Evaluation of the Degree of Rate Control via Automatic Differentiation - supporting information

Yilin Yang, Siddarth K. Achar and John R. Kitchin

July 26, 2021

This supporting information contains the code to calculate the degree of the rate control for the three cases using the automatic differentiation. The code is in Julia.

Note DifferentialEquations requires sundials to be installed. On a Mac this can be installed with

```
brew install sundials
```

Each Case below should be run independently, e.g. if you use a Jupyter notebook you need to restart the kernel for each one.

1 Case I

1.1 Analytic solution

In this example we show that automatic differentiation is equivalent to an analytical derivative.

```
using GRUtils
using DifferentialEquations
using DiffEqSensitivity, ForwardDiff
using LaTeXStrings
```

We first define functions for the rate, and for the analytical derivatives that define each DRC.

```
function rate(k1, k2, aA, aB, t)
    theta_A = 1 / (1 + 1.0e5)
    return (k1 * aA) .* (1 .- exp.(-k2 * aB .* t)) .+ (k2 * aB * theta_A) .* exp.( -k2 .* aB .* t)
end

function drc1(k1, k2, aA, aB, t, rs)
    return (k1 ./ rs) .* aA .* (1 .- exp.(-k2 .* aB .* t))
end

function drc2(k1, k2, aA, aB, t, rs)
    theta_A = 1 / (1 + 1.0e5)
```

```
    term1 = (k1 * aA * aB) .* t .* exp.(-k2 .* aB .* t)
    term2 = (aB * theta_A) .* exp.(-k2 .* aB .* t)
    term3 = (k2 * aB^2 * theta_A) .* t .* exp.(-k2 .* aB .* t)
    return k2 ./ rs .* (term1 + term2 - term3)
end
```

```
drc2 (generic function with 1 method)
```

This simply evaluates the analytical derivative functions.

```
ts = LinRange(0, 4, 401)
k1 = 1.0e-5
k2 = 1.0
aA = 1.0
aB = 3.0
rs = rate(k1, k2, aA, aB, ts)
drc1_sol = drc1(k1, k2, aA, aB, ts, rs)
drc2_sol = drc2(k1, k2, aA, aB, ts, rs)
```

```
401-element Vector{Float64}:
  1.0
  0.970151497606985
  0.9406119414204311
  0.9113901749347935
  0.8824949171261274
  0.8539347450774003
  0.825718076597347
  0.7978531528975842
  0.7703480213941957
  0.7432105187010817
  0.7164482538830794
  0.6900685920371175
  0.6640786382695216

 -0.0001738281415268283
 -0.0001691884421955314 6
 -0.0001646711555140406 6
 -0.0001602730985310884
 -0.0001559911695070205 5
 -0.0001518223458939878 5
 -0.0001477636823645692
 -0.0001438123088877371 6
 -0.0001399654288510818 2
 -0.0001362203172282495 2
 -0.0001325743187905546
 -0.0001290248463617641
```

1.2 Automatic Differentiation

To use automatic differentiation, we define the ODEs for the mole balances.

```
function state_eqn(dy, y, kf, t)
    aA = 1.0
    aB = 3.0
    kr1 = 0.0
    dy[1] = eq1 = kf[1] * aA * y[2] - kr1 * y[1] - kf[2] * aB * y[1]
    dy[2] = eq2 = -kf[1] * aA * y[2] + kr1 * y[1] + kf[2] * aB * y[1]
end

function calc_rate(y, kf)
    aB = 3.0
    rate = kf[2] * aB * y[1]
    return rate
end
```

```
calc_rate (generic function with 1 method)
```

Next, we integrate the ODEs to get the solution as a function of time.

```
tspan = (0., 4.)
theta_A = 1 / (1 + 1.0e5)
y0 = [theta_A, 1.0 - theta_A]
kf = [1.0e-5, 1.0]
prob = ODEProblem(state_eqn, y0, tspan, kf)
```

```
ODEProblem with uType Vector{Float64} and tType Float64. In-place: true
timespan: (0.0, 4.0)
u0: 2-element Vector{Float64}:
 9.99990000099999e-6
 0.999990000099999
```

We define a wrapper function that we will take the derivative of.

```
function rate_wrapper(lnk)
    kf = exp.(lnk)
    nt = 401
    _prob = remake(prob, p=kf)  # must set "p=parameter" no matter the name of parameter

    theta_sol = Array(solve(_prob, RK4(), saveat=LinRange(0., 4., nt), sensealg=ForwardDiffSensitivity()))'  # [nt, nu]
    kf_matrix = reshape(kf, 1, size(kf, 1))
    kf_repeat = repeat(kf_matrix, nt, 1)
    r = Array{Real, 2}(undef, nt, 1)  # an vector with length of nt
    for i in 1:nt
        r[i, 1] = calc_rate(theta_sol[i, :], kf_repeat[i, :])
    end
    return log.(r)
end
```

```
rate_wrapper (generic function with 1 method)
```

Finally, we compute the derivative of the wrapper function with respect to $log(k_f)$.

```
ad_drcs = ForwardDiff.jacobian(rate_wrapper, log.(kf))
```

```
401×2 Matrix{Float64}:
 0.0         1.0
 0.0100502   0.970146
 0.0201983   0.940594
 0.03044     0.911362
 0.0407714   0.882463
 0.0511884   0.853909
 0.0616871   0.825711
 0.0722636   0.797877
 0.0829145   0.77041
 0.0936362   0.743313
 0.104426    0.716585
 0.115281    0.69022
 0.126197    0.664224

 0.999059    0.00240508
 0.999067    0.00238952
 0.999077    0.00236915
 0.999088    0.00234382
 0.999101    0.00231336
 0.999114    0.00227764
 0.999129    0.0022365
 0.999145    0.00218979
 0.999163    0.00213736
 0.999182    0.00207907
 0.999203    0.00201475
 0.999226    0.00194426
```

This shows that the analytical DRC and AD DRCs are visibly indistinguishable.

```
fig = Figure((6, 4), "in")
plot(ts, drc1_sol,
     linewidth=6, xlabel="Time (s)", ylabel="Degree of Rate Control",
     label="DRC-1-Analytic", dpi=300, linecolor=0x8CDCDA)
hold(true)
plot(ts, drc2_sol, linewidth=6, label="DRC-2-Analytic", dpi=300, linecolor=0x4D4D4D)
plot(ts, ad_drcs[:, 1], linewidth=3, label="DRC-1-AD", dpi=300, linecolor=0xF16A70)
plot(ts, ad_drcs[:, 2], linewidth=3, label="DRC-2-AD", dpi=300, linecolor=0xB1D877)

legend(location=5)
savefig("si-2.png")
```

