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ONE STEP KINETIC MODEL OF COAL PYROLYSIS FOR CFD APPLICATIONS

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OBJECTIVE

Aim of this work is the development of a simplified kinetic model for coal devolatilization, suitable for CFD applications, able not only to describe the conversion of coal but also the relative yields of solid, tar and gaseous species, in term of hydrocarbon, sulphur and nitrogen compounds.

DETAILED MODEL OF COAL PYROLYSIS

Three different detailed kinetic models have been considered:

1. Kinetic model for the release of Hydrocarbon species [1].
2. Kinetic model for the release of Sulfur compounds [2].
3. **Kinetic model for the release of Nitrogen compound.**

Nitrogen Kinetic Model

Nitrogen Matrix Characterization:

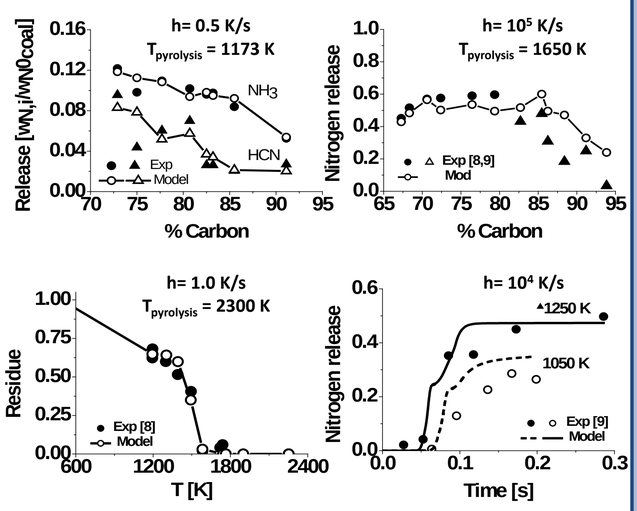
Has been applied the same criterion used to characterize the effect solid phase composition on the release of hydrocarbon species [3,4].

Kinetic Mechanism

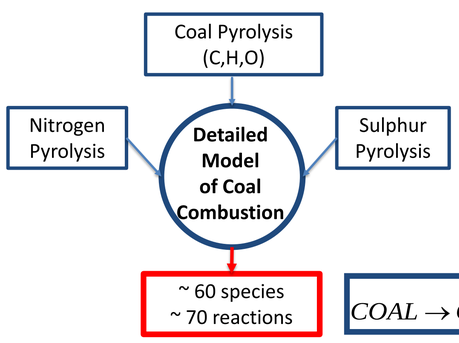
		A (*)	E_{ATT} (*)
1	COAL-N_1 →0.1 NH_3^* + 0.05 HCN^* + 0.85 N_{CHAR}	9.0×10^7	40000
2	COAL-N_1 →N_{TAR}^*	1.0×10^8	40000
3	COAL-N_1 →0.05 NH_3 + 0.3 HCN + 0.65 N_{CHAR}	1.6×10^{15}	75000
4	COAL-N_1 →N_{TAR}	1.0×10^{14}	75000
5	COAL-N_2 →0.15 NH_3^* + 0.03 HCN^* + 0.82 N_{CHAR}	7.6×10^{10}	36000
6	COAL-N_2 →N_{TAR}^*	5.0×10^{10}	36000
7	COAL-N_2 →0.15 NH_3 + 0.3 HCN + 0.55 N_{CHAR}	3.0×10^{17}	63000
8	COAL-N_2 →N_{TAR}	4.0×10^{17}	63000
9	COAL-N_3 →0.15 NH_3* + 0.15 HCN* + 0.7 N_{CHAR}	4.0×10^{10}	33000
10	COAL-N_3 →N_{TAR}^*	1.6×10^9	33000
11	COAL-N_3 →0.15 NH_3 + 0.1 HCN + 0.75 N_{CHAR}	5.0×10^{18}	61000
12	COAL-N_3 →N_{TAR}	2.0×10^{18}	61000
13	N_{CHAR} + N_{TAR} →0.05 NH_3 + 0.1 HCN + 1.85 N_{CHAR}	2.1×10^6	32500
14	N_{TAR}^* →N_{TAR}	3.0×10^8	32500
15	NH_3^* →NH_3	1.0×10^3	23000
16	HCN^* →HCN	4.0×10^2	23000
17	N_{CHAR} →$CHAR_C$+HCN	2.0×10^9	80000

