MECHANISMS OF PYROLYSIS

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WHAT IS PYROLYSIS?

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the thermal decomposition of carbonaceous materials in the absence of oxygen

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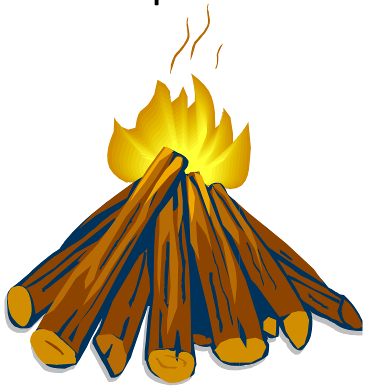
Pyrolysis is:

the first step in combustion



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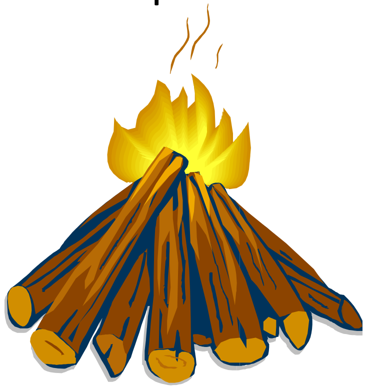

How?

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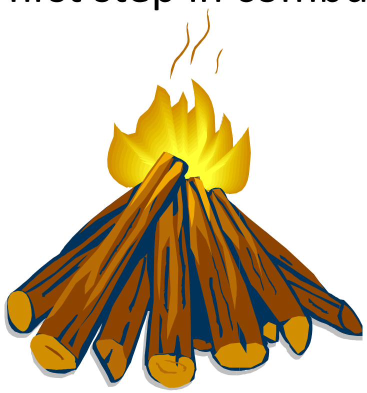

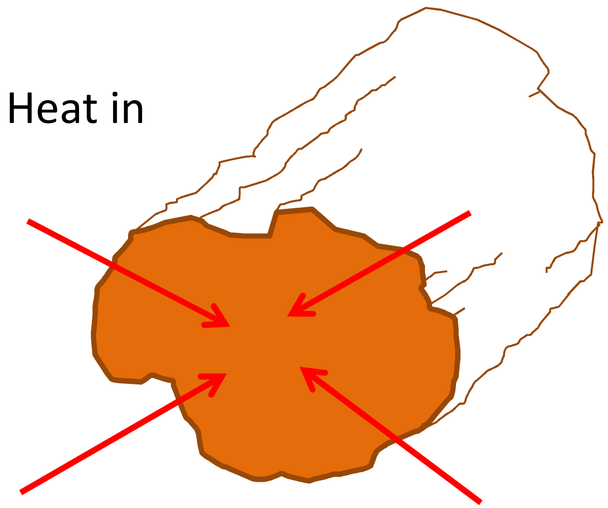

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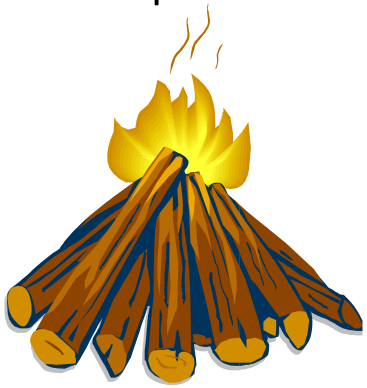
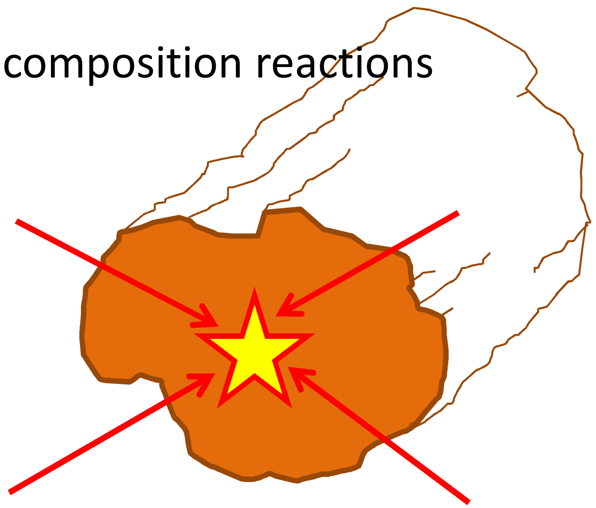


Decomposition reactions



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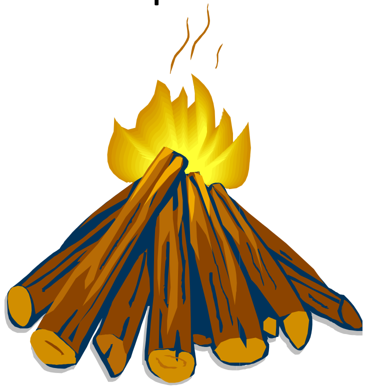

