RAC detailed scheme for biomass pyrolysis

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Introduction

Pyrolysis mechanisms have been reviewed in detail in [1]. Detailed schemes are required to be able to describe the complex reactions that take place during biomass pyrolysis and to predict a detailed product composition, as well as the influence of process conditions.

The most advanced schemes in literature for biomass pyrolysis are based on the semi-detailed scheme for primary pyrolysis from Ranzi et al. [2]. This scheme has been adapted by Anca-Couce et al. [3] in order to consider the presence of heterogeneous secondary charring reactions taking place during the pyrolysis process (not to be confused with the homogeneous tar cracking which can take place in the gas phase at higher temperatures, i.e. more than 500°C). Therefore, the RAC scheme integrates primary pyrolysis and secondary charring. The first version of the RAC (Ranzi-Anca-Couce) scheme has been applied to describe product composition in fixed-bed pyrolysis [3] and torrefaction [4] [5], as well as mass loss in TGA experiments [4] (methods to accurately calculate mass loss kinetics in TGA pyrolysis experiments are described in [6]).

Furthermore, a new version of the RAC scheme has been coupled with a single particle model in [7] and [8]. This second version of the RAC scheme is based on the updated primary pyrolysis scheme from Corbetta et al. [9], which has been improved besides the introduction of secondary charring. It has been shown that the combination of the RAC scheme with a particle model can predict mass loss, temperatures and online release of the most relevant volatiles species in single particle experiments [7] and it can accurately predict the heat of reaction for pyrolysis [8].

Biomass composition

Representative compositions for hardwood and softwood in in ash-free % mass [4].

	Hardwood	Softwood
Cellulose	44.0	44.0
Hemicellulose	34.0	26.0
LIG-C	6.0	17.5
LIG-H	7.0	9.5
LIG-O	9.0	3.0
Total lignin	22.0	30.0
% C	48.6	51.0
% H	6.0	6.0
% O	45.4	43.0

Secondary charring reactions

Recommended values for the “x” parameters representing the amount of secondary charring reactions for cellulose, hemicellulose, lignin and G{} forms in wood pyrolysis [7]. Big particle and bed sizes and slow heating rates enhance secondary charring [1].

	Low charring conditions	High charring conditions
X_CELL	0.025	0.1
X_HCE	0.05	0.2
X _LIG	0.075	0.3
X_G{}	0.1	0.4
Sugar formation in R3 and R8	Yes	No

List of species

Abbreviation	Name	Atomic composition	Net calorific value (kJ/g)
Solids			
CELL	Cellulose	$C_5H_8O_4$	16.32
CELLA	Activated cellulose	$C_5H_8O_4$	16.32
HCE	Hemicellulose	$C_5H_8O_4$	16.66
HCEHW	Hemicellulose (hardwoods)	10 * ($C_5H_8O_4$) + 4 * ($C_2H_4O_2$)	16.38
HCESW	Hemicellulose (softwoods)	10 * ($C_5H_8O_4$) + ($C_2H_4O_2$)	16.58
HCEA1	Activated hemicellulose 1	$C_5H_8O_4$	16.66
HCEA2	Activated hemicellulose 2	$C_5H_8O_4$	16.66
LIG-C	Carbon-rich lignin	$C_{15}H_{14}O_4$	26.99
LIG-H	Hydrogen-rich lignin	$C_{22}H_{28}O_9$	23.87
LIG-O	Oxygen-rich lignin	$C_{20}H_{22}O_{10}$	20.93
LIG-CC	Carbon-rich lignin 2	$C_{15}H_{14}O_4$	26.99
LIG-OH	OH-rich lignin	$C_{19}H_{22}O_8$	23.13
LIG	Intermediate lignin	$C_{11}H_{12}O_4$	24.50
G{CO_2}	Trapped CO_2	CO_2	0.0
G{CO}	Trapped CO	CO	10.11
G{COH_2}	Trapped COH_2	CH_2O	14.83
G{H_2}	Trapped H_2	H_2	95.78
G{CH_4}	Trapped CH_4	CH_4	50.13
G{CH_3OH}	Trapped CH_3OH	CH_4O	21.12
G{C_2H_4}	Trapped C_2H_4	C_2H_4	43.61
Char	Char	C	32.79
Volatiles			
HAA / AA	Hydroxyacetaldehyde / Acetic acid	$C_2H_4O_2$	16.05
HCOOH	Formic acid	CH_2O_2	5.58
GLYOX	Glyoxal	$C_2H_2O_2$	14.09
C_3H_6O	Propanal (Acetone)	C_3H_6O	29.61
$C_3H_4O_2$	Propanedial	$C_3H_4O_2$	19.29
HMFU	5-hydroxymethyl-furfural	$C_6H_6O_3$	21.85
LVG	Levoglucosan	$C_6H_{10}O_5$	16.85
XYL	Xylose monomer	$C_5H_8O_4$	17.43
pCOUMARYL	Paracoumaryl alcohol	$C_9H_{10}O_2$	30.28
PHENOL	Phenol	C_6H_6O	31.72
FE2MACR	Sinapaldehyde	$C_{11}H_{12}O_4$	25.45
H_2	Hydrogen	H_2	120.9
CO	Carbon monoxide	CO	10.11
CO_2	Carbon dioxide	CO_2	0.0
CH_4	Methane	CH_4	50.14
CH_2O	Formaldehyde	CH_2O	17.31
CH_3OH	Methanol	CH_4O	21.12
C_2H_4	Ethylene	C_2H_4	47.25
CH_3CHO	Acetaldehyde	C_2H_4O	25.10
ETOH	Ethanol	C_2H_6O	27.76
H_2O	Water vapour	H_2O	0.0

