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A strategy for kinetic parameter estimation in the pyrolysis of lignin

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Estimation of Kinetic Parameters for the Pyrolysis of Lignin

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Pyrolysis

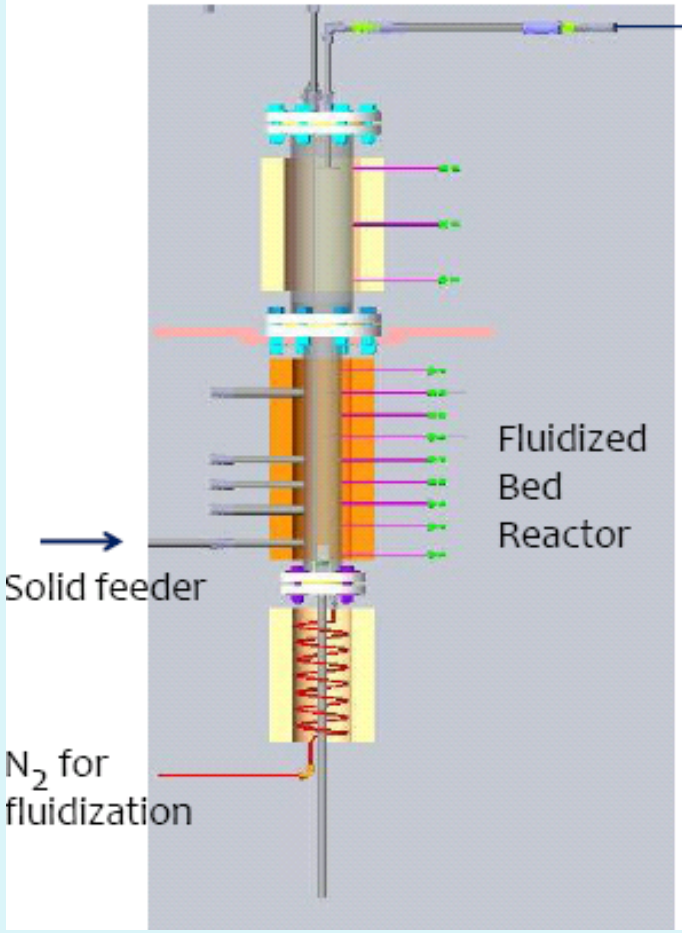
Fluidised bed pyrolyser (temperature 300-600 °C)

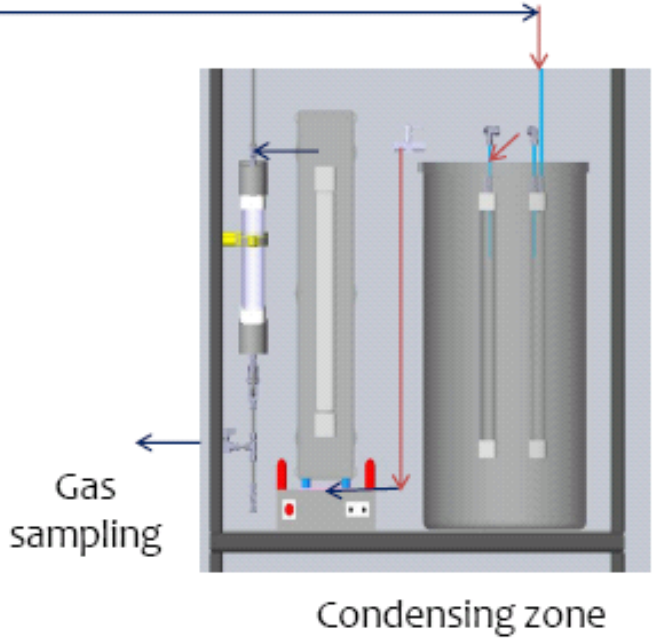
Gases: most commonly detected gas species are CO, CO_2, CH_4, CH_2O, CH_3CHO, H_2O, H_2

