Problem Solving Using Differential Algebraic Equations (DAE) to Optimisation Formulations: Pyrolysis Kinetic and Concentration Profile Study

Dr Jhuma Sadhukhan
FIChemE, CEng, CSci
jhumasadhukhan@gmail.com

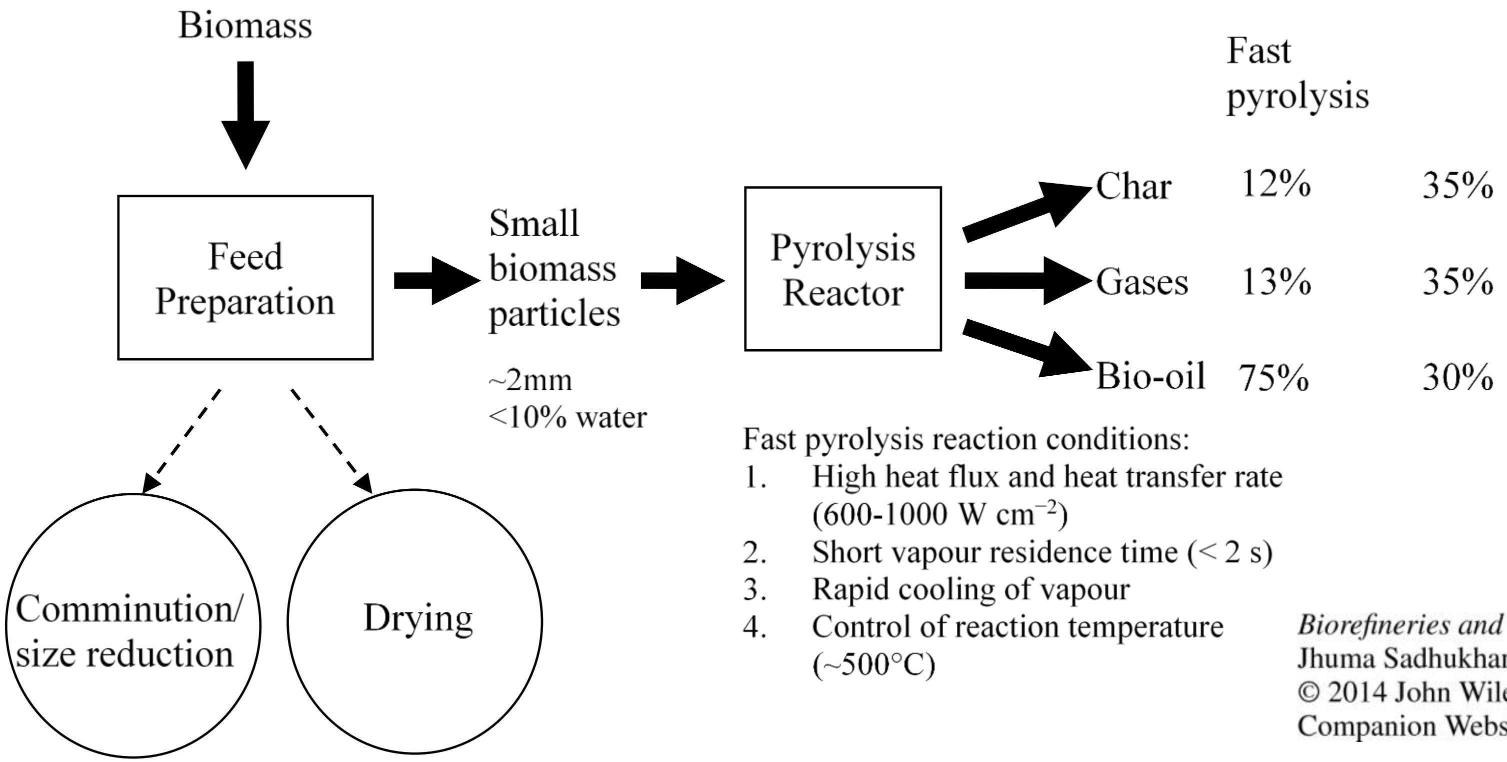
"A biorefinery is an integrated system with efficient and flexible conversion of biomass feedstocks, through a combination of physical, chemical, biochemical and thermochemical processes, into multiple products."

