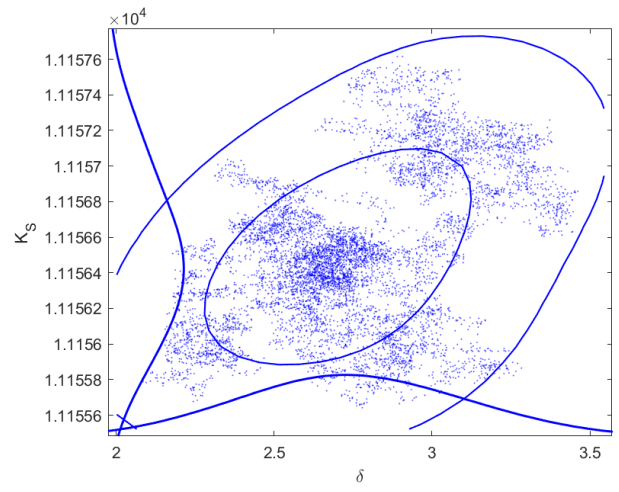
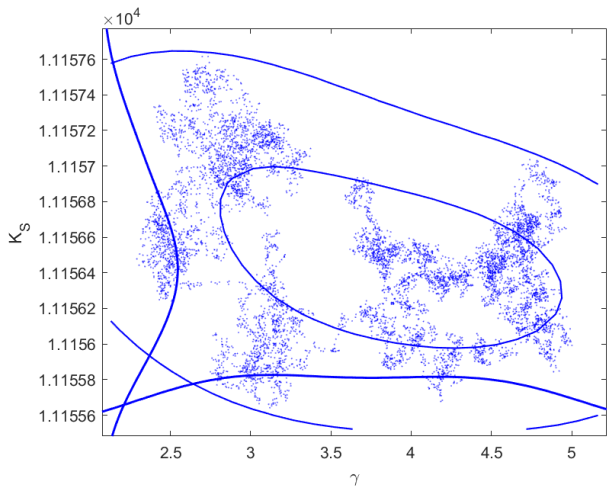