Bio-oil: Phenolic oily fraction and carbohydrate-rich water fraction

Bio-char: carbon and ashes

Equipment



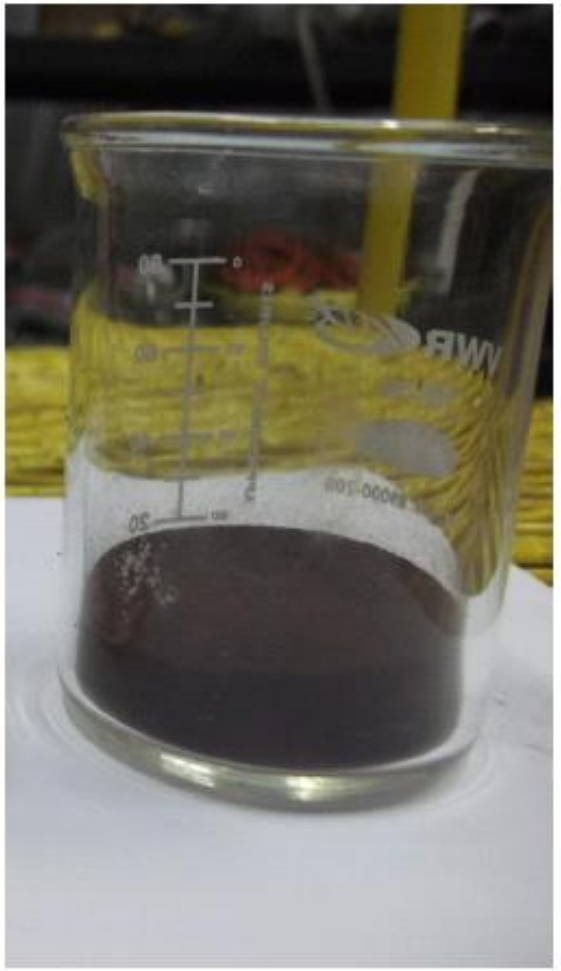


Reactor diameter = 7.5 cm (3 in)

1.5 kg of sand with d_{psm} = 180 μm

Lignin

- Very fine particles (< 30 μm)
- Particle density = 575 kg/m^3

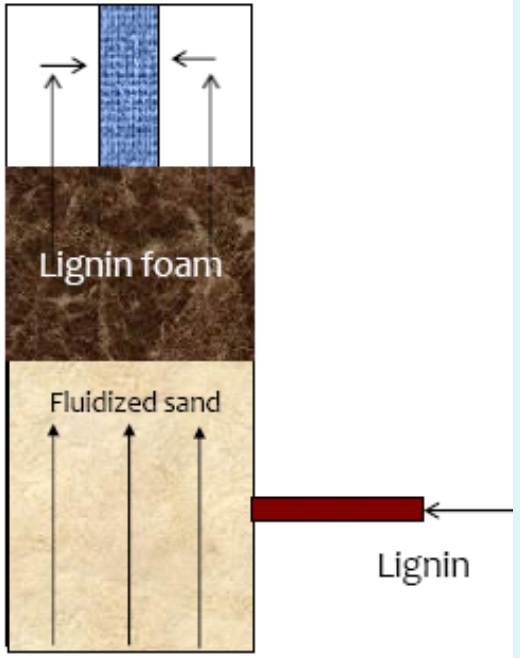


Why is lignin difficult to pyrolyze?

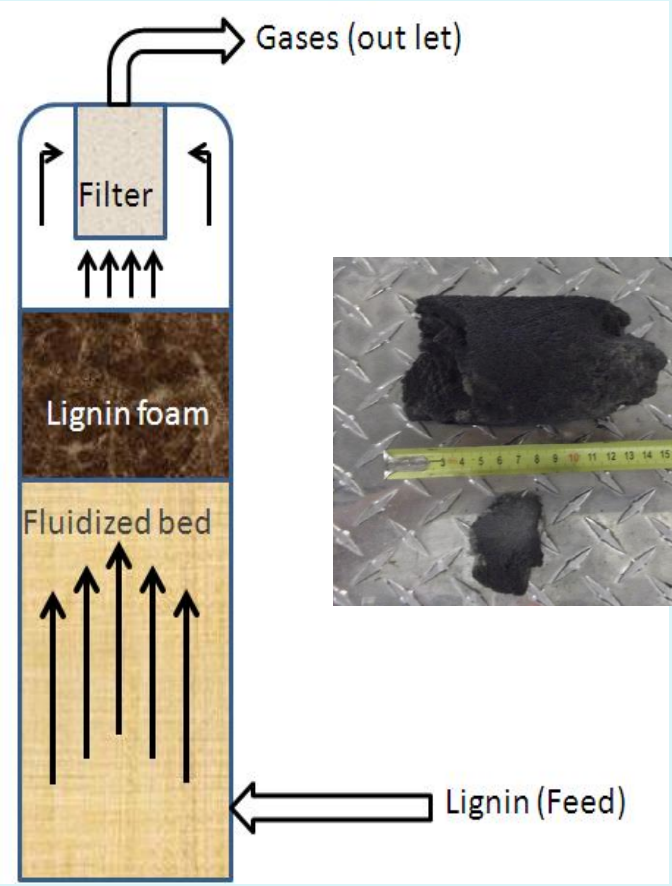
- Lignin starts melting at low temperature: 150 – 200 ºC
- Lignin needs a high reactor temperature to crack fully

