Modelling the Pyrolysis of Lignin

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Outline

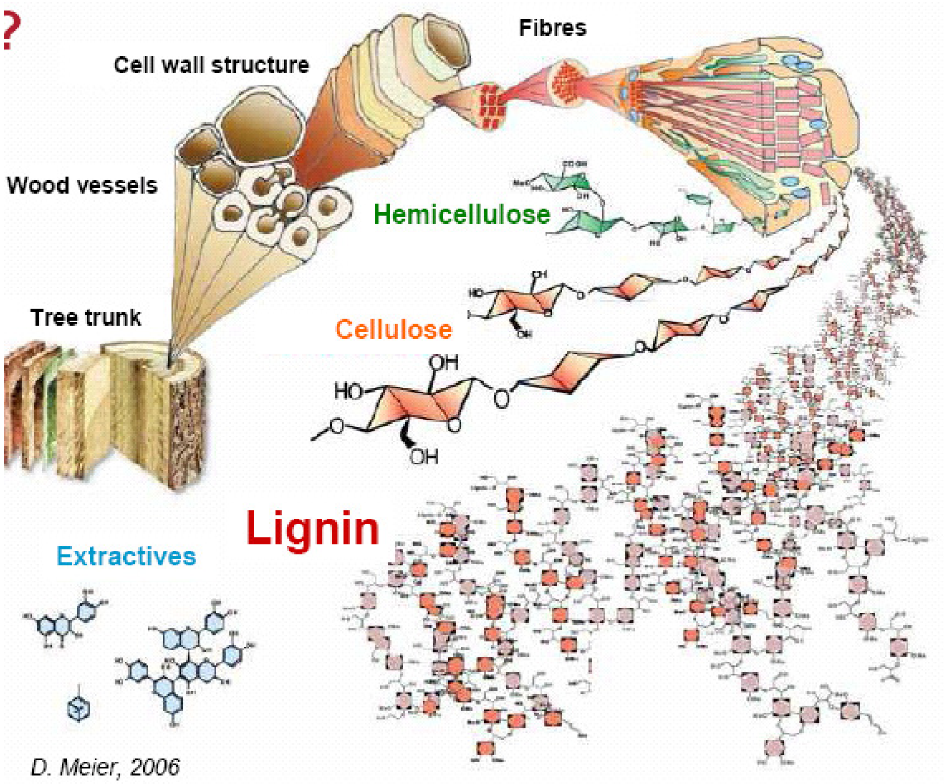
- **Lignin**
  - What is Lignin
  - Pyrolysis

- **Experimental**

- **Modelling –Development of a Working Tool**
  - Methodology
  - Assumptions

- **Model Solution**
  - Results
  - Validation

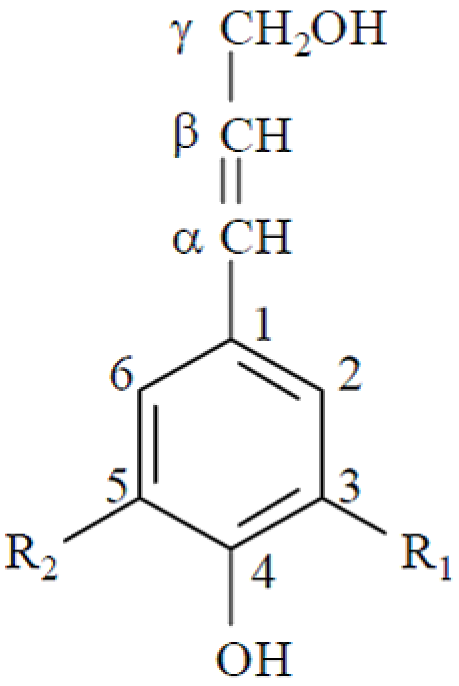
What is Lignin ?