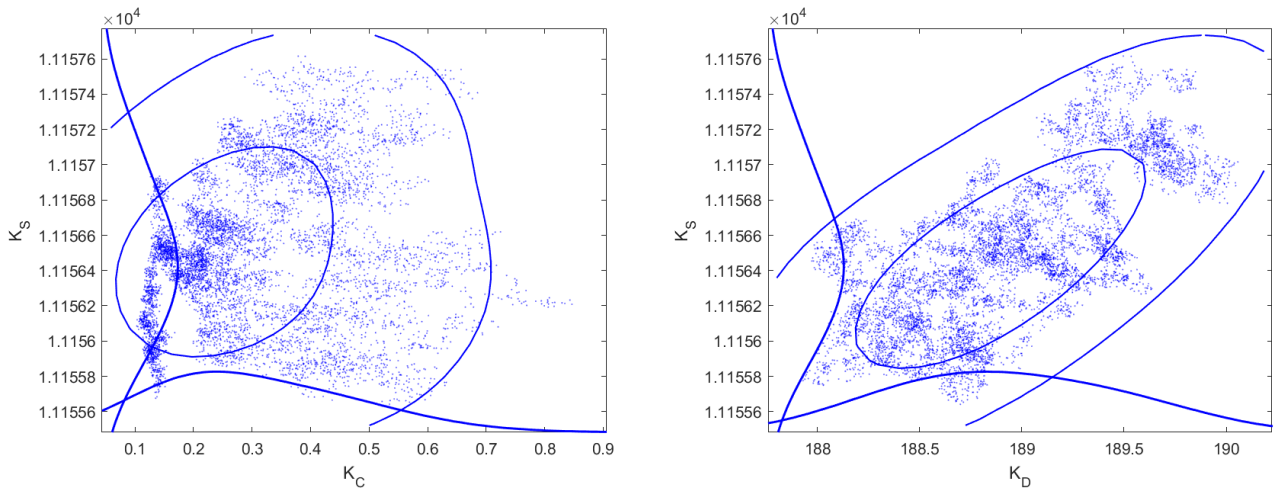












4.3. Marginal distributions for the LHI model

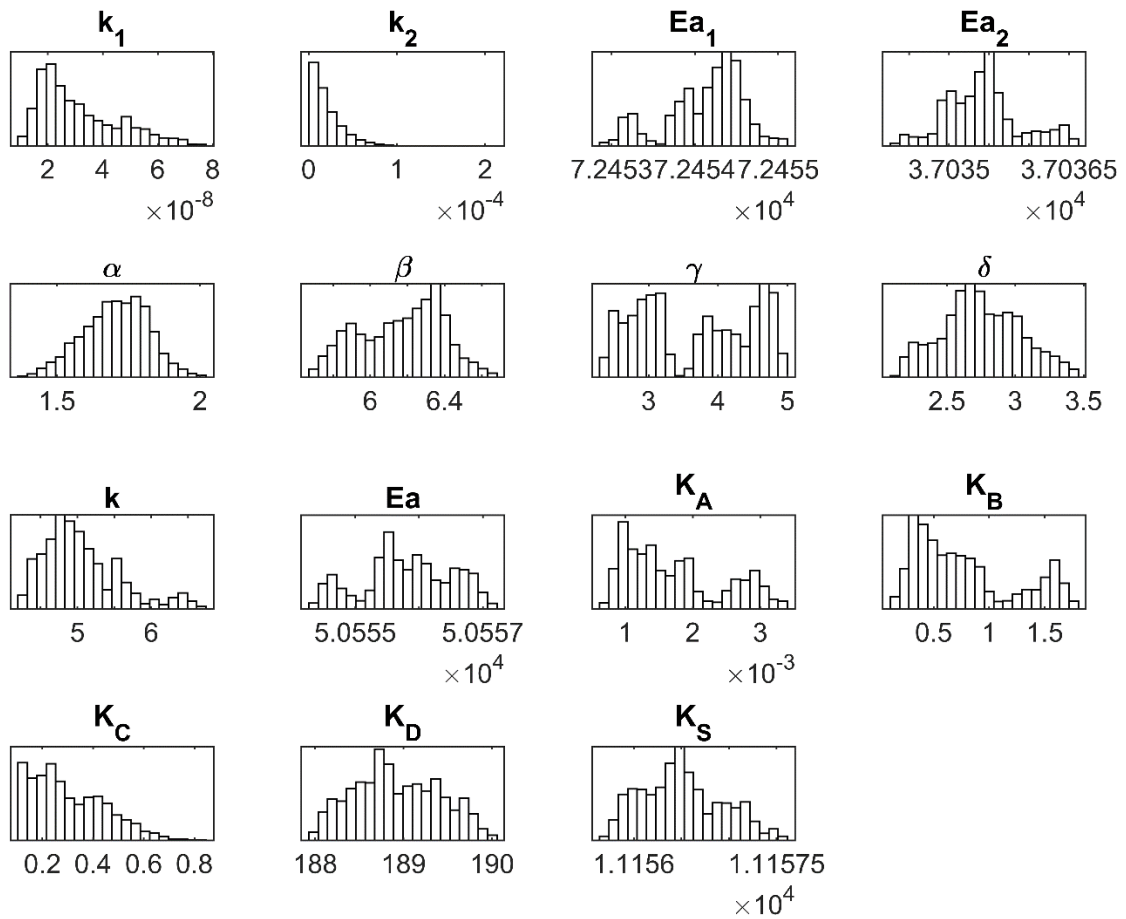


Fig. S8. MCMC distributions of parameters determined through nonlinear regression for the heterogeneous model LHI.

5. Codes for optimization of kinetic parameters using ModEst software using LHI + pseudo-homogeneous model

5.1. Project definition

```
&project
  projectname = 'LA'
/

&files
  nsets = 10
  datafile(1) = 'Exp1.txt'
  datafile(2) = 'Exp2.txt'
  datafile(3) = 'Exp3.txt'
  datafile(4) = 'Exp4.txt'
  datafile(5) = 'Exp5.txt'
  datafile(6) = 'Exp6.txt'
  datafile(7) = 'Exp7.txt'
  datafile(8) = 'Exp8.txt'
  datafile(9) = 'Exp9.txt'
  datafile(10) = 'Exp10.txt'

!weightfile(1)='Wx1.txt'
!weightfile(2)='Wx2.txt'
!weightfile(3)='Wx3.txt'
!weightfile(4)='Wx4.txt'
!weightfile(5)='Wx5.txt'

!dumpfile = 'LA.dmp'
dumpfile = 'LA.bin'
resultfile = 'LA.est'
reportfile = 'LA.sta'
optfile = 'LA.res'
ndumpp    = 100
restartfile = 'LA.res'

/

&problem
  task = 'est'
  model = 'ode'
  odesolver = 'odessa'
  optimizer = 'simlev'
  objfun = 'lsq'
/

&modelpar
  nstates = 4
  nsaux   = 0

modelvar = 'Tmean_global 100'
```

```
k1 global 1
k2 global 1
Ea1 global 50000
Ea2 global 90000
a global 5
b global 5
c global 5
d global 5
k global 1
Ea global 45000
KA global 1
KB global 1
KC global 1
KD global 1
KS global 1
```

```
Vr control file
Temp control file
mcat control file
time Odevar file;
```

```
s0(1:4) initval file;
           file;
           file;
           file;
```

```
target = '
k1 0 100
k2 0 100
Ea1 1e3 1.5e5
Ea2 1e3 2.5e5
a -10 10
b -10 10
c -10 10
d -10 10
k 0 100
Ea 1e3 1.0e5
KA 0 1e5
KB 0 1e5
KC 0 1e5
KD 0 1e5
KS 0 1e5
```

```
,
```

```
/
dstep = 1e-6
```

```
&filepar
combined = 0
usew = 0
nobs(1) = 9 9 9 9 9 9 9 9 9
ncolxy(1) = 8
nydata(1) = 4
indx(1,1) = 1 6 7 8
indy(1,1) = 2 3 4 5
/
```

```
&print
echo = 1
echodata = 1
optmonit = 1
stats = 1
debug = 1
jacout = 1
/
```

```
.\Lev_Acid
&design
/
```

```
&simflex
abstols = 1.00E-16
reltols = 1.00E-16
sizes = .1
itmaxs = 3000
/
```

```
&levmar
reltollm=1.0d-10
iterdfm=100
/
```

```
&newton
/
```

```
&odessa
satol = 1.0e-9
srtol = 1.0e-9
/
```

```
&euler
stpeul = 1e-3
/
```

```
&mcmc
```



```

nsimu    = 80000 ! length of the chain
doadapt  = 0     ! do we adapt
adaptint  = 200  ! intervall for adaptation
burnintime = 5000 ! initial burn in time
doburnin  = 1
drscale   = 5    ! scaling factor for second stage DR
! sstype  = 0    ! how SS is calculated: 0 = normal, 1 = sqrt, 2 = lognormal
sstrans   = 1
printint  = 1000 ! interval to print statistics
filepars  = 0    ! read initial values from files instead of modest? (1=yes)
updatesigma = 1  ! update error variance? (1=yes)
N0        = 1    ! prior for error variance,
S02       = 0    ! 1/s^2 ~ Gamma(N0/2,2/N/S02)
chainfile  = 'chain.mat' ! file to save the chain
s2file     = 's2chain.mat' ! file to save sigma2 chain
dumpint    = 50
/