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Pyrolysis

- Thermal conversion (destruction) of organics into liquid in the absence of oxygen
- This process does not involve the interaction with air or oxygen and occurs at a temperature around 300-700°C. This is a thermal degradation process, where large molecules are broken down into smaller fragments, producing bio-oil as the main product from the middle, gas from the top and tar from the bottom. Bio-oil is an important platform chemical.

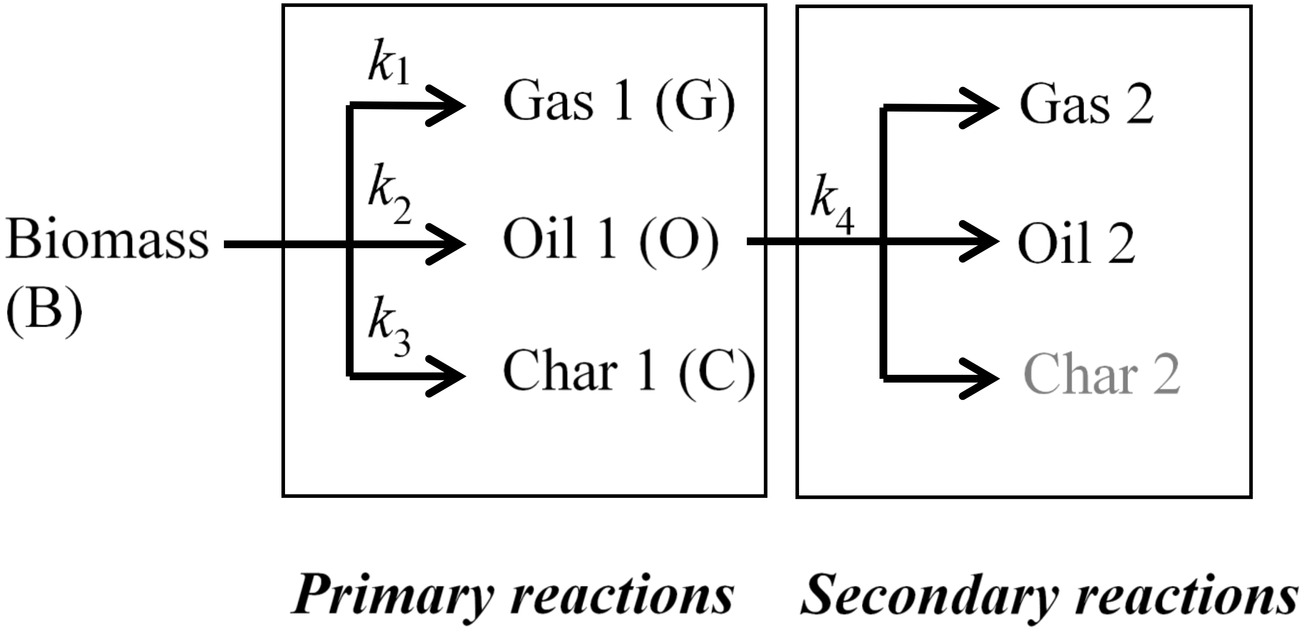


Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

*Slow pyrolysis (also known as carbonisation) has a longer vapour residence time and the reaction occurs at a lower temperature compared to fast pyrolysis, leading to a different distribution of products.