D. Meier, 2006

An organic polymer and the second most abundant renewable carbon source on Earth, after cellulose. Lignin is not one compound but many complex polymers; the commonality between all of them is their phenylpropane structure, that is, a benzene ring with a tail of three carbons

Simplified Structure:



R_1=OMe, R_2=H: Coniferyl alcohol/guaiacyl

R_1=R_2=OMe: Sinapyl alcohol/syringyl

R_1=R_2=H: *p*-Coumaryl alcohol

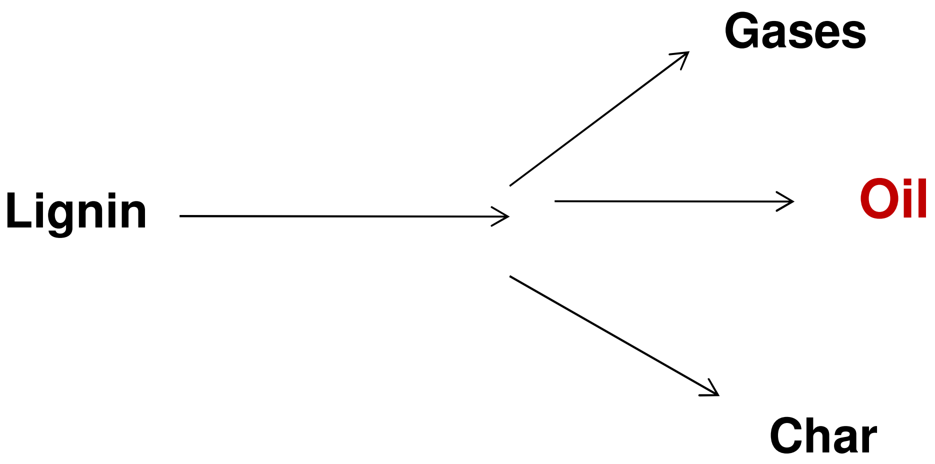
The three building blocks of lignin.

Experimental:

Institute for Chemicals and Fuels
from Alternative Resources
The University of Western Ontario

icfar

Thermal Degradation:



Gases

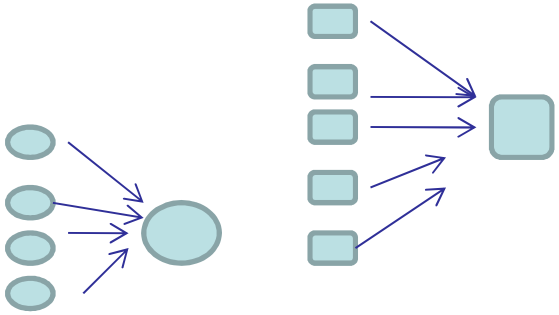
Lignin

Oil

Char

How to approach the problem

- Substitute to the real mixture an equivalent one of (fewer) “pseudo-component” which mimics more or less exactly the behaviour of the real mixture



– DISCRETE Lumping

- Interest only in “global” quantities (which are usually the only accessible to measurement)

– CONTINUUM Lumping

The problem:

In all systems where the number of species is relatively large and the difference between “adjacent” species is relatively slight

Motivation:

Create a smaller and more manageable system → lower the order of the system

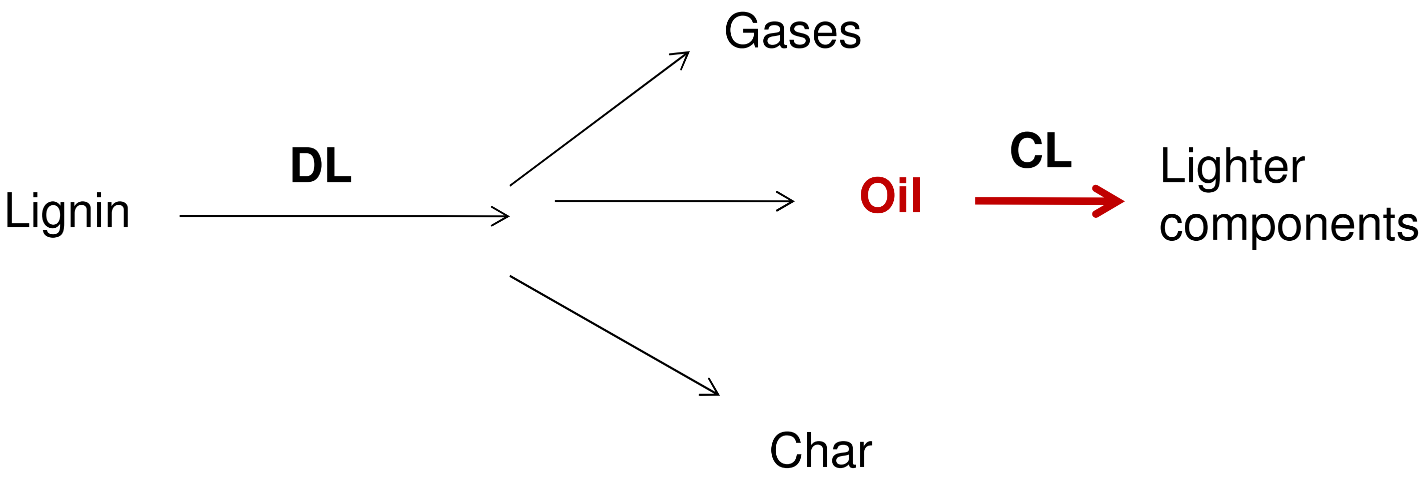
When continuous lumping is more useful:

In all systems where the number of species is relatively large and the difference between “adjacent” species is relatively slight

Olefin Mixture:

Carbon no	**Olefin isomers**
3	**1**
6	**18**
10	**895**
15	**185,310**
20	**46,224,031**
25	**12,704,949,506**

Thermal Degradation:



Gases

DL

Lignin

Oil

CL

Lighter components

Char

Continuum Lumping Kinetics

- CLK is **one** of the methodologies available for reduction of a large system of reactive species to a more manageable one

- Individual species are “lumped” together –describing the mixture in terms of “global” quantity, e.g. “lumped concentration”, “lumped rate of reaction”, etc

$$C(t) = \sum c_i(t) \qquad -\frac{dC}{dt} = R(C)$$

- **Direct Problem** -Given a well characterised feed, the global concentration *C(t)* is calculated at each time

Continuum Lumping Kinetics

- What continuum lumping can do. It can:
  - describe the "collective" kinetic or thermodynamic behaviour of a multi-component mixture;
  - give information on the "lumped" concentration;
  - give information on the "lumped" kinetics.

- What continuum lumping cannot do. It cannot:
  - give detailed information on the kinetics of each single reaction and the corresponding precise rate expressions.

Applying the CLK (Direct Problem)

- Label the species (e.g., identify each species with a unique characteristic)
- Devise the kinetic model (e.g. linear kinetics)
- Write the governing equations (mass balance)
- Calculate the lumped (global) concentration
- Calculate the lumped rate of reaction

Labelling the Components

- Identify a label which can be attributed univocally to "a" species –*x*

- The concentration *c(x,t)* is the concentration at time *t* of the species in the interval *(x, x+dx)*

$$c(x) = C_0 h(x) dx$$

With C_0 the lumped initial concentration (at t=0) and *h(x,)* a distribution function which is normalised to assure mass conservation:

$$\int_0^\infty x h(x) dx = 1$$

Labelling the Components -Hydrocracking

- The label is the Boiling Point (BP) [carbon number], BPi

- The normalised BP can be defined with respect the highest, $BP(h)$ and the lowest $BP(l)$:

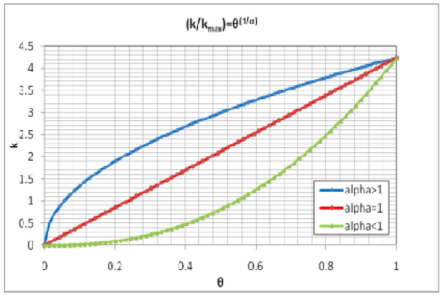
$$\theta = \frac{BP(i) - BP(l)}{BP(h) - BP(l)}$$

- The concentration of the generic component i can then be expressed as:

$$c_i(t) = c(\theta, t)d\theta$$

- Assume that the carbon cumber is univocally related to the reactivity, the relation between θ and k being monotonic:

$$\frac{k}{k_{\max}} = \theta^{1/\alpha}$$



Labelling the components

- In terms of reactivity, *k:*

$$C(\theta,t)d\theta = c(k,t)D(k)dk$$

- The function *D(k):*
  - It represents the way to transform the *i* (*C*) domain into the *k* domain, i.e., in the new domain each component is now identified by its kinetic constant *k*:

$$D(k_i) = \frac{\Delta i}{\Delta k_i} = \frac{(i+1)-i}{k_{i+1}-k_i} = \frac{1}{\Delta k_i}$$