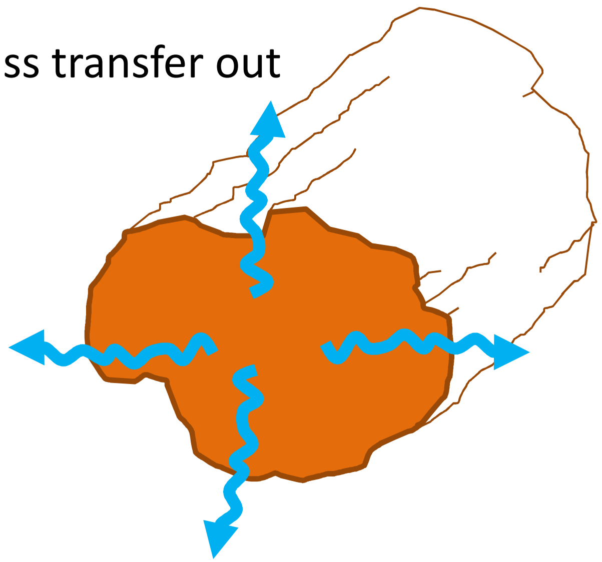

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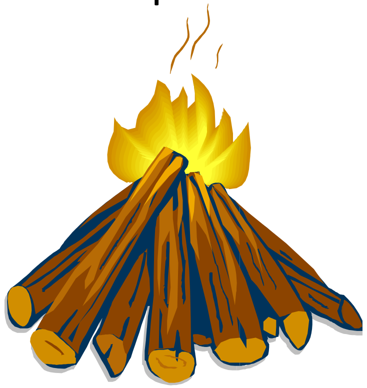
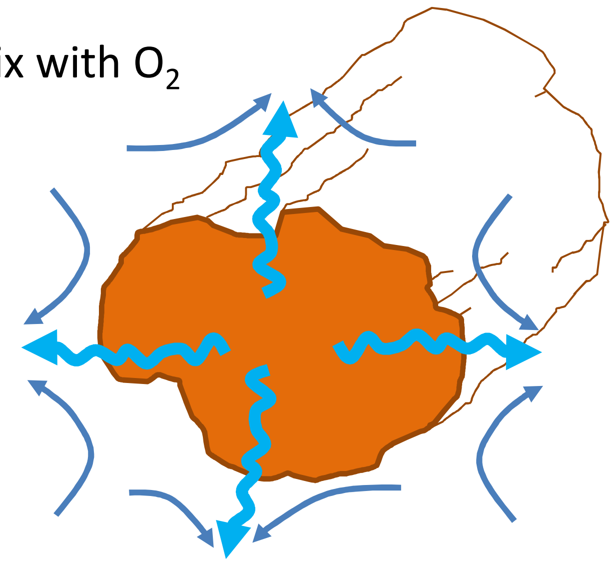


Mix with O_2



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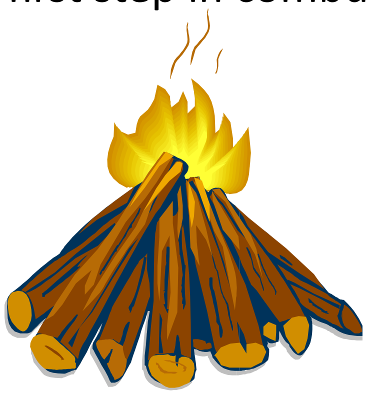
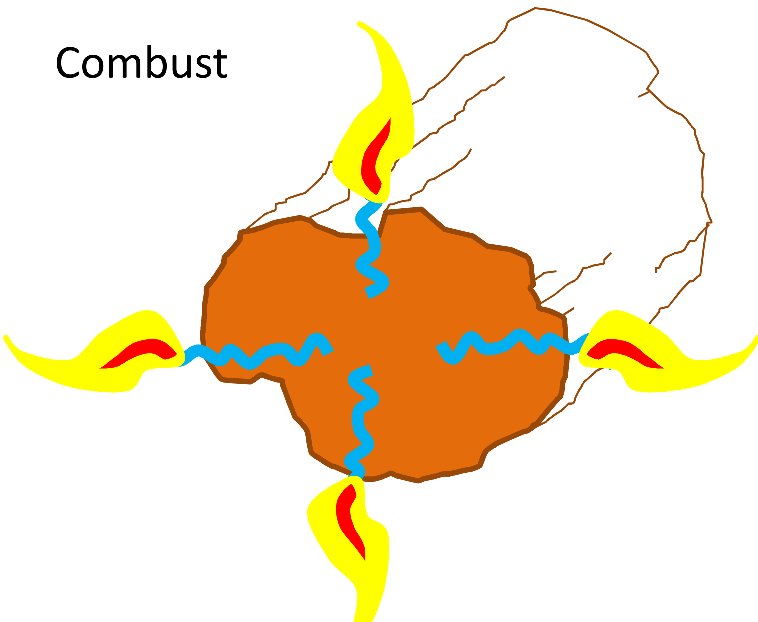
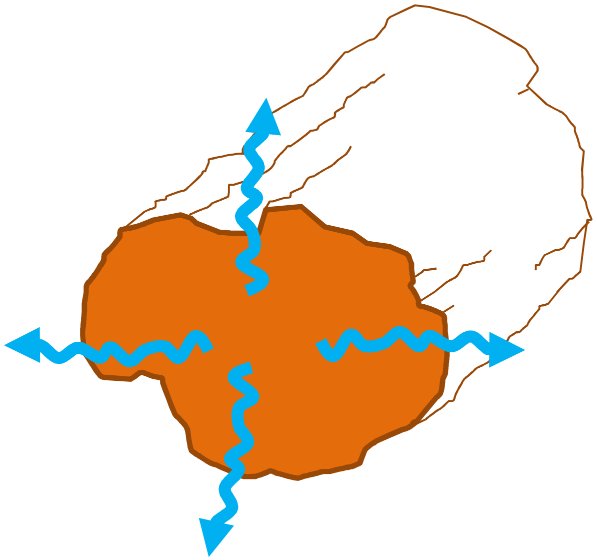




WHEN THERE IS NO AIR



Pyrolysis forms three products:

- Charcoal
- Condensable liquids (tar)
- Non condensable gases

WHAT IS THE ISSUE?

Pyrolysis is:

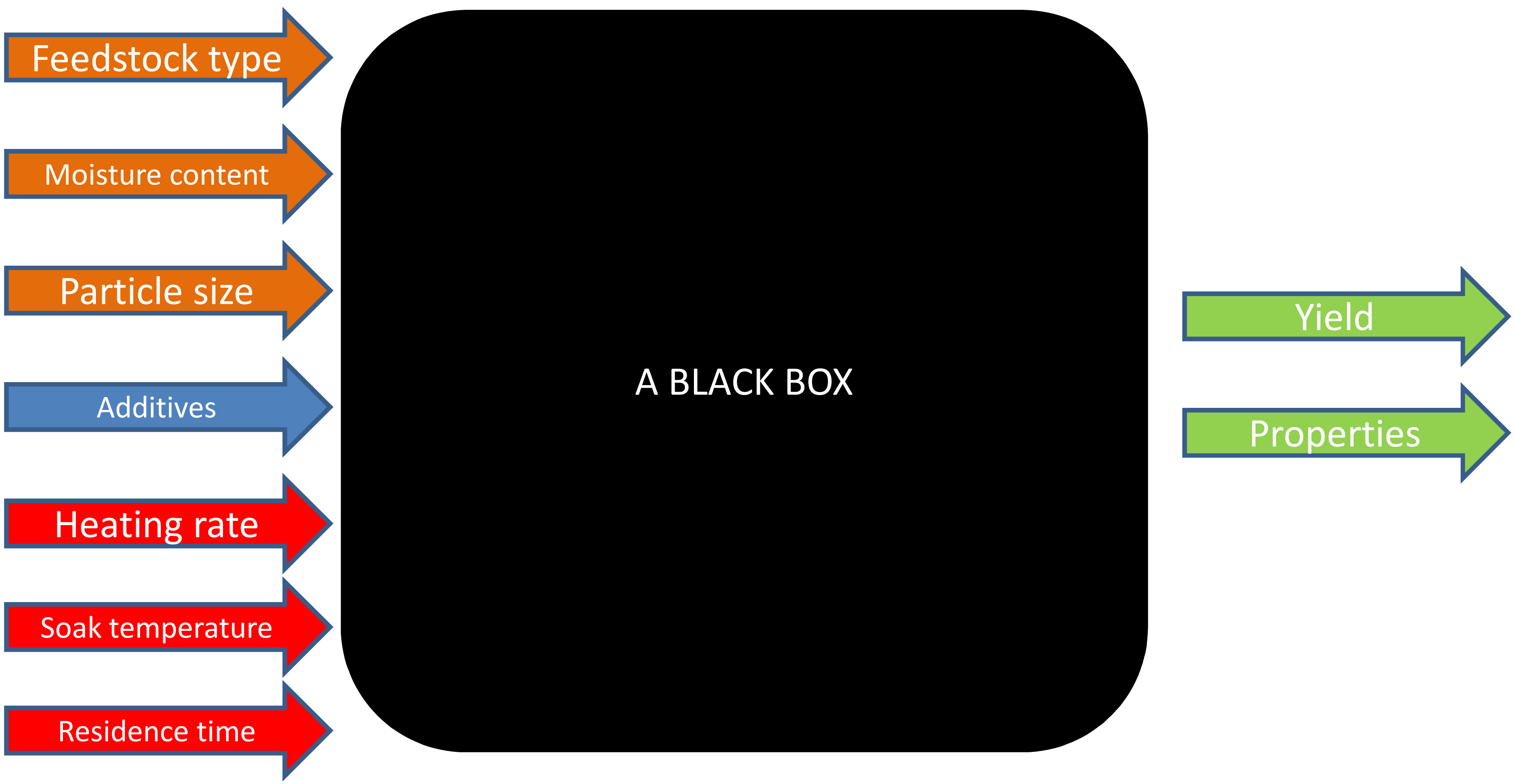
A BLACK BOX

WHAT IS THE ISSUE?

Pyrolysis is:

We set inputs

We observe outputs



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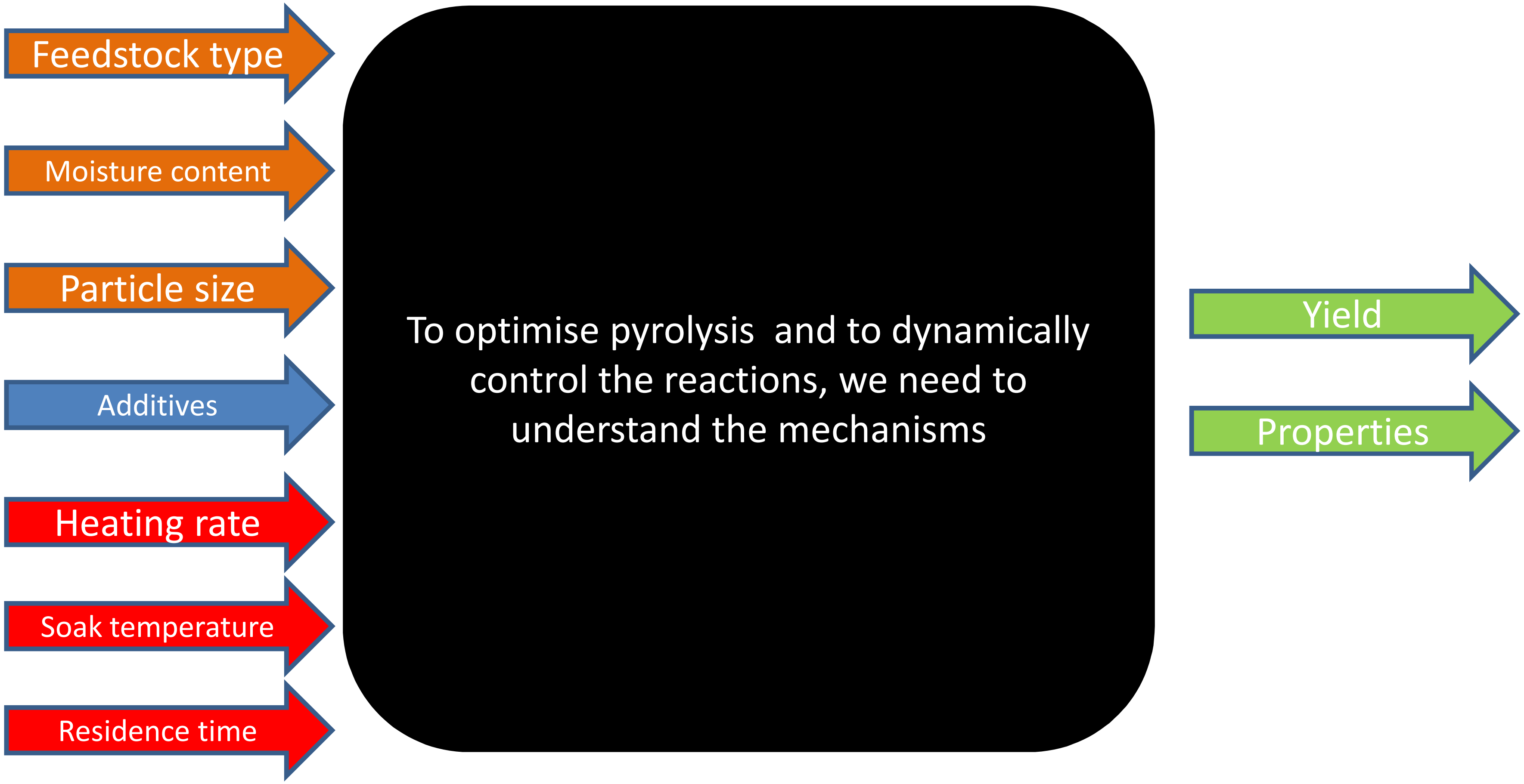
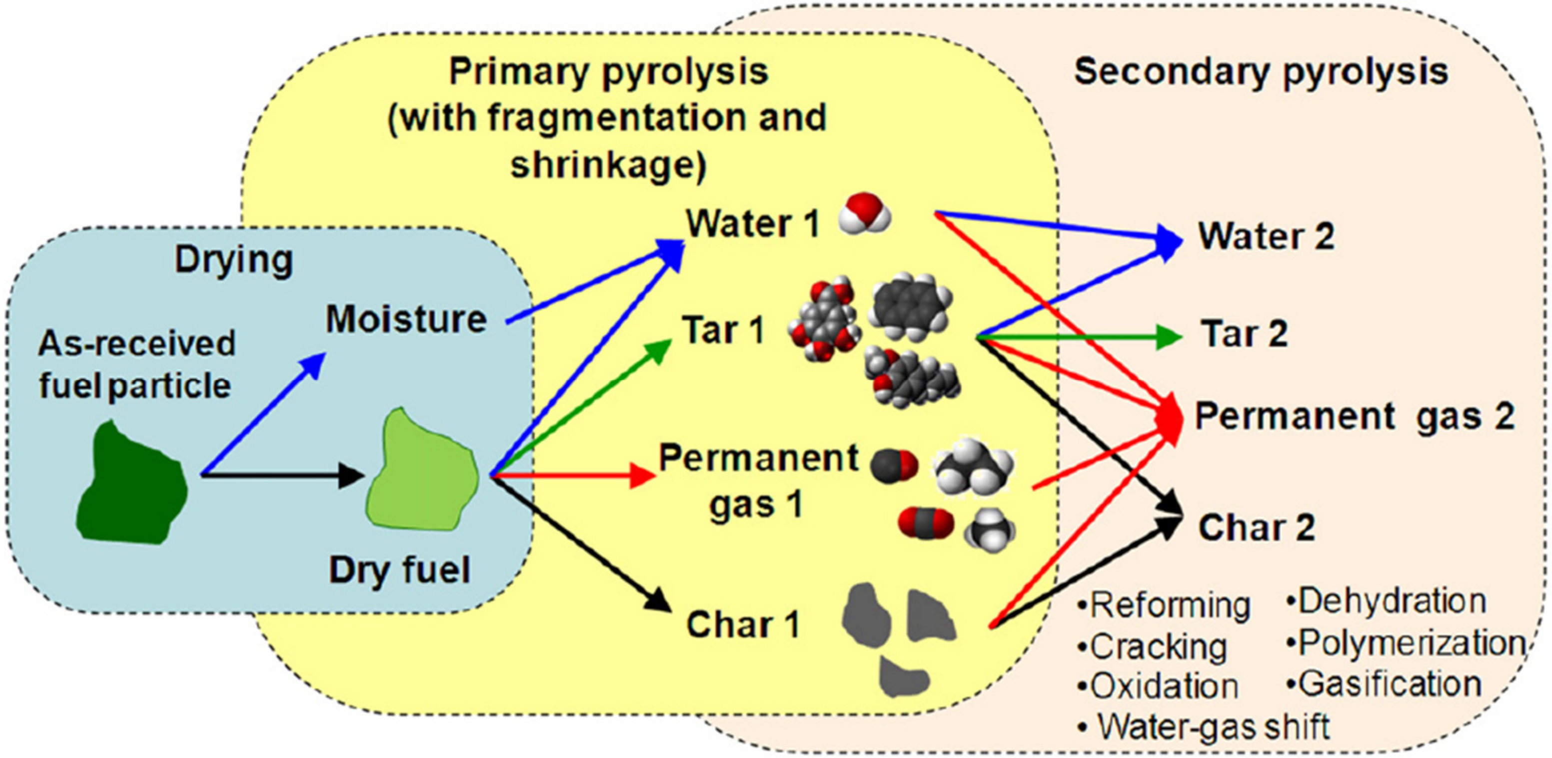