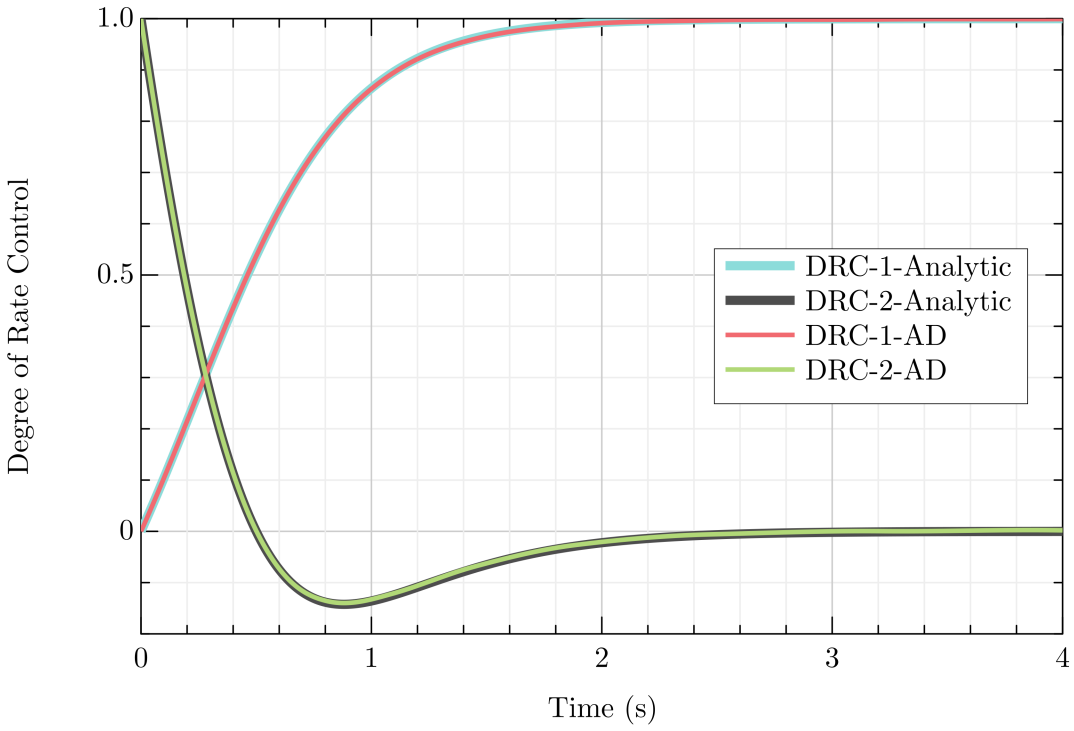


Figure 1: This is equivalent to figure 2 in the manuscript.

2 Case II

```
using GRUtils
using DifferentialEquations
using DiffEqSensitivity, ForwardDiff
using LaTeXStrings
```

```
kf0 = Array([1.33e8, 2.01e11, 2.64e6, 5.24e1, 2.05e5, 1.48e12, 5.32e2])
K = Array([2.15e2, 5.93e-5, 6.28e-2, 1.18e-5, 1.03e3, 1.92e5, 4.50e1])
```

```
7-element Vector{Float64}:
    215.0
      5.93e-5
      0.0628
      1.18e-5
   1030.0
 192000.0
     45.0
```

```
function calc_rate2(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.07, 0.21, 0.085, 0.38])
```

```
    press = press .* 1.01325
    fwd_factor = Array([press[1] * y[1], press[2] * y[1], y[3] * y[1], y[5] *
        y[1], y[2] * y[6], y[7], y[4]^2])
    rev_factor = Array([y[2], y[3], y[4] * y[5], y[4] * y[6], y[7] * y[1],
                        press[3] * y[1], press[4] * y[1]^2])
    r = kf .* fwd_factor .- kr .* rev_factor
    return r
end

function calc_overall_rate2(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.07, 0.21, 0.085, 0.38])
    press = press .* 1.01325
    r1 = kf[7] * y[4]^2 - kr[7] * press[4] * y[1]^2
    return r1
end

function state_eqn2(y, kf, t)
    r = calc_rate2(y, kf)
    eq1 = -r[1] - r[2] -r[3] -r[4] + r[5] + r[6] + 2 * r[7] # *
    eq2 = r[1] - r[5] # CO*
    eq3 = r[2] - r[3] # H2O*
    eq4 = r[3] + r[4] - 2 * r[7] # H*
    eq5 = r[3] - r[4] # OH*
    eq6 = r[4] - r[5] # O*
    eq7 = r[5] - r[6] # CO2*
    Array([eq1, eq2, eq3, eq4, eq5, eq6, eq7])
end
```

```
state_eqn2 (generic function with 1 method)
```

```
tspan = (0., 50.)
y0 = [0.9; 0.01; 0.01; 0.01; 0.01; 0.01; 0.05]
prob2 = ODEProblem(state_eqn2, y0, tspan, kf0)
```

```
ODEProblem with uType Vector{Float64} and tType Float64. In-place: false
timespan: (0.0, 50.0)
u0: 7-element Vector{Float64}:
 0.9
 0.01
 0.01
 0.01
 0.01
 0.01
 0.05
```

```
function rate_wrapper2(p)
    p = exp.(p)
    nt = 501
    _prob = remake(prob2, p=p)
    theta_sol = Array(solve(_prob, Kvaerno5(), saveat=LinRange(2.0, 50.0, nt),
                            sensealg=ForwardDiffSensitivity(), atol=1e-8, rtol=1e-8))' # [nt, nu]
    p_matrix = reshape(p, 1, size(p, 1)) # [1, np]
    p_repeat = repeat(p_matrix, nt, 1) # [nt, np]
    r = Array{Real, 1}(undef, nt)
    for i in 1:nt
        r[i] = calc_overall_rate2(theta_sol[i, :], p_repeat[i, :])
```

```
    end
    return log.(r)
end
```

```
rate_wrapper2 (generic function with 1 method)
```

```
drdp = ForwardDiff.jacobian(rate_wrapper2, log.(kf0))
```

```
501×7 Matrix{Float64}:
 -0.000135567  -3.87846e-12  ...   0.109851  -6.23875e-11  -0.100164
 -0.000124538  -3.56207e-12       0.110363  -5.72342e-11  -0.0940927
 -9.62604e-5   -2.75081e-12       0.111673  -4.40216e-11  -0.0734419
 -5.89023e-5   -1.67903e-12       0.113404  -2.65662e-11  -0.044846
 -2.08788e-5   -5.88169e-13       0.115167  -8.7999e-12   -0.0151252
  9.01706e-6    2.69496e-13  ...   0.116552   5.16877e-12   0.00860227
  2.17123e-5    6.33651e-13       0.117141   1.11006e-11   0.0189906
  1.01098e-5    3.00673e-13       0.116603   5.67931e-12   0.0102476
 -5.92857e-6   -1.59557e-13       0.11586   -1.81454e-12  -0.00206998
 -1.90208e-5   -5.35239e-13       0.115253  -7.93183e-12  -0.0121397
 -2.94084e-5   -8.33302e-13  ...   0.114771  -1.27854e-11  -0.0201459
 -3.73228e-5   -1.06039e-12       0.114405  -1.64834e-11  -0.0262655
 -4.29879e-5   -1.22293e-12       0.114142  -1.91303e-11  -0.0306692

 -1.04946e-9    1.11172e-14       0.116134   9.55184e-13   4.91593e-5
 -7.7989e-10    1.11032e-14  ...   0.116134   9.5531e-13    4.94355e-5
 -5.42121e-10   1.10881e-14       0.116134   9.55421e-13   4.96775e-5
 -3.36712e-10   1.1072e-14        0.116134   9.55517e-13   4.9885e-5
 -1.64218e-10   1.10548e-14       0.116134   9.55597e-13   5.00572e-5
 -2.51956e-11   1.10365e-14       0.116134   9.55662e-13   5.01936e-5
  7.97984e-11   1.10171e-14  ...   0.116134   9.55711e-13   5.02936e-5
  1.50208e-10   1.09966e-14       0.116134   9.55744e-13   5.03566e-5
  1.85477e-10   1.0975e-14        0.116134   9.5576e-13    5.0382e-5
  1.85049e-10   1.09522e-14       0.116134   9.5576e-13    5.03691e-5
  1.48368e-10   1.09283e-14       0.116134   9.55742e-13   5.03175e-5
  7.48777e-11   1.09032e-14  ...   0.116134   9.55708e-13   5.02265e-5
```

```
fig2 = Figure((6, 4), "in")
xs = ["1", "2", "3", "4", "5", "6", "7"]
barplot(xs, drdp[end, :], dpi=300)
ylim((0, 1))
ylabel("Degree of Rate Control")
xlabel("Step id")
savefig("si-3.png")
```