1) Solids feeder plugs

2) Low density foam forms at the bed surface



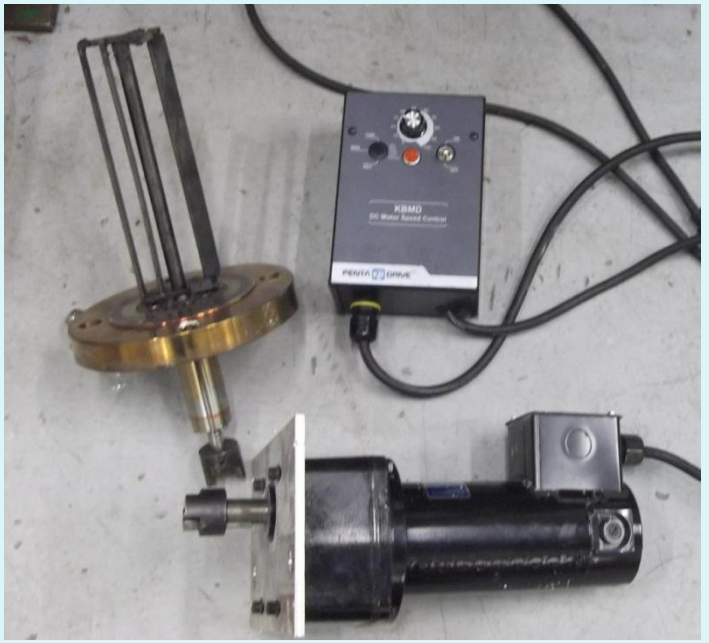
Mechanical Stirrer



No mixer: 200g of lignin fed

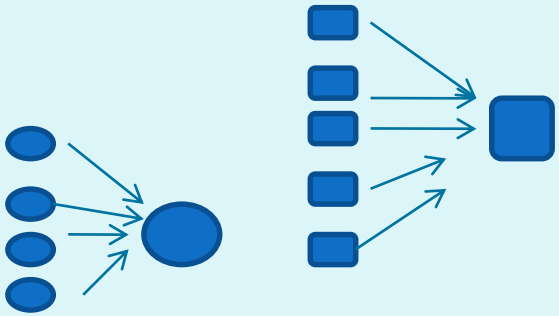
Mixer: 80 rpm
200g of lignin fed

Mechanical Stirrer



Lumping of Multi-Component Reactive Mixtures

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

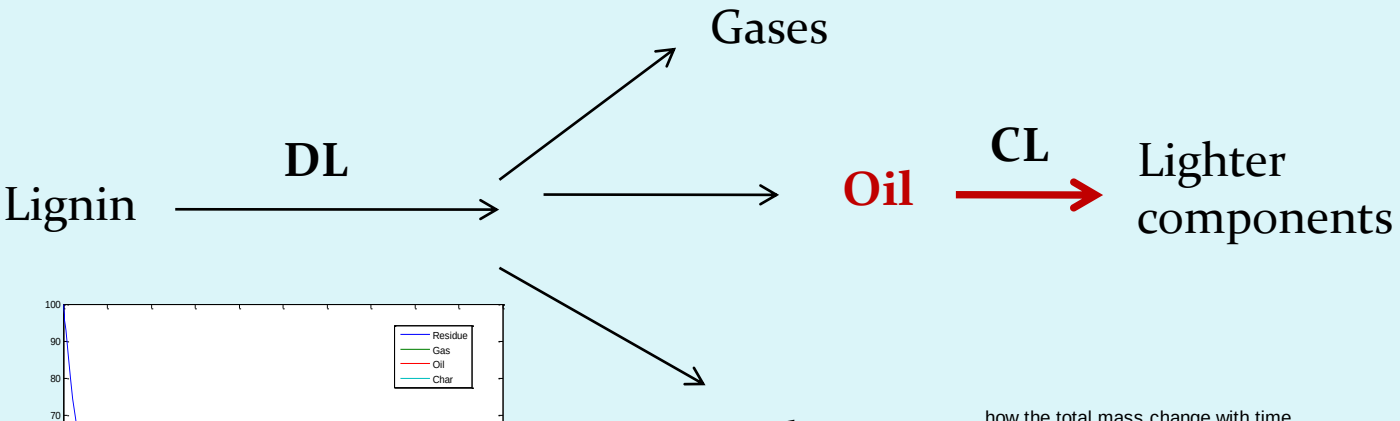


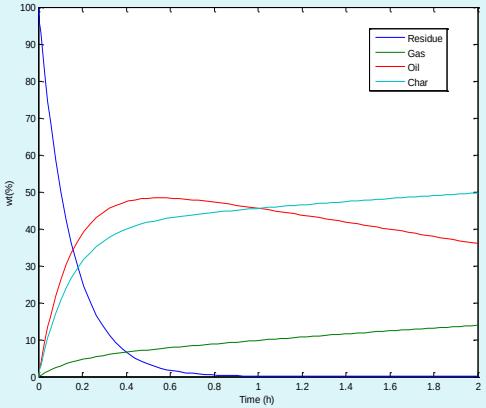
– **DISCRETE Lumping**

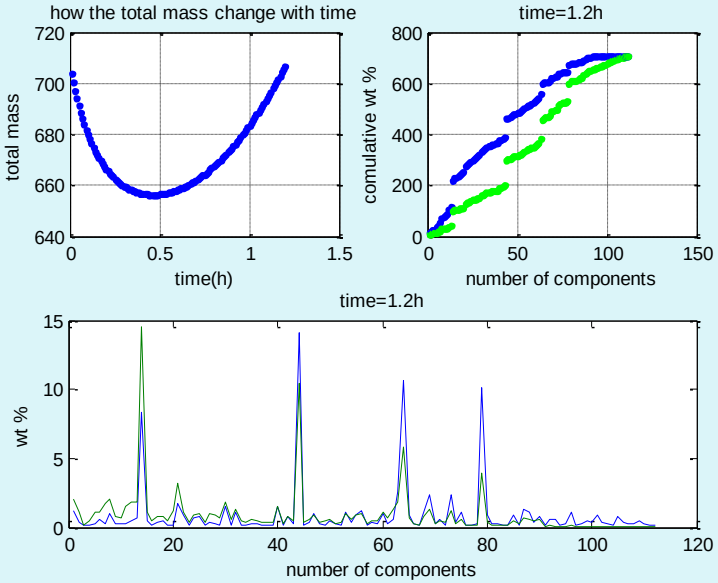
- Interest only in "global" quantities (which are usually the only accessible to measurement)

– **CONTINUUM Lumping**