Pyrolysis: Waterloo kinetics



$$\frac{dm_B(t)}{dt} = -(k_1 + k_2 + k_3)\, m_B(t) = -k\, m_B(t)$$

$$\frac{dm_G(t)}{dt} = k_1 m_B(t) + k_4\, m_O(t)$$

$$\frac{dm_O(t)}{dt} = k_2 m_B(t) - k_4\, m_O(t)$$

$$\frac{dm_C(t)}{dt} = k_3\, m_B(t)$$

At $t = 0$, $m_B = 1$, $m_G = 0$, $m_O = 0$ and $m_C = 0$

The problem is defined as Initial Value Problem (IVP)

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Waterloo kinetics: Rate constants expressed as Arrhenius equations

$$\frac{dm_B(t)}{dt} = -(k_1 + k_2 + k_3)m_B(t) = -k\,m_B(t)$$

$$\frac{dm_G(t)}{dt} = k_1 m_B(t) + k_4\,m_O(t)$$

$$\frac{dm_O(t)}{dt} = k_2 m_B(t) - k_4\,m_O(t)$$

$$\frac{dm_C(t)}{dt} = k_3\,m_B(t)$$

$$k_1 = 14300 \exp\left(\frac{-106500}{RT}\right)$$

$$k_3 = \frac{m_{C,\infty}}{1 - m_{C,\infty}}(k_1 + k_2)$$

$$k_4 = 7900 \exp\left(\frac{-81000}{RT}\right)$$

At $t = 0$, $m_B = 1$, $m_G = 0$, $m_O = 0$ and $m_C = 0$

$$k = k_1 + k_2 + k_3$$

The problem is defined as DAE Initial Value Problem (DAE-IVP)

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Waterloo kinetics: Boundary value conditions

$$\frac{dm_B(t)}{dt} = -\left(k_1 + k_2 + k_3\right) m_B(t) = -k\, m_B(t)$$

$$\frac{dm_G(t)}{dt} = k_1 m_B(t) + k_4\, m_O(t)$$

$$\frac{dm_O(t)}{dt} = k_2 m_B(t) - k_4\, m_O(t)$$

$$\frac{dm_C(t)}{dt} = k_3\, m_B(t)$$

$$k_1 = 14300 \exp\left(\frac{-106500}{RT}\right)$$

$$k_3 = \frac{m_{C,\infty}}{1 - m_{C,\infty}}\left(k_1 + k_2\right)$$

$$k_4 = 7900 \exp\left(\frac{-81000}{RT}\right)$$

$$k = k_1 + k_2 + k_3$$

Slow pyrolysis	300°C	$m_G = 0.35$	$m_O = 0.3$	$m_C = 0.35$
Fast pyrolysis	500°C	$m_G = 0.13$	$m_O = 0.75$	$m_C = 0.12$

At $t = 0$, $m_B = 1$, $m_G = 0$, $m_O = 0$ and $m_C = 0$

The problem is defined as DAE Boundary Value Problem (DAE-BVP)

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Waterloo kinetics: Analytical expressions of the differential equations

$$m_B(t) = \exp(-kt)$$

$$m_G(t) = -\frac{k-k_4}{k}\left[kk_1\exp(-kt) - k_1k_4\exp(-kt) - k_2k_4\exp(-kt) + kk_2\exp(-k_4t) - kk_1 + k_1k_4 - kk_2 + k_2k_4\right]$$

$$m_O(t) = -\frac{k_2}{k-k_4}\exp(-k_4t)\left[\exp(-t(k-k_4)) - 1\right]$$

$$m_C(t) = \frac{k_3}{k}\left[1-\exp(-kt)\right]$$

$$k_1 = 14300\exp\left(\frac{-106500}{RT}\right)$$

$$k_3 = \frac{m_{C,\infty}}{1-m_{C,\infty}}\left(k_1+k_2\right)$$

$$k_4 = 7900\exp\left(\frac{-81000}{RT}\right)$$

$$k = k_1 + k_2 + k_3$$

Slow pyrolysis	300°C	$m_G = 0.35$	$m_O = 0.3$	$m_C = 0.35$
Fast pyrolysis	500°C	$m_G = 0.13$	$m_O = 0.75$	$m_C = 0.12$

At $t = 0$, $m_B = 1$, $m_G = 0$, $m_O = 0$ and $m_C = 0$

There are 8 equations and 9 variables. Hence, the problem is an optimisation problem.