  - Different constitutive assumption can be made depending on the relative value of kinetic constants, for instance, the condition:

$$\Delta k_{i-1} < \Delta k_i < \Delta k_{i+1}$$

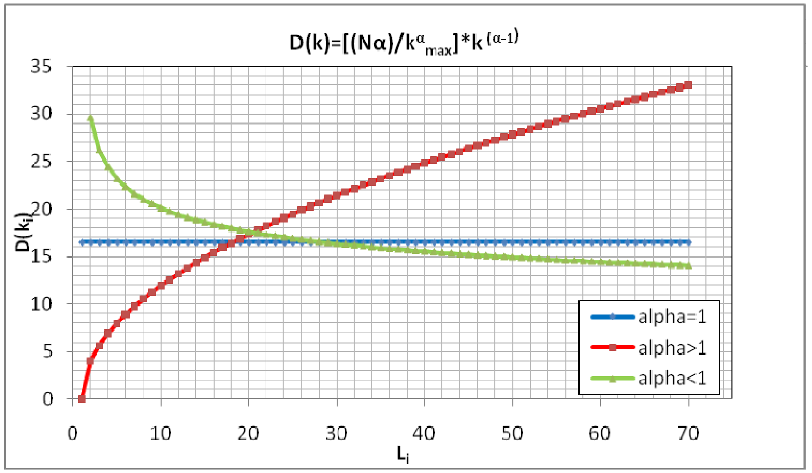
means that higher molecular weight species (species with higher kinetic constant) crack faster than those with lower molecular weight

The Species-Type Distribution

- The species-type distribution, ***D*(*k*)** contains the kinetics and it **is a characteristic of the feed only**:

$$D(k) = \frac{di}{d\theta}\frac{d\theta}{dk} = N\frac{d\theta}{dk}$$

- With the assumed relationship between θ and k:



Model Formulation

- The mass balance (model) for generic component of reactivity *k* is:

$$\frac{dc(k,t)}{dt} = -\underbrace{kc(k,t)}_{\text{Disappearance}} + \int_{k^{+}}^{k_{\max}} \underbrace{p(k,K)Kc(K,t)D(K)dK}_{\text{Production from all the components with a higher reactivity (namely higher carbon no)}}$$

- First order kinetics is assumed in agreement with a number of papers in the field (e.g. Ho, 2008)

Model Formulation

- The term:

$$\int_{k^+}^{k_{\max}} p(k,K)Kc(K,t)D(K)dK$$

contains all the constitutive hypothesis about the model

- $p(k,K)$ is the yield distribution function and needs to have the shape of a skewed Gaussian. It contains three parameters that determine the peak location and constraint the distribution to verify the total mass balance.

The Yield Function

- $p(k,K)$ has to be zero when $k=K$ (the species of reactivity k cannot yield to itself upon cracking)
- $p(k,K)=0$ for $k>K$ since dimerisation is not significant in hydrocracking
- $p(k,K)$ has to satisfy a material balance
- $p(k,K)$ should be a finite, small nonzero value when $k=0$ (this property is a consequence of the experimentally observed fact that, when a component of reactivity K cracks, even the smallest reactivity components are formed in traces)
- $p(k,K)$ should always be positive

The Yield Function

$$p(k,K)=\frac{1}{S_0\sqrt{2\pi}}\left\{\exp\left[-\left(\frac{(k/K)^{a_0}-0.5}{a_1}\right)^2\right]-A+B\right\}$$

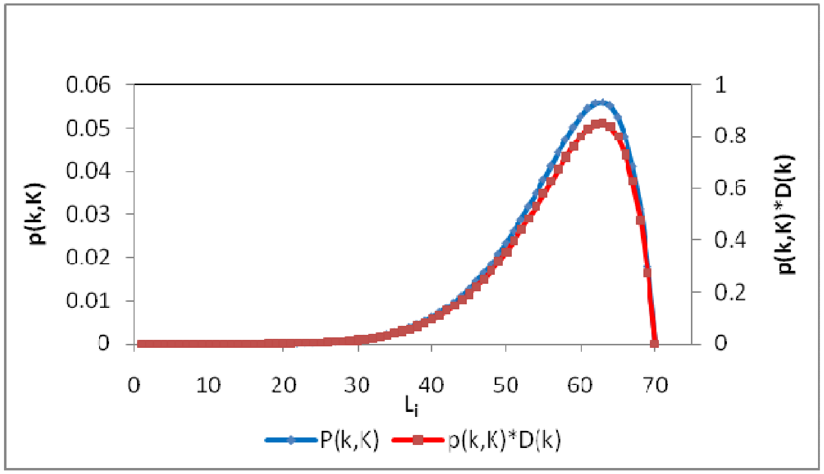
$$A=e^{-(0.5/a_1)^2}$$

$$B=\delta\left(1-\frac{k}{K}\right)$$

$$S_0=\int_0^K\frac{1}{\sqrt{2\pi}}\left\{\exp\left[\left(\frac{(k/K)^{a_0}-0.5}{a_1}\right)^2\right]-A+B\right\}D(k)dk$$