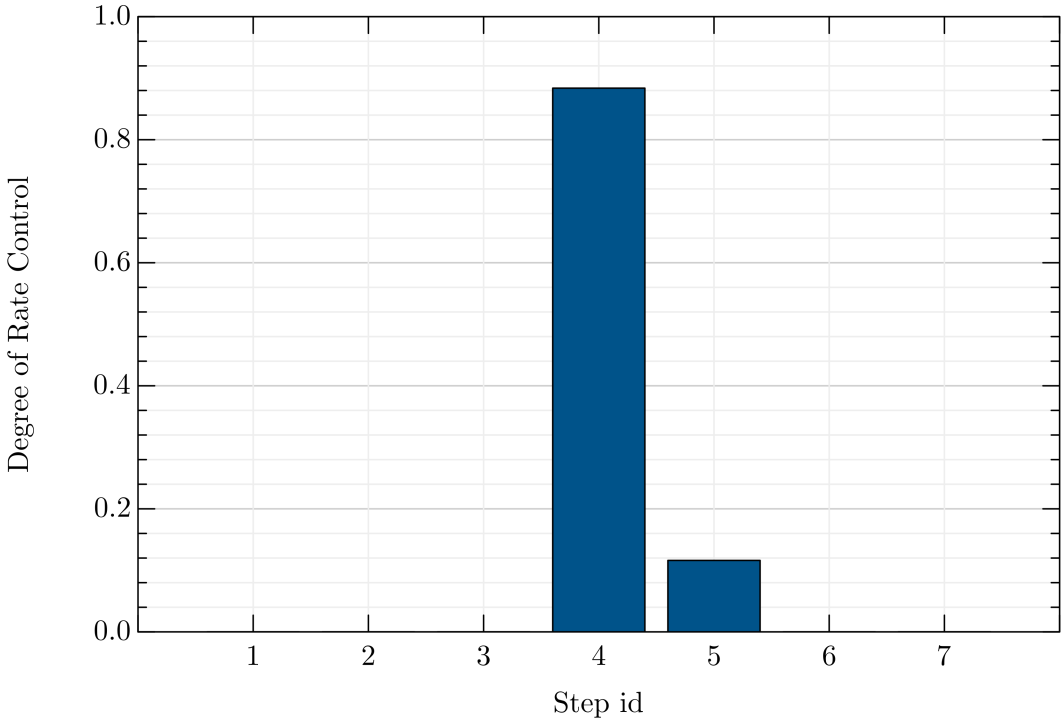


Figure 2: This is Figure 3 in the manuscript.