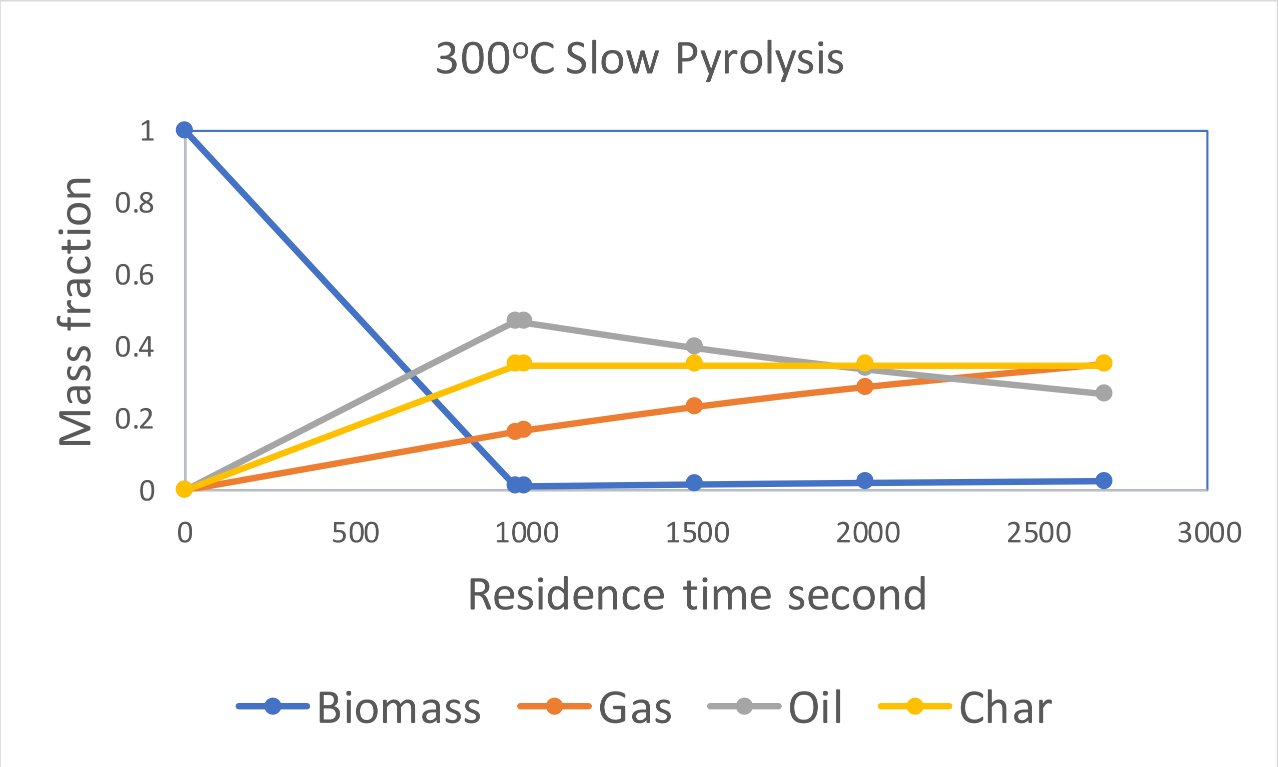
The optimisation problem can be solved for k_2 using the GRG method.