2nd version RAC: list of reactions. Taken from [7] (version V3) & [8] (SW: softwood, HW: hardwood).

			Reaction	*A* [s^{-1}]	*E* [kJ/mol]	*Δh* *[kJ/g]*
1	CELL	→	CELLA	4×10^{13}	188.37	0.0
2	CELLA	→	$(1\text{-}x_{CELL})$ * (0.45 HAA + 0.2 GLYOX + 0.3 C_3H_6O + 0.25 HMFU + 0.05 H_2 + 0.31 CO + 0.41 CO_2 + 0.4 CH_2O + 0.15 CH_3OH + 0.1 CH_3CHO + 0.83 H_2O + 0.02 HCOOH + 0.05 G{H_2} + 0.2 G{CH_4} + 0.61 Char) + x_{CELL} * (5.5 Char + 4 H_2O + 0.5 CO_2 + H_2)	2×10^{6}	80.0	0.56 $(1\text{-}x_{CELL})$ – 1.47 x_{CELL}
3	CELLA	→	$(1\text{-}x_{CELL})$ * (LVG / same products as R2) + x_{CELL} * (5.5 Char + 4 H_2O + 0.5 CO_2 + H_2)	4 × T	41.86	0.53 $(1\text{-}x_{CELL})$ – 1.47 x_{CELL}
4			Not included			
5	HCE	→	0.4 AA (HW) / 0.1 AA (SW) + 0.58 HCEA1 + 0.42 HCEA2	1×10^{10}	129.77	0.0
6	HCEA1	→	$(1\text{-}x_{HCE})$ * (0.5 CO + 0.5 CO_2 + 0.325 CH_4 + 0.8 CH_2O + 0.1 CH_3OH + 0.25 C_2H_4 + 0.125 ETOH + 0.025 H_2O + 0.025 HCOOH + 0.275 G{CO_2} + 0.4 G{COH_2} + 0.125 G{H_2} + 0.45 G{CH_3OH} + 0.875 Char) + x_{HCE} * (4.5 Char + 3 H_2O + 0.5 CO_2 + H_2)	1.2×10^{9}	125.58	0.25 $(1\text{-}x_{HCE})$ – 1.42 x_{HCE}
7	HCEA1	→	$(1\text{-}x_{HCE})$ * (0.1 CO + 0.8 CO_2 + 0.3 CH_2O + 0.25 H_2O + 0.05 HCOOH + 0.15 G{CO_2} + 0.15 G{CO} + 1.2 G{COH_2} + 0.2 G{H_2} + 0.625 G{CH_4} + 0.375 G{C_2H_4} + 0.875 Char) + x_{HCE} * (4.5 Char + 3 H_2O + 0.5 CO_2 + H_2)	0.15 × T	33.5	- 0.64 $(1\text{-}x_{HCE})$ – 1.42 x_{HCE}
8	HCEA1	→	$(1\text{-}x_{HCE})$ * (XYL / same as R6) + x_{HCE} * (4.5 Char + 3 H_2O + 0.5 CO_2 + H_2)	3 × T	46.05	0.77 $(1\text{-}x_{HCE})$ – 1.42 x_{HCE}
9	HCEA2	→	$(1\text{-}x_{HCE})$ * (0.2 HAA + 0.175 CO + 0.275 CO_2 + 0.5 CH_2O + 0.1 ETOH + 0.2 H_2O + 0.025 HCOOH + 0.4 G{CO_2} + 0.925 G{COH_2} + 0.25 G{CH_4} + 0.3 G{CH_3OH} + 0.275 G{C_2H_4} + Char) + x_{HCE} * (4.5 Char + 3 H_2O + 0.5 CO_2 + H_2)	0.5×10^{10}	138.14	- 0.14 $(1\text{-}x_{HCE})$ – 1.42 x_{HCE}
10	LIG-C	→	0.35 LIG-CC + 0.1 pCOUMARYL + 0.08 PHENOL + 0.32 CO + 0.3 CH_2O + H_2O + 0.7 G{COH_2} + 0.495 G{CH_4} + 0.41 G{C_2H_4} + 5.735 Char	1.33×10^{15}	203.02	- 0.47
11	LIG-H	→	LIG-OH + 0.25 HAA + 0.5 C_3H_6O + 0.5 G{C_2H_4}	0.67×10^{13}	156.97	0.10
12	LIG-O	→	LIG-OH + CO_2	0.33×10^{9}	106.74	- 0.21
13	LIG-CC	→	$(1\text{-}x_{LIG})$ * (0.35 HAA + 0.3 pCOUMARYL + 0.2 PHENOL + 0.4 CO + 0.65 CH_4 + 0.6 C_2H_4 + 0.7 H_2O + 0.4 G{CO} + G{COH_2} + 6.75 Char) + x_{LIG} * (15 Char + 4 H_2O + 3 H_2)	3×10^{7}	131.86	- 0.09 $(1\text{-}x_{LIG})$ – 1.30 x_{LIG}
14	LIG-OH	→	LIG + 0.55 CO + 0.05 CO_2 + 0.1 CH_4 + 0.6 CH_3OH + 0.9 H_2O + 0.05 HCOOH + 0.6 G{CO} + 0.85 G{COH_2} + 0.1 G{H_2} + 0.35 {CH_4} + 0.3 G{CH_3OH} + 0.2 G{C_2H_4} + 4.15 Char	1×10^{8}	125.58	- 0.17
15	LIG	→	$(1\text{-}x_{LIG})$ * FE2MACR + x_{LIG} * (10.5 Char + 3 H_2O + 0.5 CO_2 + 3 H_2)	4 × T	50.2	0.95 $(1\text{-}x_{LIG})$ – 1.52 x_{LIG}
16	LIG	→	$(1\text{-}x_{LIG})$ * (0.2 C_3H_6O + CO + 0.2 CH_4 + 0.2 CH_2O + 0.4 CH_3OH + 0.2 CH_3CHO + 0.95 H_2O + 0.05 HCOOH + 0.45 G{CO} + 0.5 G{COH_2} + 0.4 {CH_4} + 0.65 G{C_2H_4} + 5.5 Char) + x_{LIG} * (10.5 Char + 3 H_2O + 0.5 CO_2 + 3 H_2)	0.4×10^{9}	125.58	- 0.35 $(1\text{-}x_{LIG})$ – 1.52 x_{LIG}
17	LIG	→	$(1\text{-}x_{LIG})$ * (0.4 CO + 0.2 CH_4 + 0.4 CH_2O + 0.6 H_2O + 0.2 G{CO} + 2 G{COH_2} + 0.4 {CH_4} + 0.4 G{CH_3OH} + 0.5 G{C_2H_4} + 6 Char)	0.083 × T	33.5	- 0.50 $(1\text{-}x_{LIG})$ – 1.52 x_{LIG}