WHAT IS THE ISSUE?

Pyrolysis is:

QUALITATIVELY

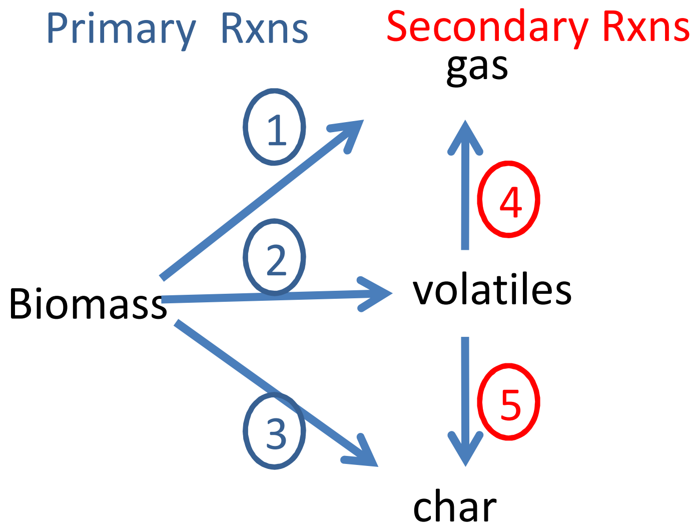
...we understand the mechanisms at play.



"The description of the pyrolysis process is particularly challenging because it evolves a great deal of physical and chemical transformations and produces a large number of product species. As a result, existing models aiming to predict the rates or yields of the released pyrolytic volatiles are still supported by empirical data..."

[Figure and quote from Neve et al., 2011]

KINETIC MODEL 1



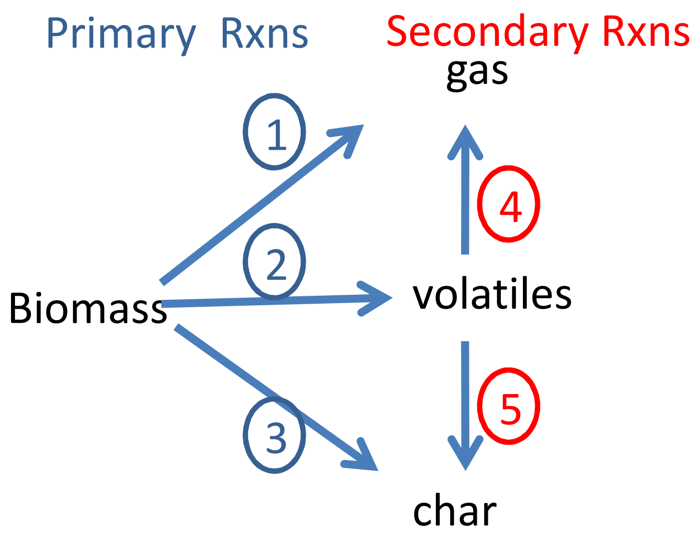
① ② ③ Endothermic

④ ⑤ Exothermic

Each reaction has:
1. a heat of reaction
2. a rate

Mechanism proposed by Shafizadeh, 1975

KINETIC MODEL 1



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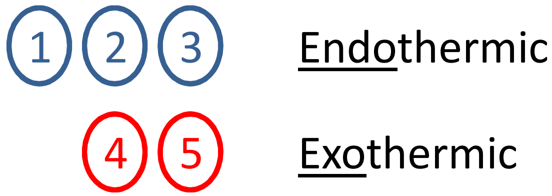
1. Heat of Reaction



Reaction No.	H [kJ/kg]
1	420
2	420
3	420
4	-40
5	-40

2. Rate of Reaction

$$k_i = A_i e^{-E_i / RT}$$

Legend

A	=pre-exponential factor [1/s]
E	=activation energy [kJ/mol]
R	= gas constant = 8.314 [J/mol/K]