Thermal Degradation (Pyrolysis)







Modelling

Discrete lumping kinetics for pyrolysis of lignin

Model 1

Lignin decomposition is described by three parallel reaction.

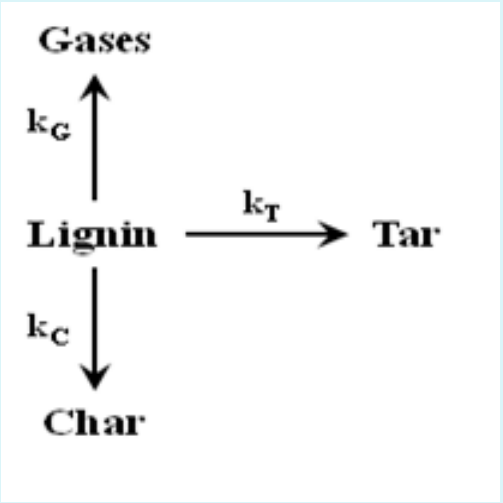
The reaction rate constants of these reactions can be determined by measuring the amount of each lump as a function of time.

$$\frac{dw_l(t)}{dt} = -(k_G + k_T + k_C)w_l(t)$$

$$\frac{dw_G(t)}{dt} = k_G\, w_l(t)$$

$$\frac{dw_T(t)}{dt} = k_T\, w_l(t)$$

$$\frac{dw_C(t)}{dt} = k_C\, w_l(t)$$



Discrete lumping kinetics for pyrolysis of lignin Model 2

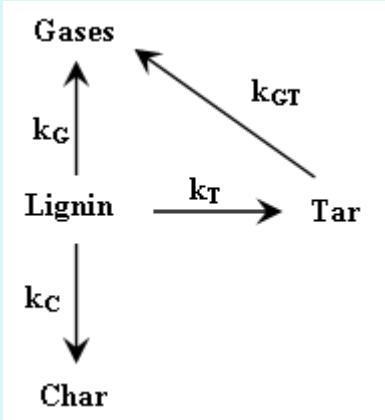
$$\frac{dw_l(t)}{dt} = -(k_G + k_T + k_C)w_l(t)$$