			+ x_{LIG} * (10.5 Char + 3 H_2O + 0.5 CO_2 + 3 H_2)			
18	G{CO_2}	→	CO_2	1×10^5	100.46	0.0
19	G{CO}	→	(1-$x_{G\{\}}$) * CO + $x_{G\{\}}$ * (0.5 Char + 0.5 CO_2)	3×10^{13}	209.3	- 3.08 $x_{G\{\}}$
20	G{COH_2}	→	0.75 G2{COH_2} + 0.25 (H_2 + 0.5 CO + 0.25 CO_2 + 0.25 Char)	1×10^6	100.46	0.31
21	G{H_2}	→	H_2	1×10^{12}	313.96	0.0
22	G{CH_4}	→	CH_4	2×10^{13}	300.0	0.0
23	G{CH_3OH}	→	(1-$x_{G\{\}}$) * CH_3OH + $x_{G\{\}}$ * (Char + H_2O + H_2)	1.2×10^{13}	209.3	- 1.27 $x_{G\{\}}$
24	G{C_2H_4}	→	0.3 C_2H_4 + 0.7 (CH_4 + Char)	1×10^6	100.46	0.46
25	G2{COH_2}	→	0.2 G3{COH_2} + 0.8 (CO + H_2)	1.5×10^9	209.3	0.0

Notes:

- The heat of reaction is calculated as the difference between the net calorific value (calculation explained in [8]) of reactants and products with the exception of the release of high temperature G{} forms (R21, R22 and R25), for which no heat of reaction is considered.
- Heterogeneous secondary reactions and the presence of alkalis lead to the fragmentation pathway for cellulose (producing in R3 the same products as in R2) and hemicellulose (producing in R8 the same products as in R6) and avoiding the formation of sugars (LVG and XYL respectively). The production of sugars is usually low for slow pyrolysis with big particle sizes (high "x" values). However, it can be high in typical fast pyrolysis conditions and especially for a low ash content (low "x" values).
- Acetic acid release from hemicellulose is considered in R5 with different typical proportions for hardwood and softwood.
- G2{COH_2} and G3{COH_2} have the same composition and calorific value as G{COH_2}. G2{COH_2} is produced from G2{COH_2} at medium temperatures in R20, at it further reacts at higher temperatures in R25 producing G3{COH_2}, which represents oxygen and hydrogen present in char and that is not released even at high temperatures (up to 1000 °C).

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