*Units: cal, mol, K, s, m

Comparison with Experimental data



GLOBAL MECHANISM and ONE STEP MODEL



MECHANISM TOO MUCH COMPLEX FOR CFD APPLICATIONS

REDUCTION

$$COAL \rightarrow CHAR + TAR + CO + CO_2 + H_2O + C_2H_4 + H_2 + H_2S + HCN \quad k = A\times e^{-\frac{E}{RT}}$$

KINETIC PARAMETERS OF ONE STEP MODEL

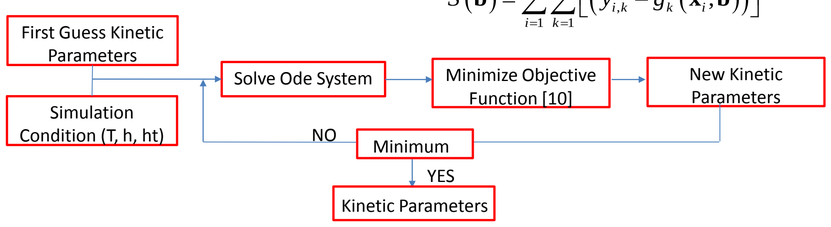
Detailed Mechanism —Oxy-Coal Conditions→ Dummy "Experimental Data"

Oxy -Coal Conditions: $10^{4\text{-}5}$ K/s and T > 1400 K

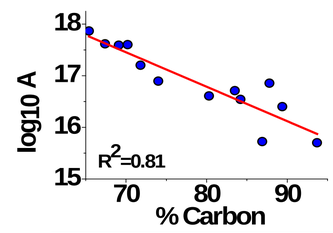
Database: 13 Coals: from Lignite (65.4% C,daf) to Anthracite (93.7% C, daf)

Non linear Regression Problem

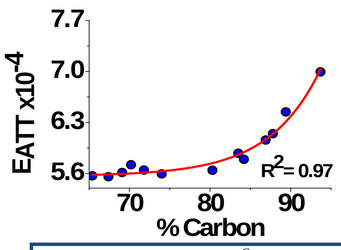
$$S(\mathbf{b}) = \sum_{i=1}^{n_E}\sum_{k=1}^{n_y}\left[\left(y_{i,k} - g_k(\mathbf{x}_i,\mathbf{b})\right)\right]^2$$



- S(b): objective function
- n_E : number of experimental point
- n_y : number of dependent variable y_i
- x_i : independent variable
- b : vector of parameters
- g_k: kinetic equations



$$\log_{10} A = 22.1 - 0.067\times C_{\%} \quad [A] = s^{-1}$$



$$E = 55650 + 5.67\times10^{-3} e^{\frac{C_{\%}}{6.35}} \quad [E] = \frac{kcal}{kmol}$$

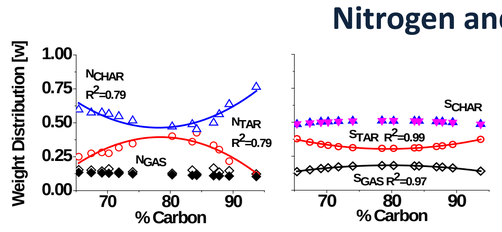
STOICHIOMETRIC COEFFICIENTS

Hydrocarbon release mechanism (high temperature)

	$CHAR_C$	H_2	CH_4	$C_{2\text{-}5}$	BTX	CO	H_2O	CO_2	TAR_1	TAR_2	TAR_3
$COAL_1$	5.13	1.50	0.38	0.50	0.00	0.00	0.00	0.00	0.50	0.00	0.00
$COAL_2$	9.41	2.69	0.32	0.10	0.15	0.82	0.09	0.00	0.10	0.09	0.00
$COAL_3$	3.64	1.35	0.26	0.59	0.11	1.91	1.23	0.64	0.09	0.00	0.29
$CHAR_C$	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Kmol j-th species per kmol of reference coal