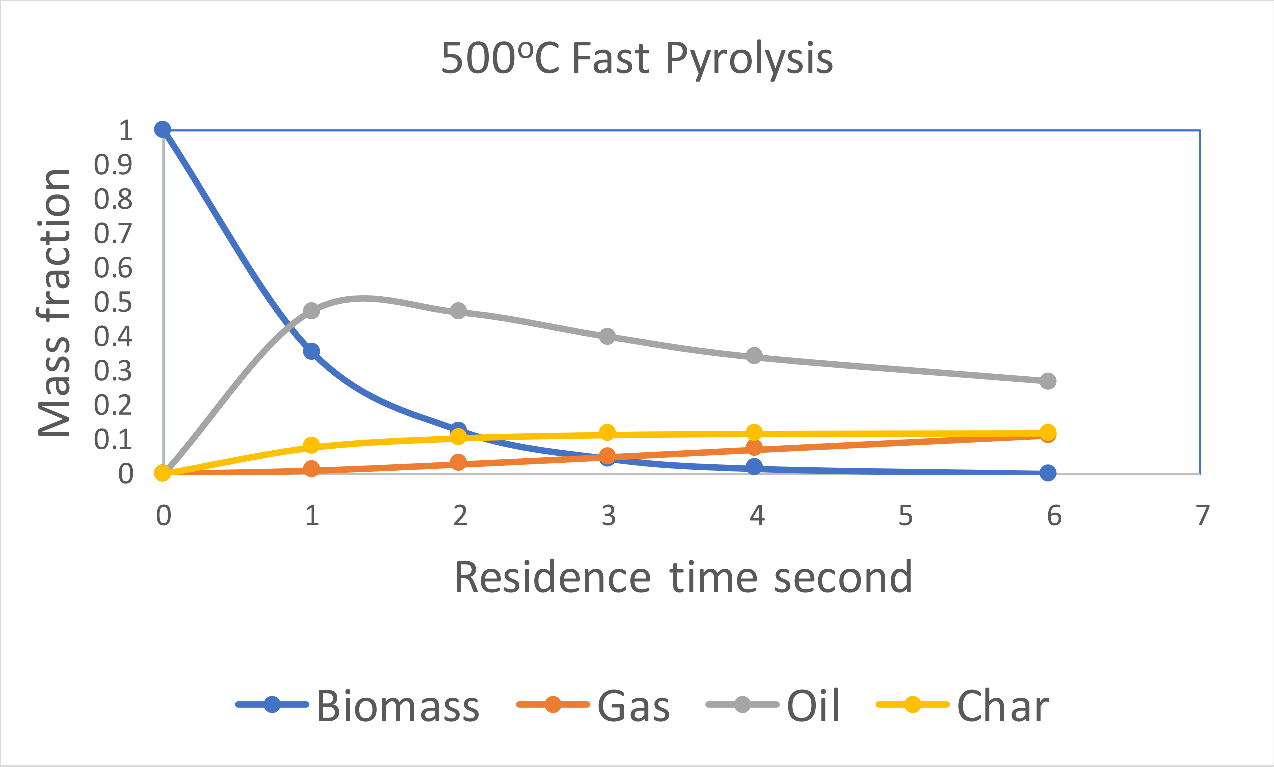
For the generalised reduced gradient method, see Chapter 8 of the reference below.