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[Data cited in Fantozzi, 2007]

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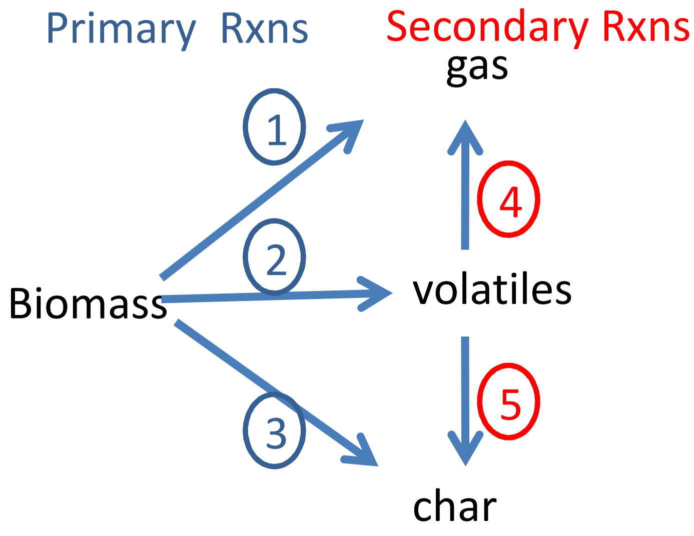

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Reaction No.	A	E	ref Temp [K]
1	1.44E+04	88.6	673
2	4.13E+06	112.7	673
3	7.38E+05	106.5	673
4	4.28E+06	107.5	673
5	1.00E+05	107.5	673

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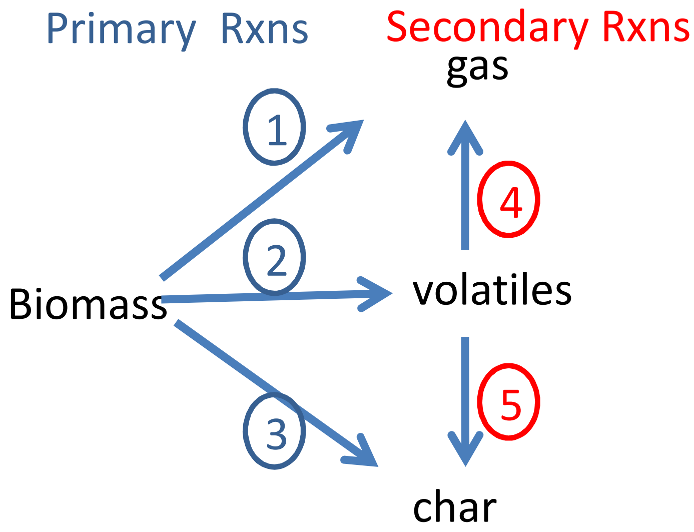

$$\frac{dm_B}{dt} = -m_B(k_1 + k_2 + k_3)$$

$$\frac{dm_{gas,1}}{dt} = m_B k_1$$

$$\frac{dm_{volatiles}}{dt} = m_B k_2 - m_{volatiles}(k_4 + k_5)$$

$$\frac{dm_{char,1}}{dt} = m_B k_3$$

$$\frac{dm_{gas,2}}{dt} = m_{volatiles} k_4$$

$$\frac{dm_{char,2}}{dt} = m_{volatiles} k_5$$

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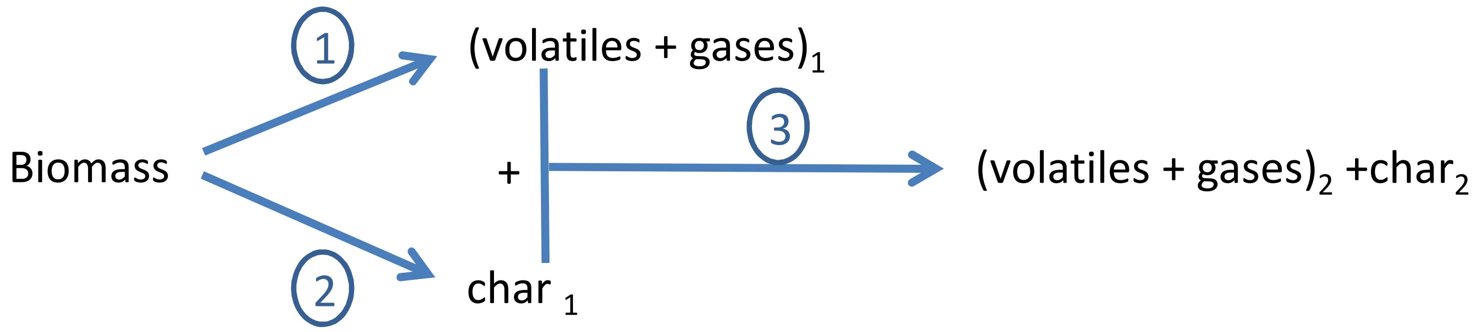
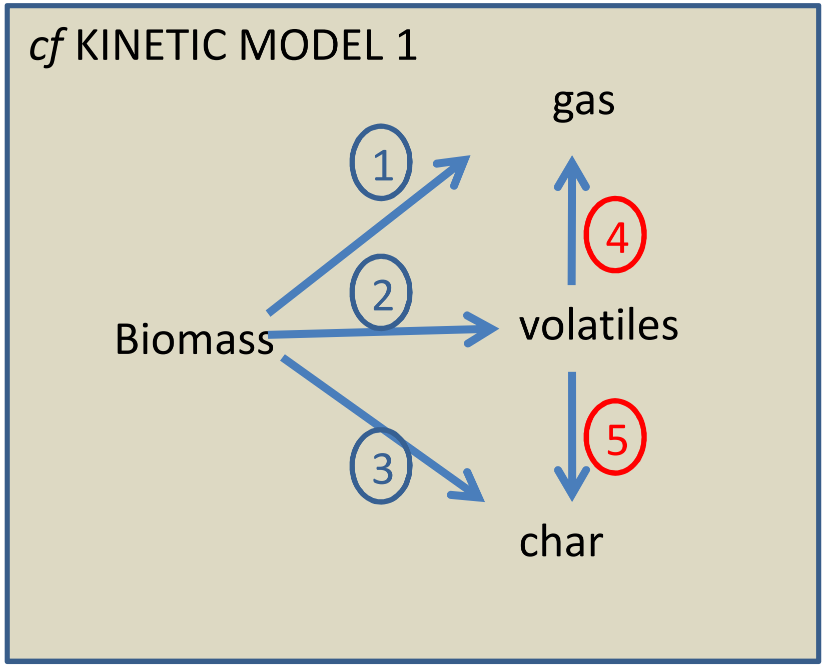
KINETIC MODEL 2