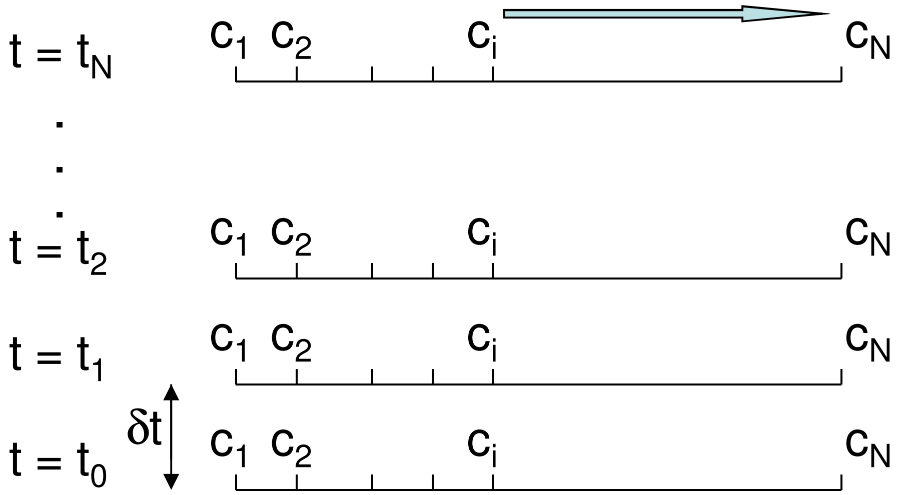
The Yield Function

- $p(k, K)$, the yield distribution function, contains 3 additional parameters, a_0, a_1, δ
  - a_0 and a_1 define the location of the peak of the distribution, the peak corresponds to the component with the highest yield
  - δ is a finite quantity that accounts for the possibility that the yield can take a small finite value when k=0. δ is assumed to be a very small (negligible) number (in the limit it will be taken equal to 0)



Model Solution

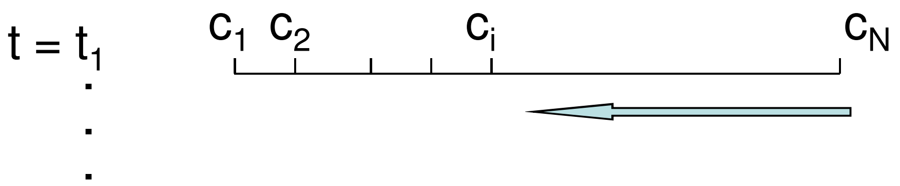
- The integro-differential equation representing the mass balance, must be solved for each component at each time. The integration space is the (c,t) plane. Schematically:



Concentrations must be obtained at each time; the generic component i is formed by the components $i+1$, $i+2$, …$i+N$; the integral must be evaluated over the interval $[c_i, c_N]$

Solution Strategy

- The integral can be solved before the differential equation if a "backward" methodology is applied, i.e.:



- The component N can only be consumed, therefore the balance reduces to:

$$\frac{dc(k_N,t)}{dt} = -k_{\max} c(k_N,t)$$

$$c(k_N,t) = c(k_N,t-\delta t)e^{-k_{\max}\delta t}$$

Starting from N, one can calculate backwards the concentrations at a given time, to then proceed to the next time step.