3 Case III

```
using GRUtils
using DifferentialEquations
using DiffEqSensitivity, ForwardDiff
using LaTeXStrings
```

```
 # Pre-calculated from the energies
kf0 = Array([1.87e8, 1.87e8, 1.87e8, 1.8883185167968056e9, 1.322049155405556e7,
             9.606108656999557e9, 1.0790409835530733e10, 3.930665236502143e7,
             2.3091859525960427e7, 561418.3516964992, 218543.129742791,
             9.818482331329404e11, 8480.066664476652, 2106.812489014142,
             1.0e13, 1.0e13, 0.19579578392147623])

K = Array([0.3200776001873334, 10.40372197634553, 13.121524676913081,
           2.732767674835581e10, 90853.07029698449, 1.8828894331792707e6,
           1.492835002616191e9, 5.543477568325298e11, 350.58978957927326, 40.07010486794337,
           0.0007668179990975123, 6060.791562549015, 5.333375260677139e-5,
           1.3250393012667561e-5, 2.592779654046556e14, 7.83206922497337e11, 9.149335697265244e-10])
```

```
17-element Vector{Float64}:
     0.3200776001873334
    10.40372197634553
    13.121524676913081
     2.732767674835581e10
```

```
 90853.07029698449
     1.8828894331792707e6
     1.492835002616191e9
     5.543477568325298e11
   350.58978957927326
    40.07010486794337
     0.0007668179990975123
  6060.791562549015
     5.333375260677139e-5
     1.3250393012667561e-5
     2.592779654046556e14
     7.83206922497337e11
     9.149335697265244e-10
```

```
function calc_rate(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.1, 0.0, 0.0, 0.0, 0.05])
    fwd_factor = Array([press[1] * y[1], press[1] * y[1], press[1] * y[1], y[2]* y[5],
                        y[3] * y[5], y[4] * y[5], y[6] * y[5], y[10] * y[7], y[8], y[9], y[12],
                        y[11], y[13], y[14], y[16] * y[15], y[17] * y[17], y[16]])
    rev_factor = Array([y[2], y[3], y[4], y[6] * y[7], y[8], y[9], y[10] * y[1],
                        y[11] * y[12], y[13] * y[1], y[14] * y[1], press[3] * y[15], press[2] * y[15],
                        press[4] * y[15], press[4] * y[15], y[5] * y[17], y[16] * y[1], press[5] * y[1]])
    r = kf .* fwd_factor .- kr .* rev_factor
    return r
end

function calc_overall_rate(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.1, 0.0, 0.0, 0.0, 0.05])
    r1 = y[13] * kf[13]
    r2 = y[14] * kf[14]
    r = r1 + r2
    return r
end

function state_eqn(dy, y, kf, t)
    r = calc_rate(y, kf)
    dy[1] = -r[1] - r[2] - r[3] + r[7] + r[9] + r[10] + r[16] + r[17] # *
    dy[2] = r[1] - r[4] # C3H6-1*
    dy[3] = r[2] - r[5] # C3H6-2*
    dy[4] = r[3] - r[6] # C3H6-3*
    dy[5] = -r[4] - r[5] - r[6] - r[7] + r[15] # O*
    dy[6] = r[4] - r[7] # C3H5*
    dy[7] = r[4] - r[8] # OH*
    dy[8] = r[5] - r[9] # OMP-1*
    dy[9] = r[6] - r[10] # OMP-2*
    dy[10] = r[7] - r[8] # C3H5O*
    dy[11] = r[8] - r[12] # C3H4O*
    dy[12] = r[8] - r[11] # H2O*
    dy[13] = r[9] - r[13] # PO-1*
    dy[14] = r[10] - r[14] # PO-2*
    dy[15] = r[11] + r[12] + r[13] + r[14] - r[15] # v*
    dy[16] = -r[15] + r[16] - r[17] # O2*
    dy[17] = r[15] - 2 * r[16] # O-1*
end
```

```
state_eqn (generic function with 1 method)
```

```
tspan = (0., 1.)
y0 = [0.68; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02;
      0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02]
prob = ODEProblem(state_eqn, y0, tspan, kf0)
```

```
ODEProblem with uType Vector{Float64} and tType Float64. In-place: true
timespan: (0.0, 1.0)
u0: 17-element Vector{Float64}:
 0.68
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
```

```
function rate_wrapper(p)
    p = exp.(p)
    nt = 201
    _prob = remake(prob, p=p)
    theta_sol = Array(solve(_prob, Rodas4P(), saveat=LinRange(0., 0.02, 201),
                            sensealg=ForwardDiffSensitivity(), atol=1e-8, rtol=1e-8))' # [nt, nu]
    p_matrix = reshape(p, 1, size(p, 1)) # [1, np]
    p_repeat = repeat(p_matrix, nt, 1) # [nt, np]
    r = Array{Real, 1}(undef, nt)
    for i in 1:nt
        r[i] = calc_overall_rate(theta_sol[i, :], p_repeat[i, :])
    end
    return log.(r) # here, we take care with the second reaction
end
```

```
rate_wrapper (generic function with 1 method)
```

```
drdp = ForwardDiff.jacobian(rate_wrapper, log.(kf0))
```

```
201×17 Matrix{Float64}:
 0.0           0.0           0.0          ...  0.0           0.0           0.0
 0.000140291   0.000235166   0.0870994         8.9376e-8    -1.69054e-6   -0.113988
 0.000722106   0.000190174   0.198013          6.18345e-8   -1.77174e-6   -0.249245
```

```
0.00158909   0.000207795  0.292634      4.70839e-8   -1.66016e-6  -0.366824
0.00257824   0.000252158  0.370735      3.64719e-8   -1.42016e-6  -0.463347
0.00359386   0.000306132  0.432572  ...  2.83264e-8   -1.15698e-6  -0.541995
0.00458931   0.000360327  0.483395      2.19809e-8   -9.18453e-7  -0.606769
0.00550682   0.00040903   0.522706      1.69207e-8   -7.13638e-7  -0.661423
0.00635016   0.000452459  0.555768      1.31928e-8   -5.55975e-7  -0.705199
0.00713804   0.000491964  0.584273      1.03671e-8   -4.35099e-7  -0.740882
0.0077851    0.000522819  0.605404  ...  7.94471e-9   -3.30655e-7  -0.772966
0.00838304   0.000550644  0.623941      6.39215e-9   -2.6339e-7   -0.795962
0.00893695   0.000576149  0.640809      4.98357e-9   -2.02277e-7  -0.817468

0.011596     0.000684434  0.706502      2.98393e-10   2.04814e-9  -0.910095
0.011596     0.000684434  0.706502  ...  2.98393e-10   2.04814e-9  -0.910095
0.011596     0.000684434  0.706502      2.98393e-10   2.04814e-9  -0.910095
0.011596     0.000684434  0.706502      2.98393e-10   2.04815e-9  -0.910095
0.011596     0.000684434  0.706502      2.98393e-10   2.04815e-9  -0.910095
0.011596     0.000684434  0.706502      2.98392e-10   2.04815e-9  -0.910095
0.011596     0.000684434  0.706502  ...  2.98392e-10   2.04815e-9  -0.910095
0.011596     0.000684434  0.706502      2.98392e-10   2.04816e-9  -0.910095
0.011596     0.000684434  0.706502      2.98392e-10   2.04816e-9  -0.910095
0.011596     0.000684434  0.706502      2.98392e-10   2.04816e-9  -0.910095
0.011596     0.000684434  0.706502      2.98392e-10   2.04816e-9  -0.910095
0.011596     0.000684434  0.706502  ...  2.98392e-10   2.04816e-9  -0.910095
```

```
fig = Figure()
xs = ["1", "2", "3", "4", "5", "6", "7", "8", "9", "10", "11", "12", "13", "14", "15", "16", "17"]
barplot(xs, drdp[end, :], dpi=300)
ylabel("Degree of Rate Control")
xlabel("Step id")
savefig("si-4.png")
```