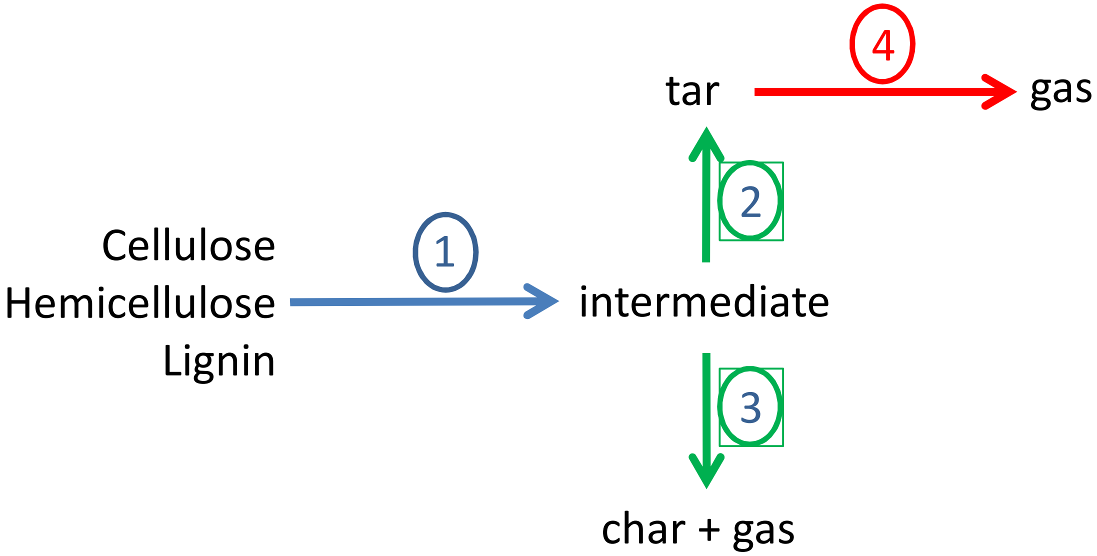
Reaction order is now flexible

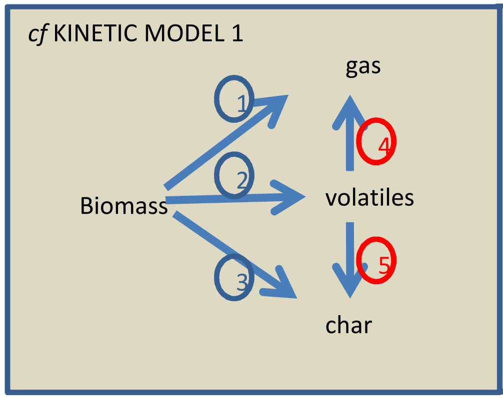


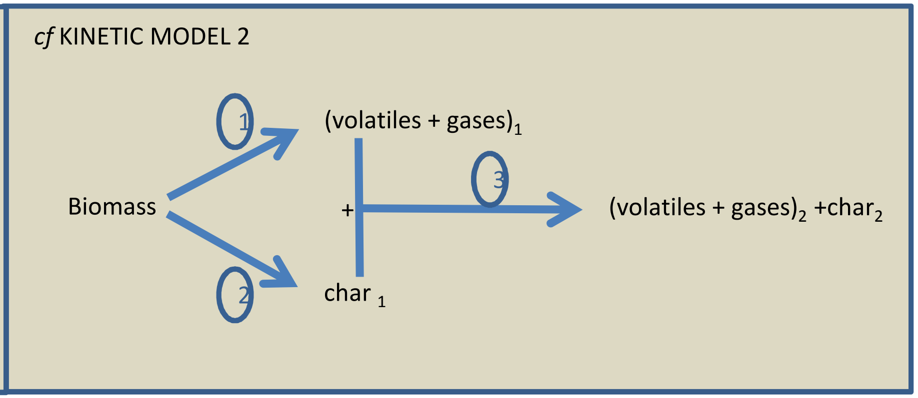
[Mechanism proposed by Koufopanos et al., 1989. Elaborated by Babu and Chaurasia, 2002]

KINETIC MODEL 3

The components of biomass each
have different decomposition kinetics







Mechanism proposed by Miller and Bellan, 1997

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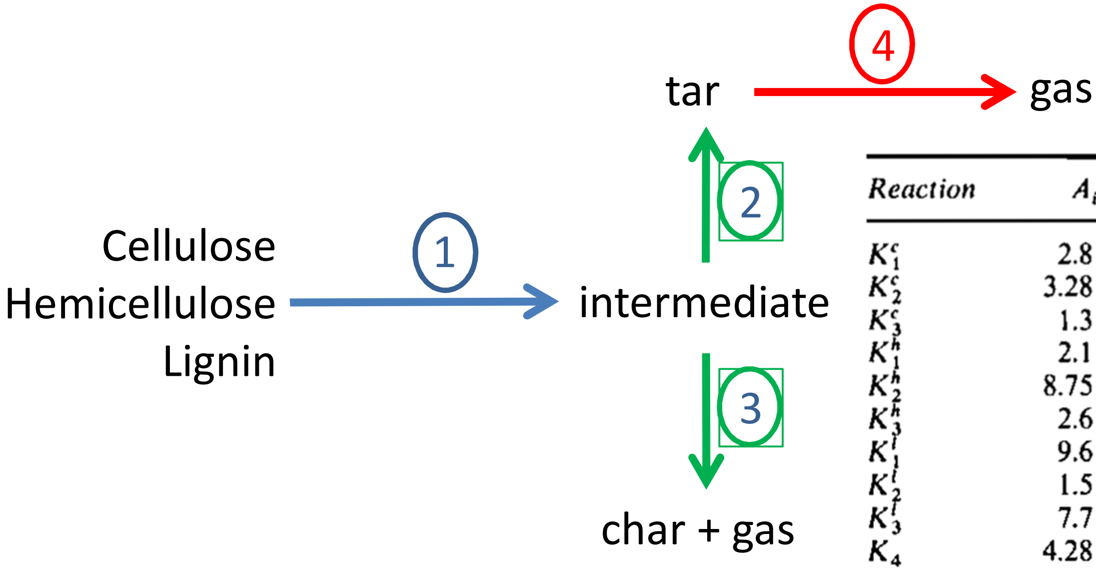
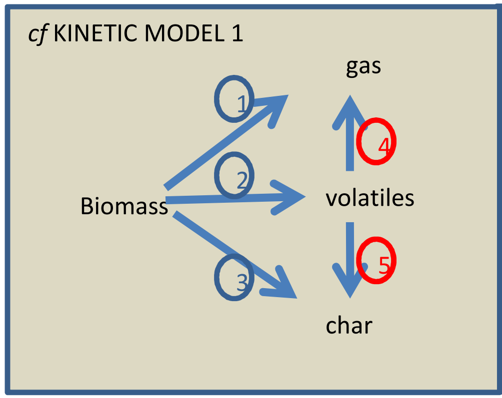
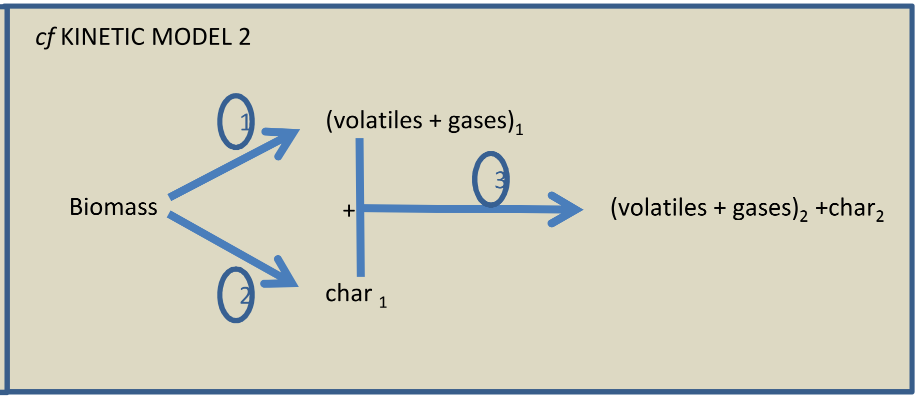