```

5.2. Method subroutine

```

subroutine fode(ns,t,s,ds,
&      xdata,nx,nobs,
&      nsaux,nstatea,
&      states0,
&      gpar,ngpar,
&      lpar,nlpar,
&      iobs,iset)

implicit none

c arguments

integer*4 ns,nsaux,nstatea !n of state variables
real*8 t !time
real*8 s(nstatea) !state variables
real*8 ds(ns) !derivatives
integer*4 nx,nobs,ngpar,nlpar
real*8 xdata(nx,nobs)
real*8 states0(nstatea)
real*8 gpar(ngpar)
real*8 lpar(nlpar)
integer*4 iobs,iset

c local variables (all user defined variables must be declared here!)
real*8 cA,cB,CC,cD,z, Den
real*8 r, rMW, rHet

include 'la.inc'

c user code:
where (s.lt.0.0d0) s = 0.0d0
CA = s(I)

```

```

CB = s(2)
CC = s(3)
CD = s(4)

Temp = Temp + 273.15
Tmean = Tmean + 273.15
z = 1.0/Temp - 1.0/Tmean
k1 = k1*exp(-Ea1/8.3143*z)
k2 = k2*exp(-Ea2/8.3143*z)
k = k*exp(-Ea/8.3143*z)
Den = (1+KA*CA+KB*CB+CC/KC+CD/KD)**2

rMW = k1*CA**a*CB**b - k2*CC**c*CD**d
rHet = k*(KA*KB*CA*CB-CC*CD/(KS*KC*KD))/Den
r = rMW + mcat*rHet/Vr

ds(1) = -r !A
ds(2) = -r !B
ds(3) = r !C
ds(4) = r !D

return

end

```

5.3. Definition of initial conditions

```

subroutine inits0(ns,t,s,
&      xdata,nx,nobs,
&      nsaux,nstatea,
&      states0,
&      gpar,ngpar,
&      lpar,nlpar,
&      iobs,iset)

implicit none

c  arguments

integer*4 ns,nsaux,nstatea !n of state variables
real*8 t !time
real*8 s(nstatea) !state variables

integer*4 nx,nobs,ngpar,nlpar
real*8 xdata(nx,nobs)
real*8 states0(ns)
real*8 gpar(ngpar)
real*8 lpar(nlpar)
integer*4 iobs,iset

* local variables (all user defined variables must be declared here!)

include 'la.inc'

```

```

* user code:
    s = states0
    t = xdata(1,1)
    return
end

```

5.4. Definition of output variables

```

subroutine observations(s,ns,yest,ny,
&    xdata,nx,nobs,
&    nsaux,nstatea,
&    states0,
&    gpar,ngpar,
&    lpar,nlpar,
&    iobs,iset)

implicit none

c  arguments

integer*4 ns,nsaux,nstatea  !n of state variables
real*8    s(nstatea) !state variables
integer*4 ny                !n of obs. vars
real*8    yest(ny)         !observed variables

integer*4 nx,nobs,ngpar,nlpar
real*8    xdata(nx,nobs)
real*8    states0(nstatea)
real*8    gpar(ngpar)
real*8    lpar(nlpar)
integer*4 iobs,iset

* local variables (all user defined variables must be declared here!)

include 'la.inc'

c  user code:
yest(1)=s(1)
yest(2)=s(2)
yest(3)=s(3)
yest(4)=s(4)

return

end

```