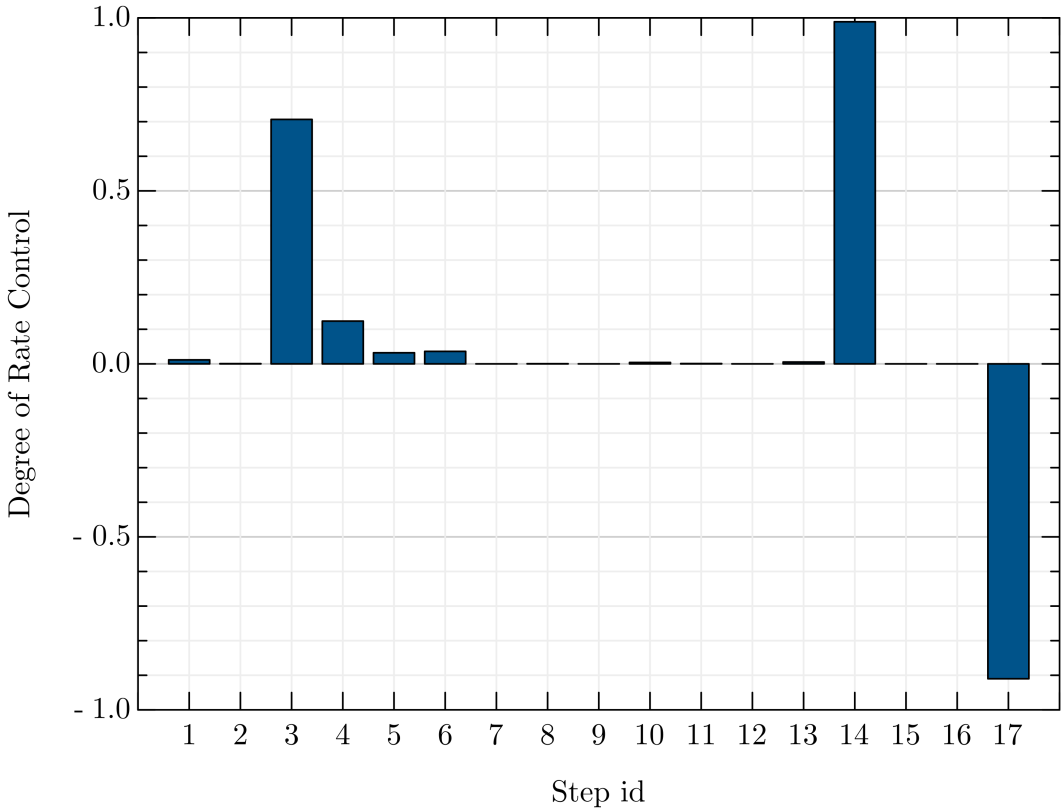


Figure 3: This corresponds to Figure 4.

```
fig = Figure()
plot(LinRange(0.0, 0.02, 201), drdp, linewidth=3,
     xlabel="Time (s)",
     ylabel="Degree of Rate Control (s)", dpi=300)

legend("DRC1", "DRC2", "DRC3", "DRC4", "DRC5", "DRC6", "DRC7", "DRC8", "DRC9",
       "DRC10", "DRC11", "DRC12", "DRC13", "DRC14", "DRC15", "DRC16", "DRC17",
       location=12)

savefig("si-4a.png")
```

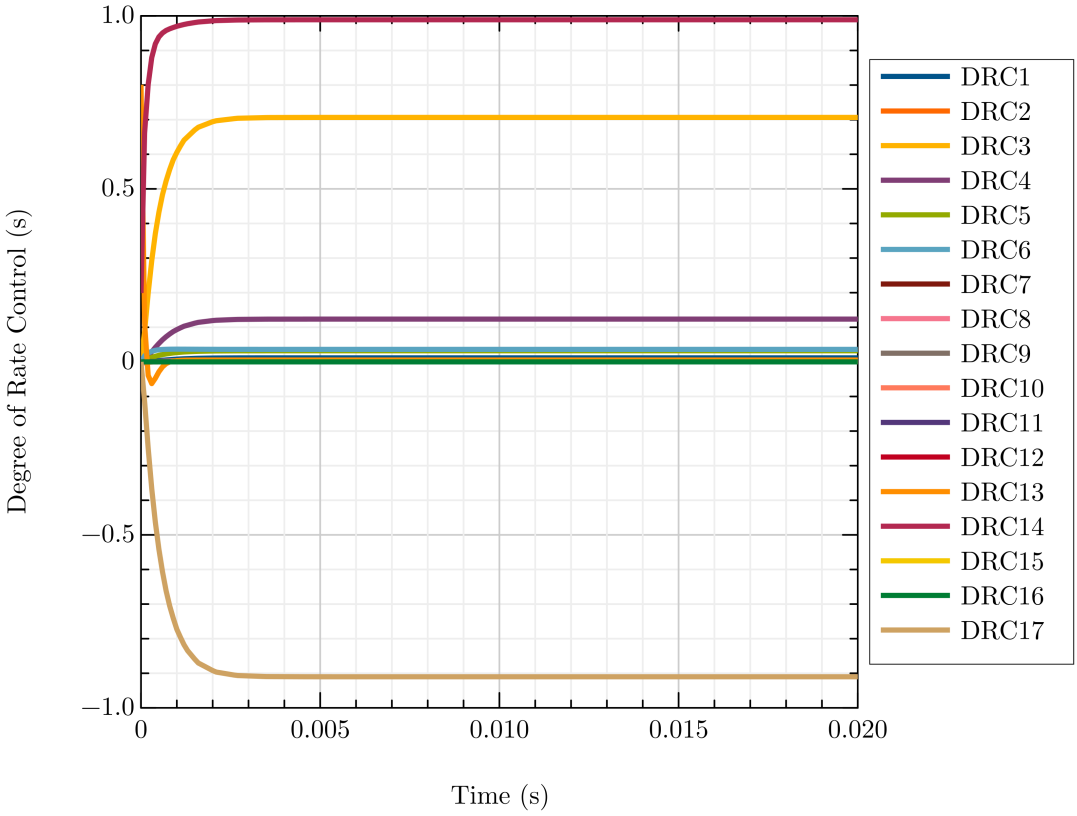


Figure 4: Time dependent DRC for each reaction (not shown in the manuscript).