Model Parameters

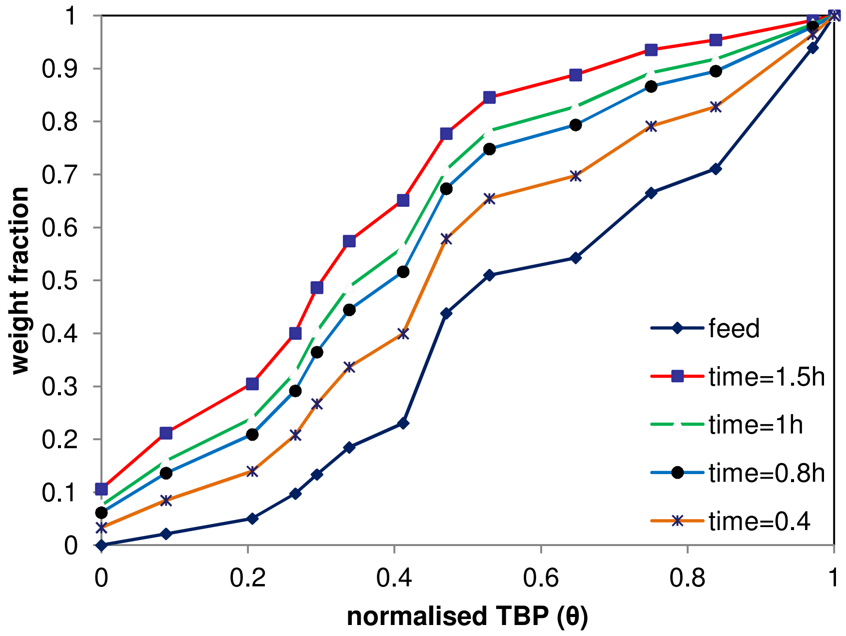
- The model was first solved with the trial values of the parameters
- Subsequently, using the a subset of the experimental data, an optimisation procedure was used to find a set of parameters to tune the model

$$Min\left[J(c(t))\right]=\sum_{i=1}^{N}\left[c(t)_{\text{experimental}}-c(t)_{\text{model}}\right]^{2}$$

- The parameters so obtained can be used for any other feedstock provided that the catalyst remain the same
- The model can be used as a **tool** to predict the composition after cracking for any given residence time –the additional experimental runs are then used to study the predictive features of the model

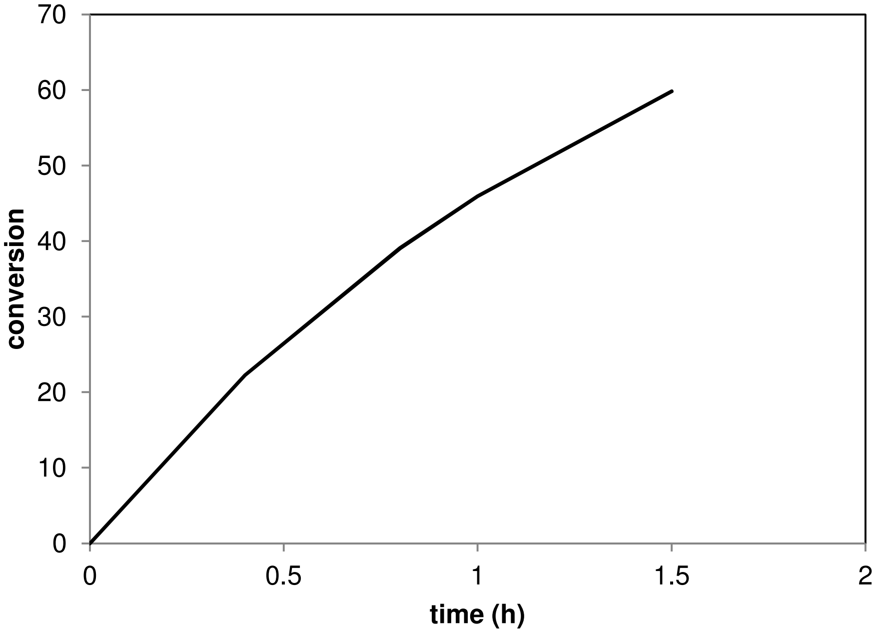
Preliminary Results

a_1= 28.15, a_0=4.41, k_{max}=1.35, α=1.35, δ= 2.67e-9



Piskorz et al., Energy and Fuels, 1989, 3, 723-726

Preliminary Results



$a_1 = 28.15$, $a_0 = 4.41$, $k_{max} = 1.35$, $\alpha = 1.35$, $\delta = 2.67e\text{-}9$

Conclusions

- The model captures the qualitative behaviour of the process

- Validation with ICFAR data
  - Parameters
  - Operating conditions

- Comprehensive modelling
  - DL (three lumps) applied to the primary pyrolysis
  - CL applied to the cracking of the bio-oil