Nitrogen and Sulphur Distribution



Nitrogen Repartition*	Sulphur Repartition*
$N_{CHAR} = 7.3 - 0.175\times C_{\%} + 1.12\times10^{-3}\times C_{\%}^2$	$S_{CHAR} = 1 - S_{TAR} - S_{GAS}$
$N_{GAS} = 1 - N_{TAR} - N_{CHAR}$	$S_{GAS} = -1.20 + 3.48\times10^{-2}\times C_{\%} - 2.182\times10^{-4}\times C_{\%}^2$
$N_{TAR} = -6.56 + 0.177\times C_{\%} - 1.13\times10^{-3}\times C_{\%}^2$	$S_{TAR} = -2.48 - 5.49\times10^{-2}\times C_{\%} + 3.45\times10^{-4}\times C_{\%}^2$

*Kg N or S in j phase respect nitrogen or sulphur content in coal parent.
j = CHAR, TAR, GAS

Solid Phase CHAR: brute formula $C_1N_xS_y$.

$$\alpha_{CHAR} = (100 - N_{\%} - S_{\%}) \times \sum_{i=1}^{NCOAL} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{COALi,CHAR_{CHO}}$$

$$x = N_{CHAR} \times \omega_{COAL}^N \times \frac{PM_{COAL}}{PM_N} \times \frac{1}{\alpha_{CHAR}}$$

$$y = S_{CHAR} \times \omega_{COAL}^S \times \frac{PM_{COAL}}{PM_S} \times \frac{1}{\alpha_{CHAR}}$$

TAR Phase TAR: brute formula $C_xH_yO_zN_kS_j$.

$$\alpha_{TAR} = \frac{(100 - N_{\%} - S_{\%})}{PM_{TAR}} \times \sum_{j=1}^{NTAR} PM_j \sum_{i=1}^{4} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{COALi,j}$$

$$\phi_{TAR} = \sum_{i=1}^{NTAR} x_{TARi} \times \phi_{TARi} \qquad x_{TAR_i} = \frac{\sum_{i=1}^{NCOAL} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{TAR,COALi}}{\sum_{i=1}^{NTAR} TAR_i} \qquad \phi = x, y, z$$

$$k = N_{TAR} \times \omega_{COAL}^N \times \frac{PM_{COAL}}{PM_N} \times \frac{1}{\alpha_{TAR}} \qquad j = S_{TAR} \times \omega_{COAL}^S \times \frac{PM_{COAL}}{PM_S} \times \frac{1}{\alpha_{TAR}}$$

Gas Phase: CO, CO_2, H_2O, C_2H_4, H_2, HCN, H_2S

$$\alpha_j = (100 - N_{\%} - S_{\%}) \times \sum_{i=1}^{4} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{COALi,j} \quad j = CO, CO_2, H_2O$$

$$\alpha_{H_2S} = S_{GAS} \times \omega_S^0 \times \frac{PM_{Coal}}{PM_S} \qquad \alpha_{HCN} = N_{GAS} \times \omega_N^0 \times \frac{PM_{Coal}}{PM_N}$$

$$\Delta C = \omega_{C,coal} - PM_C \sum_{i=1}^{Nspecie} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{COALi,j} \qquad \Delta H = \omega_{H,coal} - PM_H \sum_{i=1}^{Nspecie} \frac{\omega_{COALi}}{PM_{COALi}} \times \alpha_{COALi,j}$$