$$\frac{dw_G(t)}{dt} = k_G\, w_l(t) + \frac{dw_T(t_v)}{dt_v}$$

$$\frac{dw_T(t)}{dt} = k_T\, w_l(t) - \frac{dw_T(t_v)}{dt_v}$$

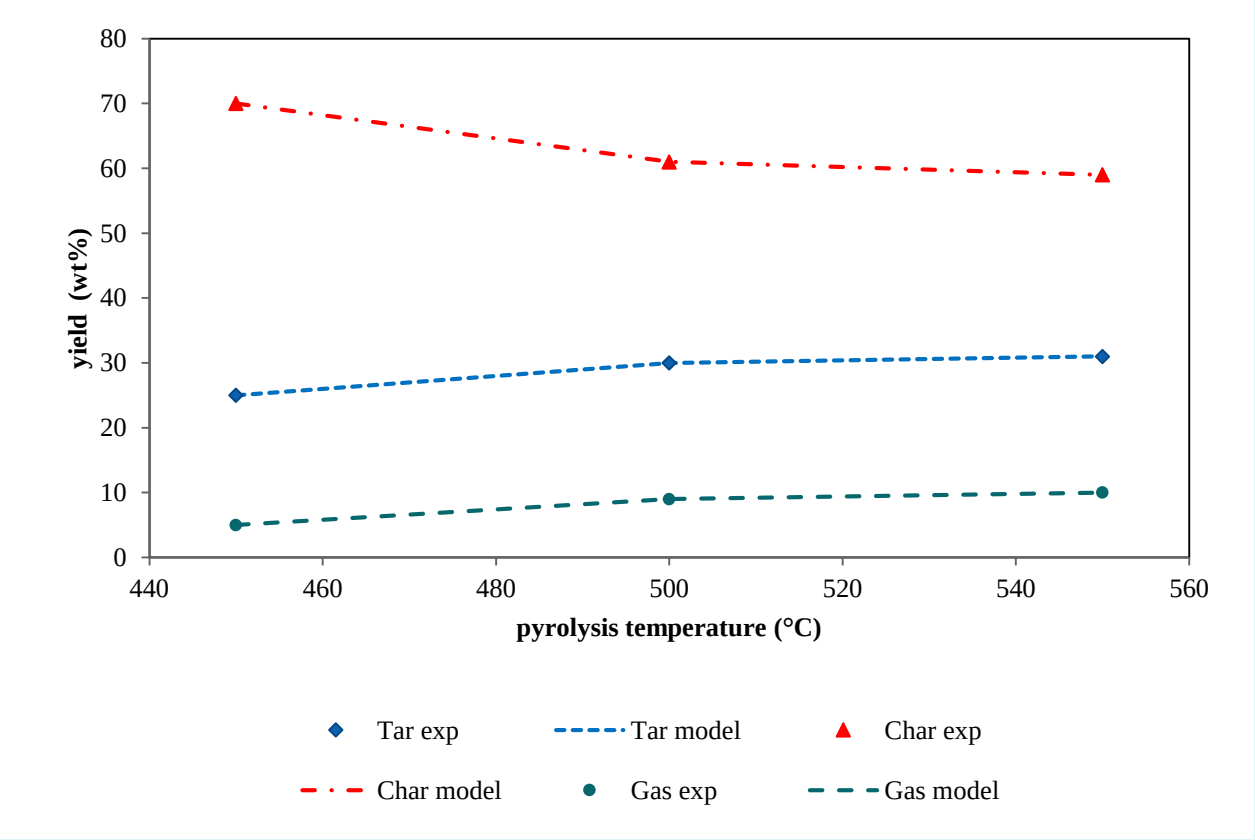
$$\frac{dw_C(t)}{dt} = k_C\, w_l(t)$$

$$\frac{dw_T(t_v)}{dt_v} = -k_{GT}\, w_T(t_v)$$



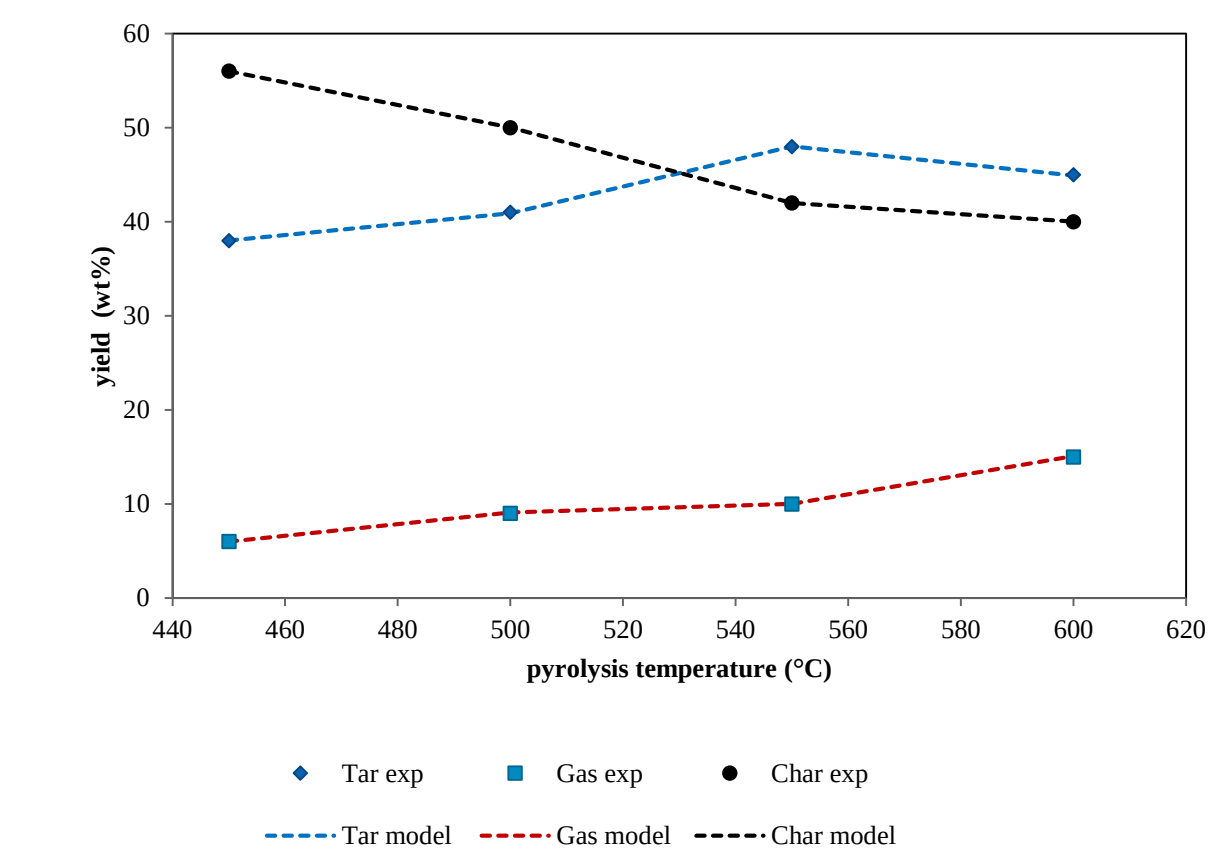
Models results

Discrete model 1 (better suited for the FB without mixing)



Models results

Discrete model 2



Applying the CL to the fractionation of bio-oil

- Label the species
- Devise the kinetic model
- Write the governing equations (mass balance)
- Calculate the lumped concentration
- Calculate the lumped rate of reaction