Reaction	$A_i[1/s]$	$E_i[KJ/mol]$	Source
K_1^c	2.8×10^{19}	242.4	Di Blasi and Russo (1994)
K_2^c	3.28×10^{14}	196.5	Di Blasi and Russo (1994)
K_3^c	1.3×10^{10}	150.5	Di Blasi and Russo (1994)
K_1^h	2.1×10^{16}	186.7	Ward & Braslaw (1985)*
K_2^h	8.75×10^{15}	202.4	Di Blasi and Russo (1994)*
K_3^h	2.6×10^{11}	145.7	Di Blasi and Russo (1994)*
K_1^l	9.6×10^{8}	107.6	Ward & Braslaw (1985)*
K_2^l	1.5×10^{9}	143.8	Koufopanos *et al.* (1989)*
K_3^l	7.7×10^{6}	111.4	Koufopanos *et al.* (1989)*
K_4	4.28×10^{6}	108.0	Di Blasi and Russo (1994)





Mechanism proposed by Miller and Bellan, 1997

NETWORK MODELS

...are focussed on emissions

They are...

"the most fundamental pyrolysis models ... which aim to
describe the physical and chemical phenomena taking place during a particle's devolatilization."

De Jong *et al*. 2007 use:

FG-DVC - Function Group - devolatilization, vaporisation and crosslinking model

It uses TG-FTIR data.

[Quote from de Jong *et al*., 2007]

NETWORK MODELS

How they work

"Network models are based on a structural description of the parent fuel...During devolatilization, the macromolecular fuel structure is changed as a result of depolymerization, vaporization and cross-linking of the fuel matrix. This causes the breakup of existing bridges connecting the aromatic rings and the formation of new bridges at rates described by network statistics. As a result, gaseous products and tars are formed, while the solid particle converts into carbonaceous char."

FG-DVC models have two parts:

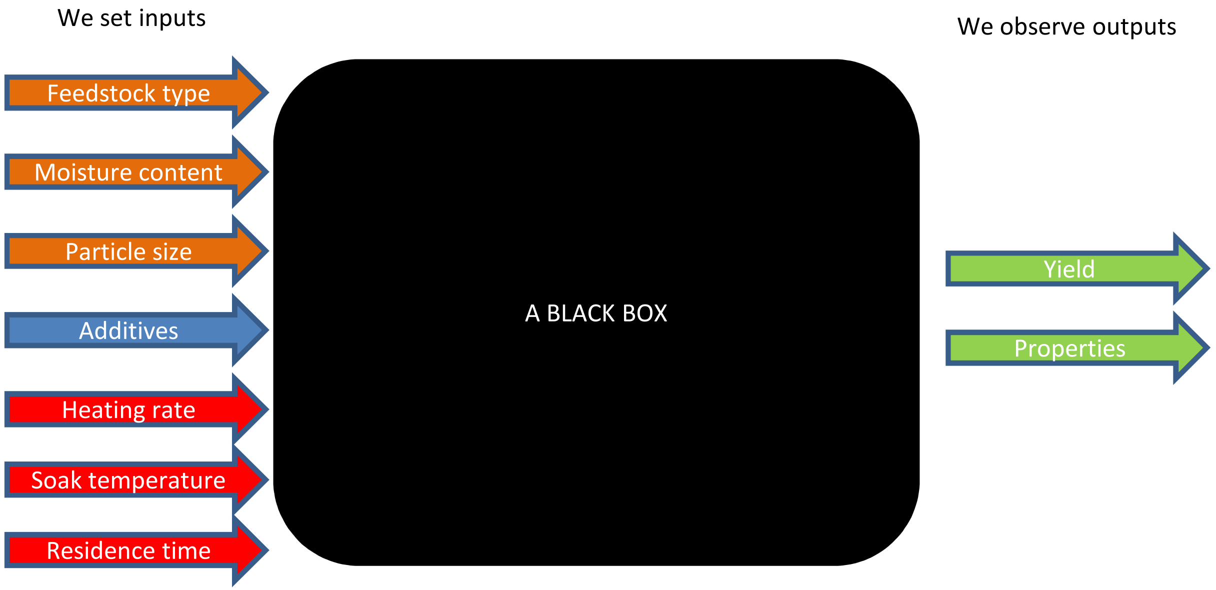
A functional group model (FG) - describes the gas evolution as well as the elemental and functional group compositions.

Depolymerization, vaporization and cross-linking model (DVC) - determines the amount and molecular weight of macromolecular fragments. The lightest of these evolve as tar.

[Quote from de Jong *et al.*, 2007]

OUTPUT = f{INPUTS} MODEL

Neve *et al*. (2011) "suggest that empirical relationships can be developed to approximate the pyrolysis behavior of most biomasses. Moreover, the literature data structured by the authors is related to a wide range of operating conditions".