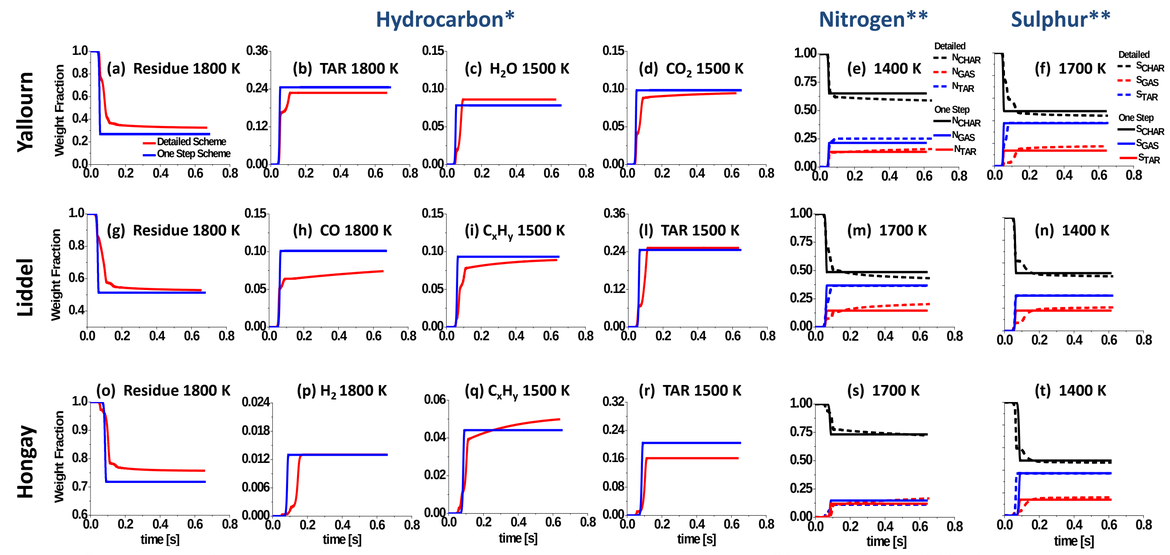
$$\alpha_{C2H4} = \frac{PM_{COAL}}{2} \times \frac{\Delta C}{PM_C} - \frac{1}{2}\alpha_{HCN} \qquad \alpha_{H2} = \frac{PM_{COAL}}{2PM_H} \Delta H - 2\times\alpha_{C2H4} + \frac{1}{2}\alpha_{N,GAS} - \alpha_{H_2S}$$

Legend

- α_i : stoichiometric coefficient for j-th species in One Step Model
- ω_{COALi} : mass fraction of i-th reference coal [1]
- $\alpha_{COALi,j}$: stoichiometric coefficient of j-th species for i-th references coal
- PM_{COALj} : molecular weight j-th reference coal [1]
- PM_j: molecular weight of j-th tar reference [1]
- PM_{TAR} : molecular weight of TAR specie
- x_{TARi} : molar fraction of i-th tar reference in tar mixture
- ϕ_{TARi} , ϕ_{TAR} :atomic content in i-th tar reference and TAR
- $\alpha_{TAR,COALi}$: stoichiometric coefficient of TAR_i reference
- $N_{\%}$, $S_{\%}$: mass % of N and S in coal
- N_x,S_x : nitrogen and sulphur distribution in x phase, with x = CHAR, TAR, GAS
- ω_N, ω_S : mass fraction of N and S in coal parent.

COMPARISON BETWEEN MODELS

One Step	% C, daf	CHAR	TAR	CO	CO_2	H_2O	C_2H_4	H_2	HCN	H_2S	A	E
Yallourn	65.3	2.219	0.143	0.721	0.222	0.432	0.323	0.632	0.0058	0.0013	5.7×10^{17}	55800
Liddel	83.5	4.146	0.144	0.356	0.022	0.074	0.317	1.209	0.0169	0.0034	3.6×10^{16}	58590
Hongay	93.7	5.880	0.128	0.066	0.000	0.007	0.150	0.634	0.0081	0.0026	7.4×10^{15}	70300



* ω on dry ash basis

** ω_N and ω_S respect initial nitrogen or sulphur in coal

CONCLUSION

In this work a simplified model for coal pyrolysis has been developed. The One Step model shows a satisfactory agreement with detailed models. Moreover the One Step model only needs the coal elemental composition as an input.

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