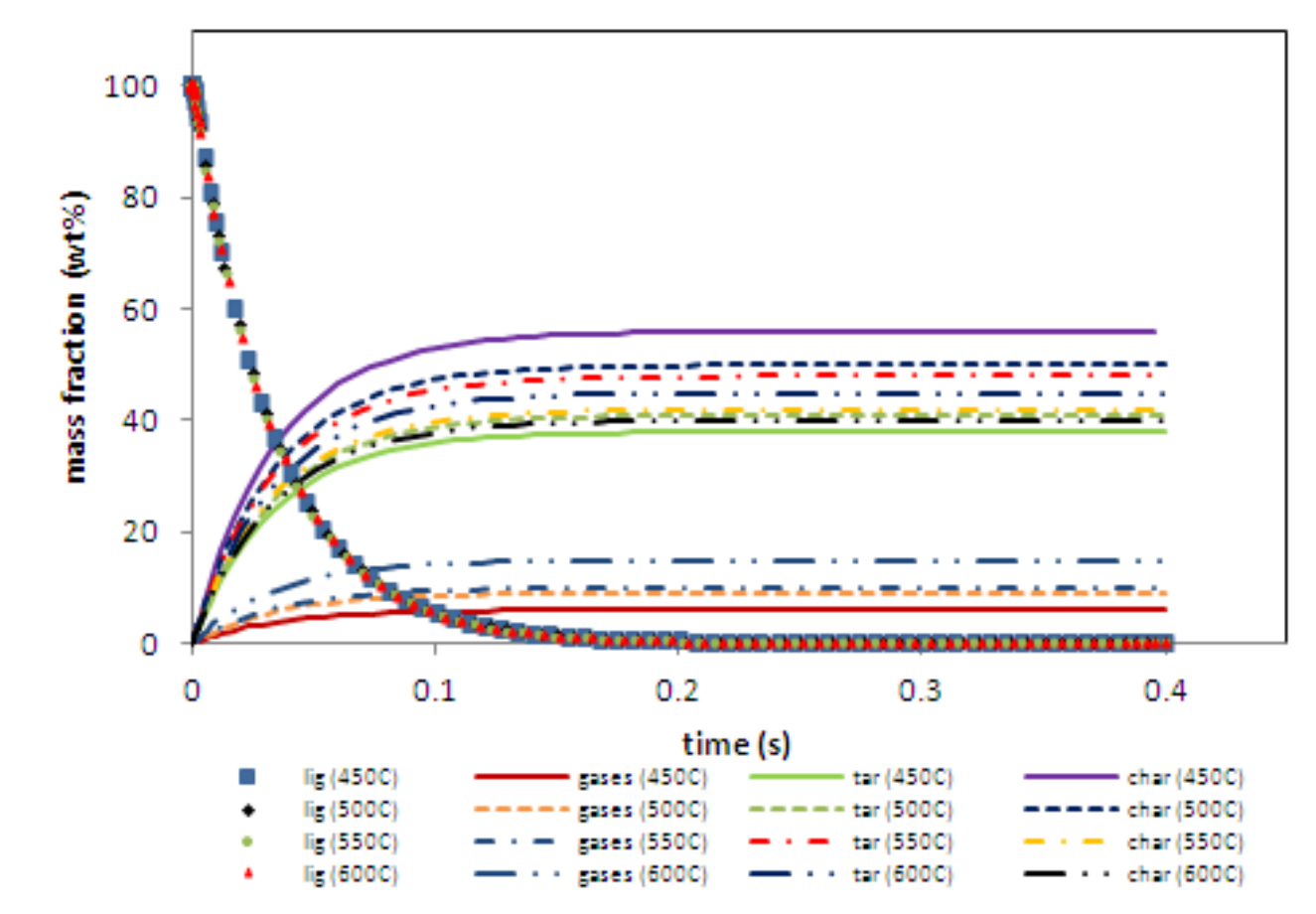
Model Formulation

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

$$\frac{dc(k,t)}{dt} = \underbrace{-kc(k,t)}_{\text{Disappearance}} + \underbrace{\int_{k^+}^{k_{\max}} p(k,K)Kc(K,t)D(K)dK}_{\text{Production from all the components with a higher reactivity}}$$

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

Model Results (short residence time)