4 Figure 5

```
using GRUtils
using DifferentialEquations
using DiffEqSensitivity, ForwardDiff
using LaTeXStrings
```

```
Eaf = Array([0.00, 0.00, 0.00, 0.36, 0.59, 0.31, 0.30, 0.54, 0.62, 0.77, 0.76, 0.10, 0.90, 0.96, 0.00, 0.00, 1.36])
Ear = Array([0.42, 0.57, 0.58, 1.40, 1.10, 0.95, 1.19, 1.72, 0.83, 0.89, 0.00, 0.00, 0.00, 0.00, 1.43, 1.18, 0.00])
Af = Array([1.87e8, 1.87e8, 1.87e8, 8.03e12, 1.17e13, 1.28e13, 1.14e13, 1.09e13, 4.10e13, 3.24e13, 1.00e13,
            1.00e13, 1.00e13, 1.00e13, 1.00e13, 1.00e13, 1.00e13, 1.00e13])
Ar = Array([1.00e13, 1.00e13, 1.00e13, 8.93e12, 1.78e13, 1.92e13, 7.14e12, 1.54e13, 1.53e13, 1.31e13, 2.85e8, 1.62e8,
            1.59e8, 1.59e8, 1.00e13, 1.00e13, 2.14e8])


# # reaction conditions
# p_C3H6 = 0.1  # 0.01 - 0.5 bar
# p_O2 = 0.05  # 0.01 - 0.5 bar, https://doi.org/10.1016/j.jcat.2010.09.002
T= 350
times = 15.0  # end time for simulation
np = 1501  # number of points
kb = 8.617333262145e-5
kf0 = Af .* exp.(-Eaf ./ (T * kb))
kr0 = Ar .* exp.(-Ear ./ (T * kb))
K = kf0 ./ kr0
```

```
17-element Vector{Float64}:
   20.872546100528705
 3016.3405010833485
 4202.173967255303
    8.495813690618929e14
    1.4502492307661682e7
    1.0952244663399394e9
    1.0438608184641424e13
    6.9367803791872456e16
 2831.1269056019605
  132.18971425689134
    3.9961041134068033e-7
 2241.5496407486125
    6.905152211410761e-9
    9.445202678799137e-10
    3.900261523392704e20
    9.800588792613136e16
    1.2202480858241735e-15
```

```
function calc_rate(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.1, 0.0, 0.0, 0.0, 0.05])
    fwd_factor = Array([press[1] * y[1], press[1] * y[1], press[1] * y[1], y[2] * y[5], y[3] * y[5], y[4] * y[5], y[6] * y[5],
                        y[10] * y[7], y[8], y[9], y[12], y[11], y[13], y[14], y[16] * y[15], y[17] * y[17], y[16]])
    rev_factor = Array([y[2], y[3], y[4], y[6] * y[7], y[8], y[9], y[10] * y[1], y[11] * y[12], y[13] * y[1], y[14] * y[1],
                        press[3] * y[15], press[2] * y[15], press[4] * y[15], press[4] * y[15], y[5] * y[17], y[16] * y[1], pres
    r = kf .* fwd_factor .- kr .* rev_factor
    return r
end


function calc_overall_rate(y, kf)
    global K
    kr = kf ./ K
    press = Array([0.1, 0.0, 0.0, 0.0, 0.05])
    r1 = y[13] * kf[13]
    r2 = y[14] * kf[14]
    r = r1 + r2
    return r
end


function state_eqn(dy, y, kf, t)
    r = calc_rate(y, kf)
    dy[1] = -r[1] - r[2] - r[3] + r[7] + r[9] + r[10] + r[16] + r[17]  # *
    dy[2] = r[1] - r[4]  # C3H6-1*
    dy[3] = r[2] - r[5]  # C3H6-2*
    dy[4] = r[3] - r[6]  # C3H6-3*
    dy[5] = -r[4] - r[5] - r[6] - r[7] + r[15]  # O*
    dy[6] =  r[4] - r[7] # C3H5*
    dy[7] =  r[4] - r[8] # OH*
    dy[8] =  r[5] - r[9] # OMP-1*
    dy[9] =  r[6] - r[10] # OMP-2*
    dy[10] = r[7] - r[8]  # C3H5O*
    dy[11] = r[8] - r[12]  # C3H4O*
    dy[12] = r[8] - r[11]  # H2O*
    dy[13] = r[9] - r[13]  # PO-1*
```

```
    dy[14] = r[10] - r[14]  # PO-2*
    dy[15] = r[11] + r[12] + r[13] + r[14] - r[15]  # v*
    dy[16] = -r[15] + r[16] - r[17]  # O2*
    dy[17] =  r[15] - 2 * r[16] # O-1*
end
```

```
state_eqn (generic function with 1 method)
```

```
tspan = (0., times + 1.0)
y0 = [0.68; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02; 0.02]
prob = ODEProblem(state_eqn, y0, tspan, kf0)
```

```
ODEProblem with uType Vector{Float64} and tType Float64. In-place: true
timespan: (0.0, 16.0)
u0: 17-element Vector{Float64}:
 0.68
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
 0.02
```

```
function rate_wrapper(p)
    p = exp.(p)
    nt = np
    _prob = remake(prob, p=p)
    theta_sol = Array(solve(_prob, Rodas4P(), saveat=LinRange(0., times, np), sensealg=ForwardDiffSensitivity(), atol=1e-8, rtol
    p_matrix = reshape(p, 1, size(p, 1))  # [1, np]
    p_repeat = repeat(p_matrix, nt, 1)  # [nt, np]
    r = Array{Real, 1}(undef, nt)
    for i in 1:nt
        r[i] = calc_overall_rate(theta_sol[i, :], p_repeat[i, :])
    end
    return log.(r)  # here, we take care with the second reaction
end
```