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

Optimisation problem solutions using the GRG method





$m_{C,\infty}$= 0.35

Optimisation solution → k_2

k_1	0
k_2	0.626104
k_3	0.337135
k_4	0.000326
k	0.963242

$$k_1 = 14300 \exp\left(\frac{-106500}{RT}\right)$$

$$k_3 = \frac{m_{C,\infty}}{1 - m_{C,\infty}}(k_1 + k_2)$$

$$k_4 = 7900 \exp\left(\frac{-81000}{RT}\right)$$

$m_{C,\infty}$= 0.12

k_1	0.000909
k_2	0.910470
k_3	0.124279
k_4	0.026543
k	1.035657

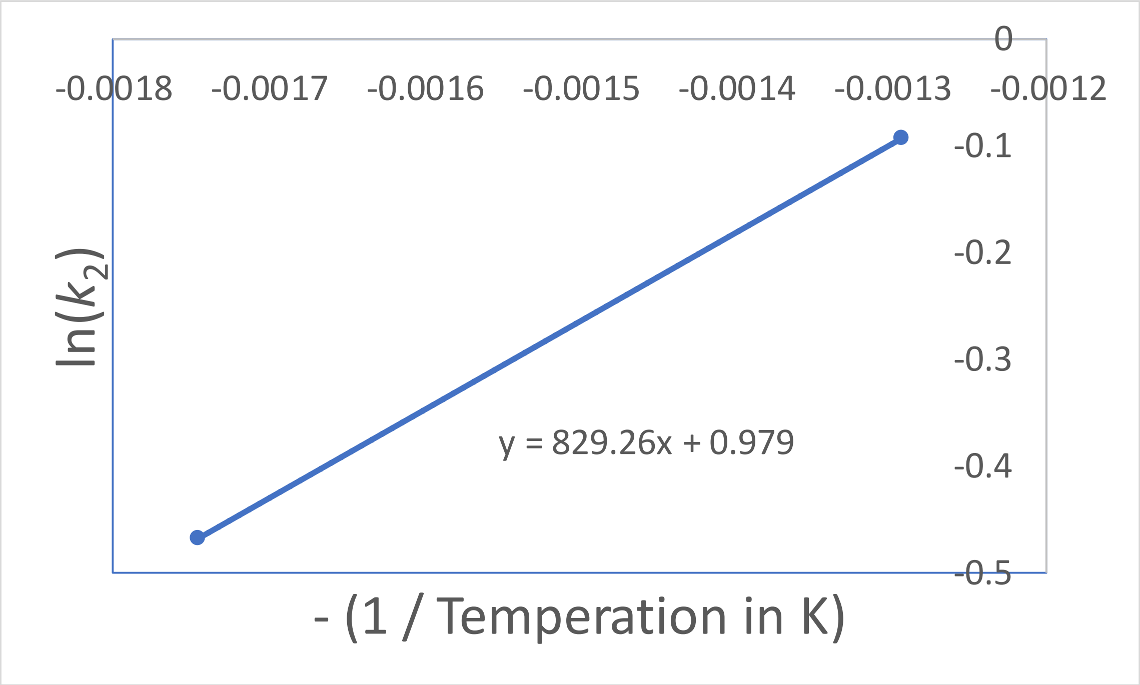
Optimisation solution

k_2 expressed as Arrhenius equations

Temperature, K	=300+273	=500+273
k_2	0.626104	0.910470

$$k_2 = k_0 \exp\left(-\frac{A}{RT}\right)$$

$$\ln k_2 = \ln k_0 + \frac{A}{R}\left(-\frac{1}{T}\right)$$



$$k_2 = 2.6618 \exp\left(-\frac{6894.4676}{RT}\right)$$

$$m_B(t) = \exp(-kt)$$

$$m_G(t) = -\frac{k-k_4}{k}\left[kk_1\exp(-kt) - k_1k_4\exp(-kt) - k_2k_4\exp(-kt) + kk_2\exp(-k_4t) - kk_1 + k_1k_4 - kk_2 + k_2k_4\right]$$

$$m_O(t) = -\frac{k_2}{k-k_4}\exp(-k_4t)\left[\exp(-t(k-k_4)) - 1\right]$$

$$m_C(t) = \frac{k_3}{k}\left[1 - \exp(-kt)\right]$$

Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis, First Edition.
Jhuma Sadhukhan, Kok Siew Ng and Elias Martinez Hernandez.

Companion Website: http://www.wiley.com/go/sadhukhan/biorefineries

$$k_1 = 14300\exp\left(\frac{-106500}{RT}\right)$$

$$\mathbf{k_2 = 2.6618\exp\left(-\frac{6894.4676}{RT}\right)}$$

$$k_3 = \frac{m_{C,\infty}}{1-m_{C,\infty}}(k_1 + k_2)$$

$$k_4 = 7900\exp\left(\frac{-81000}{RT}\right)$$

$$k = k_1 + k_2 + k_3$$

Conclusions

- Shows an example of how a DAE problem is eventually revealed as an optimisation problem.
- The whole operation was done in Excel spreadsheet.
- In real world problems, we often face data gaps, such as, in this case, biomass to oil reaction rate constant.
- From the steady state values, we can turn an IVP into a BVP.
- If analytical solutions exist for differential equations, and if the number of equations is less than the number of variables, we need to use optimisation algorithm, such as the GRG method.
- If analytical solution does not exist, we need to use numerical solution methods for DAE problems.
- Ref: https://tesarrec.web.app/modelbench for numerical solution platform.