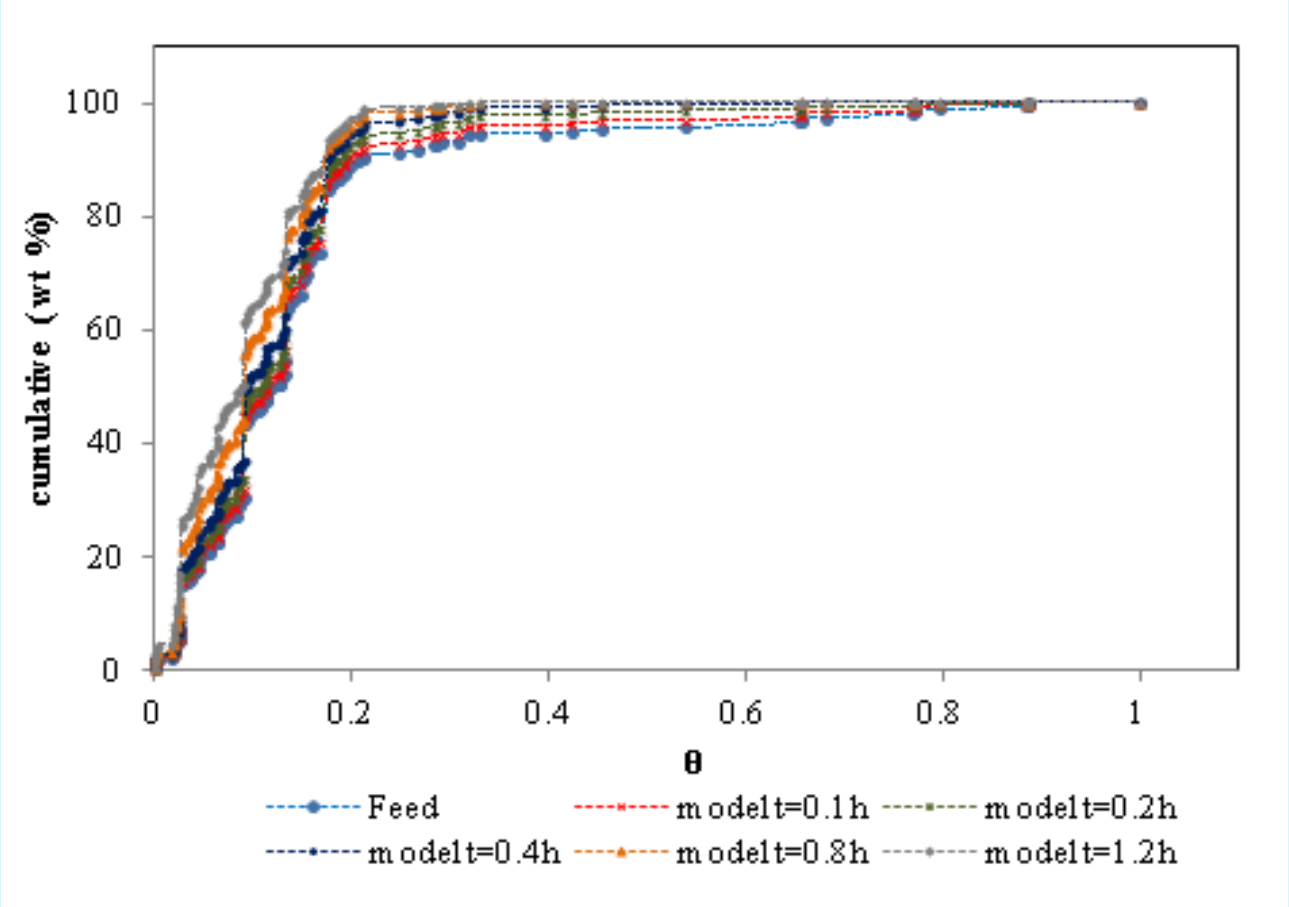


Kinetic parameters for the pyrolysis of lignin

T (◦C)	K_G	K_T	K_c
450	1.8	11.2	16.5
500	2.6	12.0	14.7
550	3.0	14.3	12.5
600	4.4	13.3	11.8

Reaction Rate Constant	Frequency Factor (s^{-1})	Activation Energy (J/mol)
K_G	69.9	35756
K_T	15.0	11785
K_C	1.6	7560

Continuum Modelling

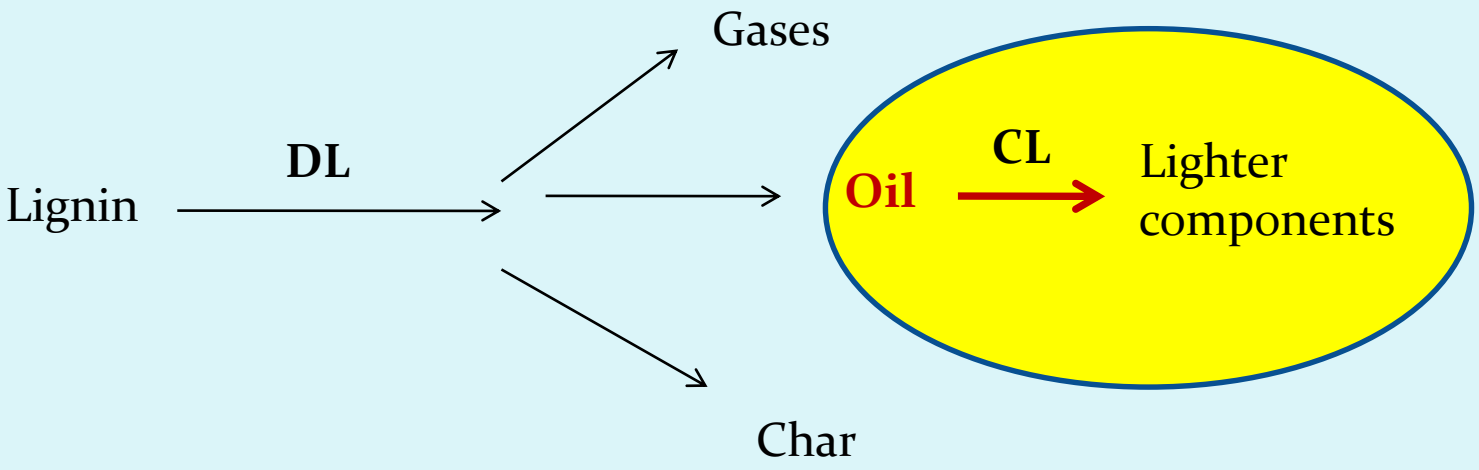


Parameters of the Continuum Model (bio-oil)

Time (h)	a_0	a_1	k_{max}	α	δ
0.1	20.2	3.8	6.28	0.58	9.052e-07
0.2	32.2	3.8	9.48	0.54	9.052e-07
0.4	34.2	3.8	11.48	0.548	9.052e-07
0.8	5.2	3.8	13.28	0.488	9.052e-07
1.2	10.32	3.8	13.68	0.556	9.052e-07

Future Work

- Further model validation
- Feed distribution function to link the CL to the DL to generate a "complete" model (the species-type distribution function, $D(k)$, "contains" the kinetics and it is a characteristic of the feed only)



Conclusions

- Discrete lumping models predict well the yields observed in FB and MF bed reactors
- The continuum model is shown to be appropriate to predict the cracking (upgrading) of bio-oil in a catalytic reactor (utilising methodologies and lessons borrowed from the fossil fuel industry)
  - Much less analytical support required (when compared with mechanistic models) –smaller number of model parameters
  - Effectively used for rapid catalyst screening/evaluation (new catalysts?)
- Polymerisation (CL)
- Monomers $\Leftrightarrow$ Oligomers (CL)

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

- The label is the molecular weight, *n(i)*

- The normalised molecular weight can be defined with respect the highest, *n*(*h*) and the lowest *n*(*l*) molecular weight:

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

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

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

- Assume that the molecular weight is univocally related to the reactivity, the relation between θ and *k* being monotonic:

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

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 net polymerisation is not significant
- $p(k,K)$ 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

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.