[Model proposed by Neve et al., 2011]

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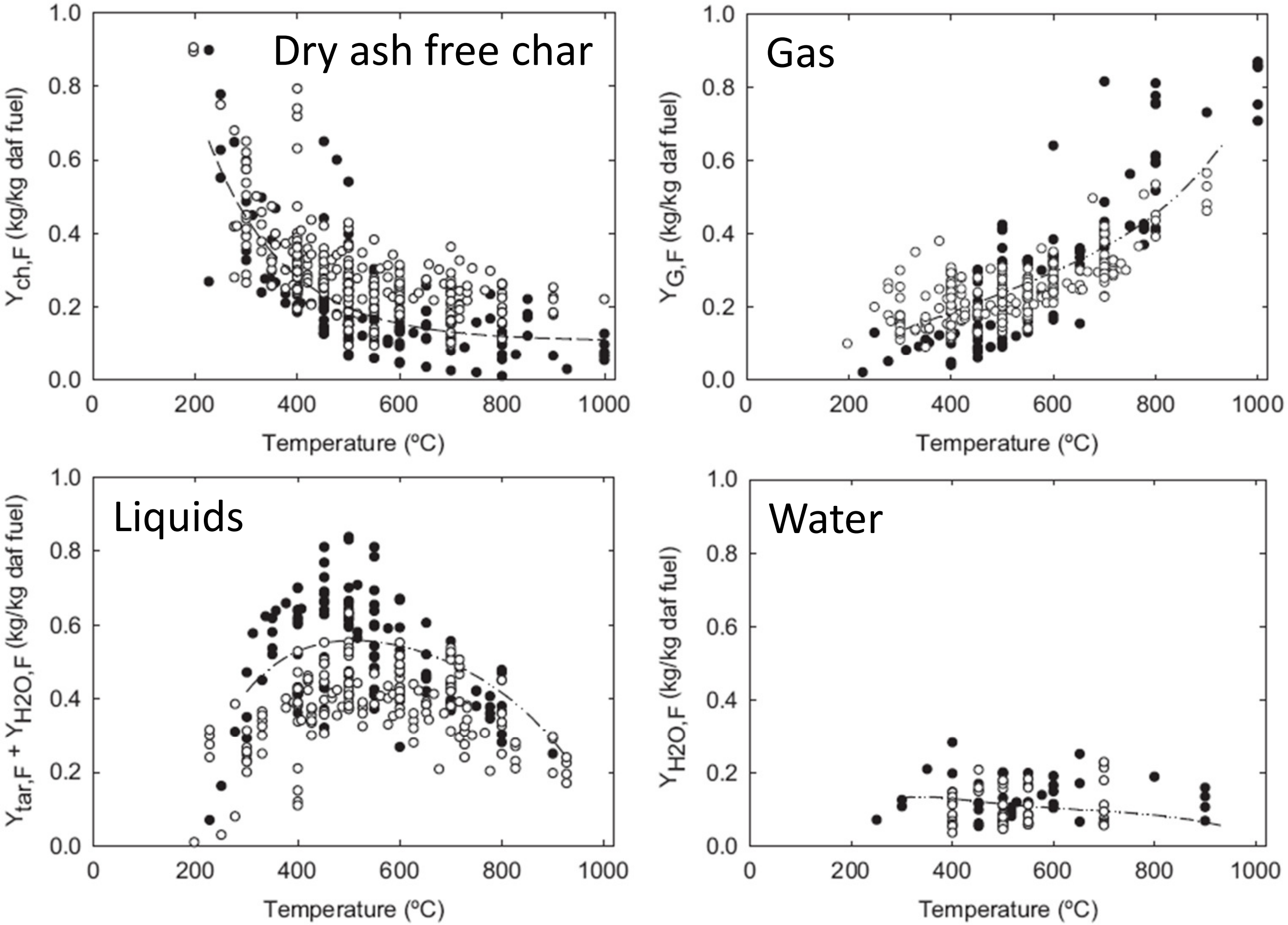
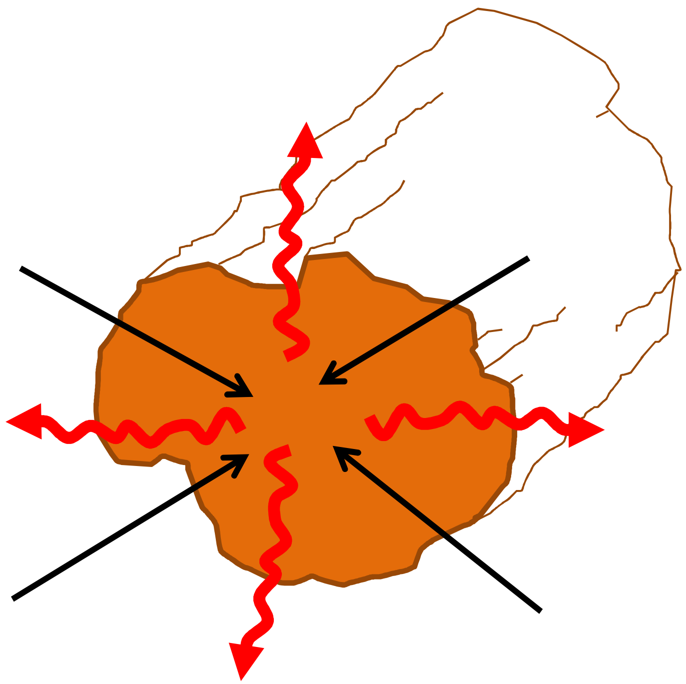


Fig. 11. Yields of daf char ($Y_{ch,F}$), total pyrolytic gas ($Y_{G,F}$), total pyrolytic liquids ($Y_{tar,F} + Y_{H_2O,F}$) and pyrolytic water ($Y_{H_2O,F}$) as a function of pyrolysis peak temperature. ● - "fast heating rate"; ○ - "slow heating rate"; ·–·· empirical model (Eq. (26)) based on a biomass with 49% carbon, 44% oxygen and 5.90% hydrogen (mass % of daf fuel) and a yield of daf char given by Eq. (27); – –yield of daf char for "fast heating rate" conditions given by Eq. (27). Data-points from [5,16,30,31,34–41,43–47,55,59,61–63,65–68,70–73,75–77,79–81,85–87,89,90, 92–94,96–102,105].

[Model proposed by Neve et al., 2011]

DON’T FORGET HEAT AND MASS TRANSFER

Larger particles have heat and mass transfer limitations



It is important to hold larger particles for longer time so that temperatures equilibrate

$$\text{Biot number} = \frac{\text{Heat transfer resistance}}{\text{Mass transfer resistance}}$$

SUMMARY

There are many approaches to understanding pyrolysis mechanisms.

Five are presented here, from purely empirical, to kinetic models with empirical constants to fundamental mechanistic models.

The degree of complexity has to relate to the end-use of the data.