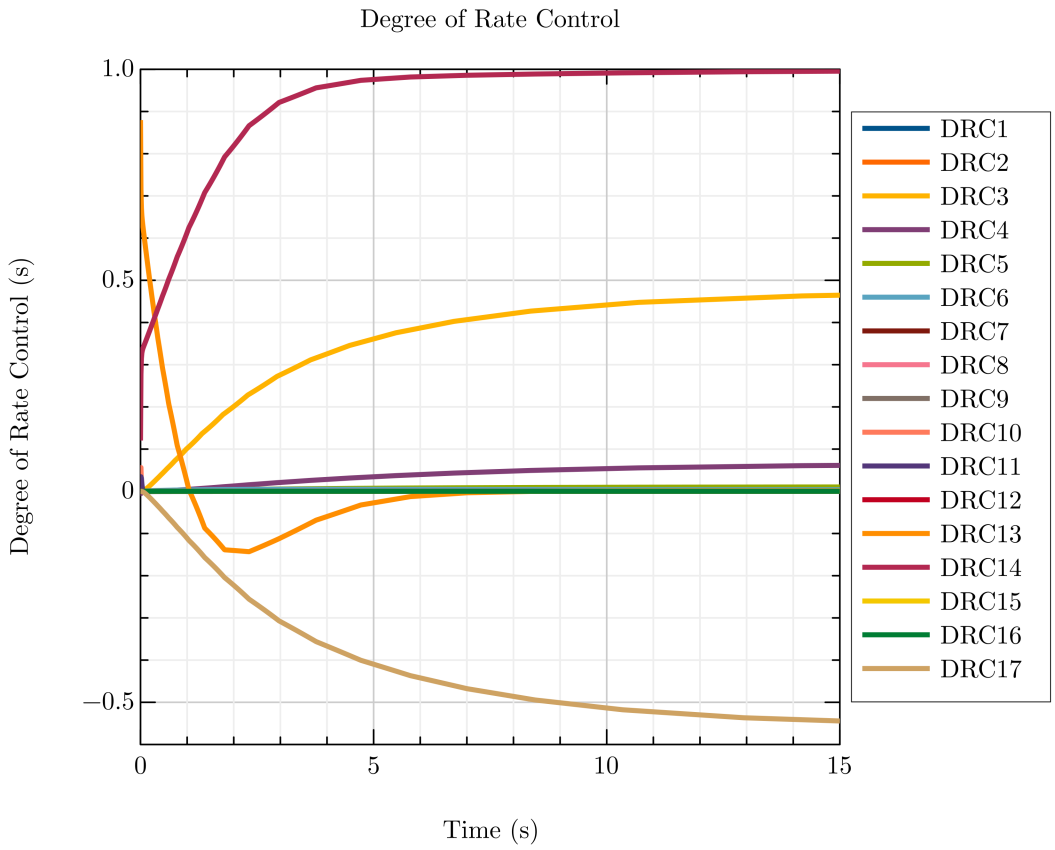
```
rate_wrapper (generic function with 1 method)
```

```
drdp = ForwardDiff.jacobian(rate_wrapper, log.(kf0))
```

```
1501×17 Matrix{Float64}:
  0.0          0.0          0.0           ...   0.0           0.0
 -0.00399755   9.61583e-5   0.0042394          6.61814e-9   -0.000584464
 -0.00154971   8.31498e-5   0.00167367         4.60157e-9   -0.000261893
 -0.000524881  6.43145e-5   0.000701612        1.13217e-10  -0.000424031
 -0.000158407  5.66038e-5   0.00048945        -2.89243e-9   -0.000688568
 -3.91155e-5   5.38658e-5   0.000678655   ...  -5.3132e-9     -0.00111
  5.09909e-6   5.26928e-5   0.00108609        -6.93231e-9   -0.00168479
  1.86994e-5   5.21626e-5   0.00164997        -7.61491e-9   -0.00236869
  2.31524e-5   5.18243e-5   0.00230405        -7.69637e-9   -0.00313166
  2.39026e-5   5.15637e-5   0.00302769        -7.53107e-9   -0.00395582
  2.3196e-5    5.13349e-5   0.00382354    ...  -7.29258e-9   -0.00482865
  2.24219e-5   5.11078e-5   0.00465954        -7.08513e-9   -0.00575532
  2.15874e-5   5.08819e-5   0.00553211        -6.92101e-9   -0.00671127

  0.0045958    8.01083e-5   0.464472          -7.91957e-10  -0.543852
  0.00459676   8.0118e-5    0.464493      ...  -7.89471e-10  -0.543889
  0.00459773   8.01278e-5   0.464515          -7.86985e-10  -0.543926
  0.00459869   8.01376e-5   0.464536          -7.84499e-10  -0.543963
  0.00459965   8.01473e-5   0.464558          -7.82013e-10  -0.544
  0.00460061   8.01571e-5   0.46458           -7.79527e-10  -0.544036
  0.00460158   8.01669e-5   0.464601      ...  -7.77041e-10  -0.544073
  0.00460254   8.01766e-5   0.464623          -7.74555e-10  -0.54411
  0.0046035    8.01864e-5   0.464644          -7.72069e-10  -0.544147
  0.00460447   8.01962e-5   0.464666          -7.69583e-10  -0.544184
  0.00460543   8.02059e-5   0.464687          -7.67096e-10  -0.544221
  0.00460639   8.02157e-5   0.464709      ...  -7.6461e-10   -0.544258
```

```
fig1 = Figure()
plot(LinRange(0., times, np), drdp, linewidth=3, xlabel = "Time (s)", ylabel = "Degree of Rate Control (s)", title = "Degree of
legend("DRC1", "DRC2", "DRC3", "DRC4", "DRC5", "DRC6", "DRC7", "DRC8", "DRC9", "DRC10", "DRC11", "DRC12", "DRC13", "DRC14", "DRC
savefig("si-5a.png")
```




```
function trans_finite_forward(old_k, pert, prob, idx_k)
    new_k_1 = deepcopy(old_k)
    new_k_2 = deepcopy(old_k)
    new_k_1[idx_k] = old_k[idx_k] * (1 - pert)
    new_k_2[idx_k] = old_k[idx_k] * (1 + pert)
    _prob_1 = remake(prob, p=new_k_1)
    new_ode_sol_1 = solve(_prob_1, Rodas4P(), saveat=LinRange(0., times, np), atol=1e-8, rtol=1e-8)
    new_coverage_1 = Array(new_ode_sol_1)  # [nc, nt]
    new_rates_1 = Array{Float64, 1}(undef, size(new_coverage_1, 2))
    for it in 1:size(new_coverage_1, 2)
        new_rates_1[it] = calc_overall_rate(new_coverage_1[:, it], new_k_1)
    end

    _prob_2 = remake(prob, p=new_k_2)
    new_ode_sol_2 = solve(_prob_2, Rodas4P(), saveat=LinRange(0., times, np), atol=1e-8, rtol=1e-8)
    new_coverage_2 = Array(new_ode_sol_2)  # [nc, nt]
    new_rates_2 = Array{Float64, 1}(undef, size(new_coverage_2, 2))
    for it in 1:size(new_coverage_2, 2)
        new_rates_2[it] = calc_overall_rate(new_coverage_2[:, it], new_k_2)
    end

    delta_ln_rate = log.(new_rates_2) .- log.(new_rates_1)
    delta_ln_k = log.(new_k_2[idx_k]) - log.(new_k_1[idx_k])
    drc = delta_ln_rate ./ delta_ln_k
    return drc
end
```

```
trans_finite_forward (generic function with 1 method)
```

```
trans_cands = 10 .^(LinRange(-1., -14., 14))

```

```
fd_trans_drcs = Array{Float64, 3}(undef, size(trans_cands, 1), size(kf0, 1), np)

for (idx, c) in enumerate(trans_cands)
    for idx_k in 1:size(kf0, 1)
        fd_trans_drcs[idx, idx_k, :] = trans_finite_forward(kf0, c, prob, idx_k)
    end
end
```

```
fig2 = Figure()

lw = 1.5
sub1 = subplot(2, 2, 1)
target_k = 3
# plot(LinRange(0., 0.02, 201), drdp[:, target_k], linewidth=3, linecolor=0x7F58AF, dpi=300, alpha=0.7)
plot(LinRange(0., times, np), drdp[:, target_k], linewidth=5, linecolor=0x000000, dpi=300, alpha=0.7)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[4, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-3", dpi=300, linecolor=0xE84D8A)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[11, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-3", dpi=300, linecolor=0x64C5EB)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[14, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-3", dpi=300, linecolor=0xFEB326)
legend("AD", "FD(1e-4)", "FD(1e-11)", "FD(1e-14)", location=4)

sub2 = subplot(2, 2, 2)
target_k = 4
plot(LinRange(0., times, np), drdp[:, target_k], linewidth=5, linecolor=0x000000, dpi=300, alpha=0.7)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[4, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-4", dpi=300, linecolor=0xE84D8A)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[11, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-4", dpi=300, linecolor=0x64C5EB)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[14, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-4", dpi=300, linecolor=0xFEB326)
hold(true)
legend("AD", "FD(1e-4)", "FD(1e-11)", "FD(1e-14)", location=4)

sub3 = subplot(2, 2, 3)
target_k = 14
plot(LinRange(0., times, np), drdp[:, target_k], linewidth=5, linecolor=0x000000, dpi=300, alpha=0.7)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[4, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-14", dpi=300, linecolor=0xE84D8A)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[11, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-14", dpi=300, linecolor=0x64C5EB)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[14, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-14", dpi=300, linecolor=0xFEB326)
hold(true)
legend("AD", "FD(1e-4)", "FD(1e-11)", "FD(1e-14)", location=4)

sub4 = subplot(2, 2, 4)
target_k = 17
plot(LinRange(0., times, np), drdp[:, target_k], linewidth=5, linecolor=0x000000, dpi=300, alpha=0.7)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[4, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-17", dpi=300, linecolor=0xE84D8A)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[11, target_k, :]), linewidth=lw, xlabel = "Time (s)",
     ylabel = "DRC-17", dpi=300, linecolor=0x64C5EB)
hold(true)
plot(LinRange(0., times, np), (fd_trans_drcs[14, target_k, :]), linewidth=lw, xlabel = "Time (s)",
```

```
    ylabel = "DRC-17", dpi=300, linecolor=0xFEB326)
hold(true)
legend("AD", "FD(1e-4)", "FD(1e-11)", "FD(1e-14)", location=4)


savefig("si-5.png")
```

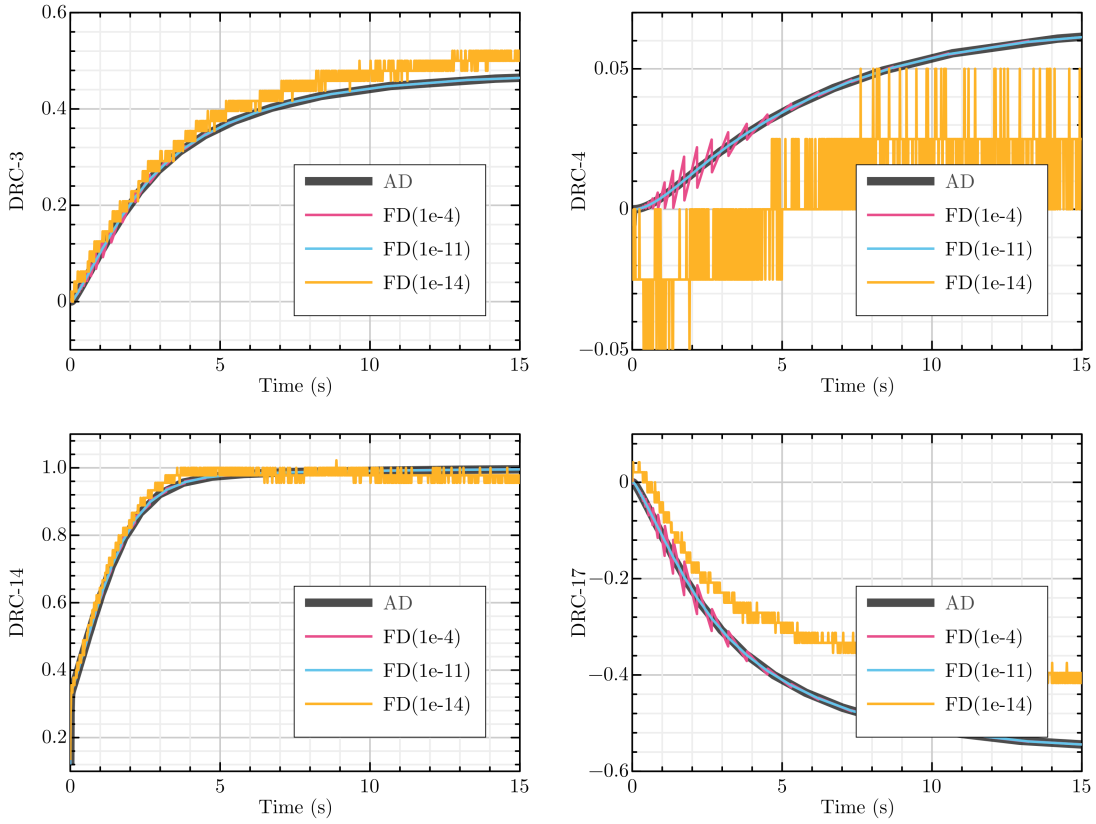


Figure 5: This is figure 5 in the manuscript.

5 DELSA for Uncertain Parameters

Please find the related code at our GitHub repo.

To generate the figures run these commands with that code:

```
julia run_drc.jl PO-input.yaml --output_path PO-output
julia run_drc.jl PO-input-delsa.yaml --output_path PO-output-delsa --delsa
```

After that, this code was used for Figure 6.

```
from matplotlib import pyplot as plt
import numpy as np

```

```
data = np.load("./autodiff-drc/PO-output-delsa/delsa-sensit.npy")

def subplot(fig, ax_index, param_index, data, title):
    ax = fig.add_subplot(1, 3, ax_index)
    ax.hist(data[:, -1, param_index], bins=15, color=[(252/255, 78/255, 3/255)], rwidth=0.9)
    ax.set_xlim([0, 1])
    ax.set_xlabel("Delsa Importance Measure")
    ax.set_ylabel("Frequency")
    ax.set_title(title)
    ax.grid()
    ax.text(0.35, 31, f"Mean: {round(data[:, -1, param_index].mean(), 3)}", fontsize=13)
    return ax


fig = plt.figure(figsize=(16, 5))
subplot(fig, 1, 2, data, r"DELSA-$k_{3}$")
subplot(fig, 2, 13, data, r"DELSA-$k_{14}$")
subplot(fig, 3, 16, data, r"DELSA-$k_{17}$");
```