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Characterization and pyrolysis kinetics of Thai Napier grass and agricultural residues

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Outline

- Introduction and background
- Study methods
- Highlights of results
- Concluding remarks

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Energy demand and production of Thailand

- The total energy demand in Thailand has been significantly increased during the last decades, as a result of the economic and life standard development.
- Approximately 57% of the total energy demand was imported, mostly in the form of conventional fuels including natural gas and crude oil.
- The Royal Thai Government has established a 10-Year Alternative Energy Development Plan (AEDP): 2012-2021, aimed at increasing the share of renewable energy to 25% of the total energy consumption by 2021.
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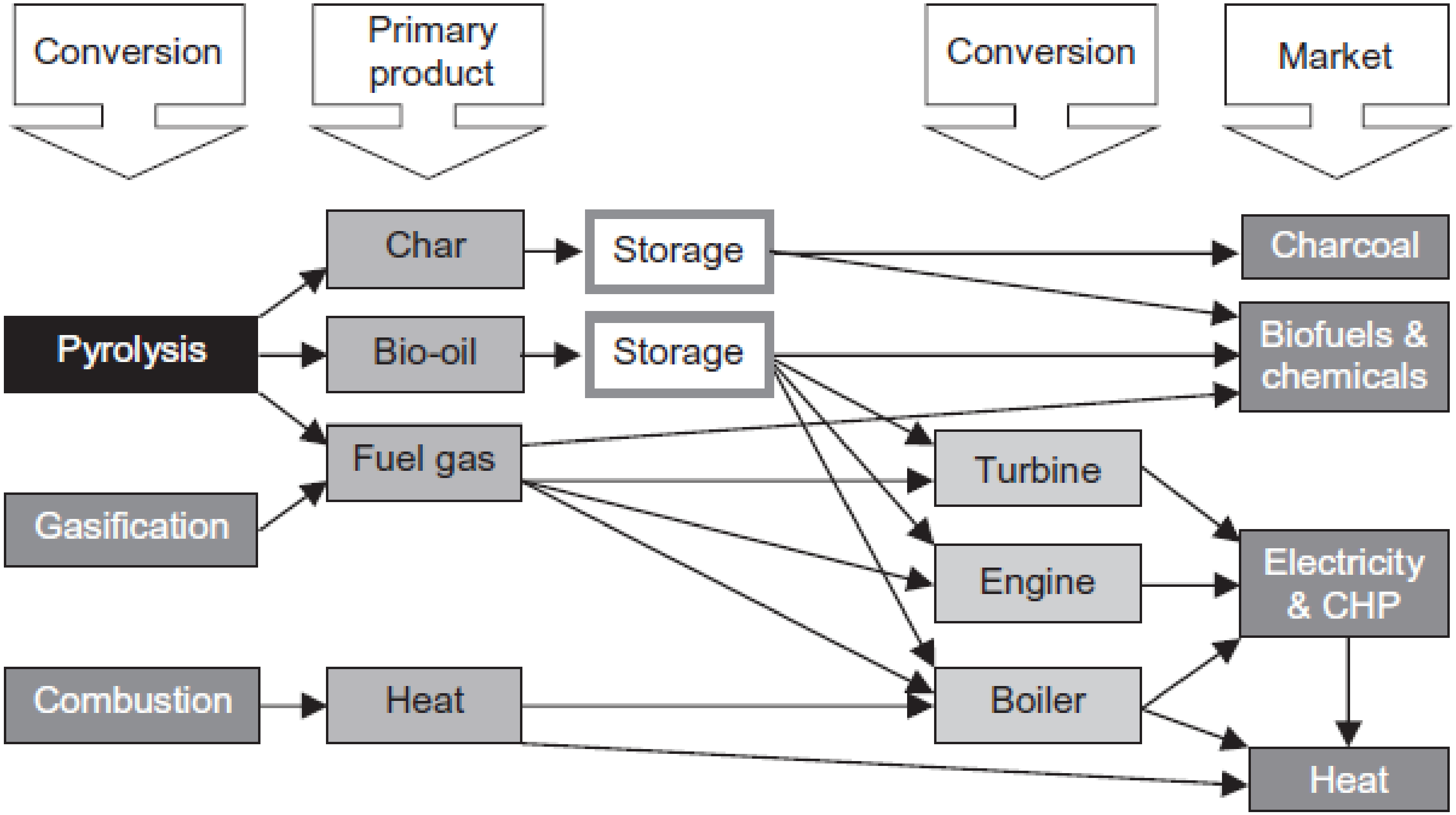
Biomass resources in Thailand

- Approx. 8-14 Mtoe (Million Tonnes of Oil Equivalent) of rice straw, annually.
- The total of agricultural residues in Thailand in 2013 was equivalent to 9.20 Mtoe, of which cassava stalk accounted for 0.50 Mtoe.
- This huge bioenergy resource would be an important factor for the achievement of AEDP´s target.

AD for power production in Thailand

- Thai government has promoted a project of electricity production from energy crops with an emphasis on Napier grass and biogas production from Napier grass by anaerobic digestion (AD).
- A drawback of AD the technology is not capable of digesting the lignin component of grasses, which normally account for one thirds of the energy content of energy crops.
- The digestate from the AD of Napier grass, containing mainly lignin, in principle can be used as fertilizer and/or solid fuel for heat and power generation via thermochemical conversion processes.

Thermochemical conversion of biomass



Main steps of solid fuel combustion

1. Drying, around 100^{o}C

2a. Devolatilization or pyrolysis, around 350^{o}C

2b. Volatiles combustion (flame, homogeneous reaction)

3. Char combustion (heterogeneous reaction)

Approaches for kinetic study

- Reaction scheme
  - Combined pyrolysis and char combustion
  - Separate pyrolysis and char combustion
- Experimental approach
  - TGA (Thermogravimetric analysis)
- Modelling approach
  - Lump kinetics for pseudo-component
  - Distributed activation energy model

Pyrolysis kinetic modelling

Solid biomass -- > char + volatile

$$\frac{d\alpha}{dt} = A.e^{\frac{-E_a}{RT}}.f(\alpha) \qquad (1)$$

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \qquad (2)$$

$$\frac{d\alpha_i}{dt} = A_i.e^{\frac{-E_{a,i}}{RT}} f(1-\alpha_i) \qquad i = 1,2,3 \qquad (3)$$

$$\frac{d\alpha}{dt} = \sum_{1}^{3} c_i \frac{d\alpha_i}{dt} \qquad (4)$$

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Distributed activation energy model

$$1-\alpha=\int_0^{\infty}\exp\left[-\int_0^{t}A\,exp\left(\frac{-E}{RT}\right)\,dt\right]f(E)dE \qquad n=1 \qquad (5)$$

$$f(E)=\frac{1}{\sigma\sqrt{2\pi}}\exp\left[-\frac{(E-E_0)^2}{2\sigma^2}\right] \qquad (6)$$

Fitting and fit quality

$$S = \sum_{i=1}^{n} [\left(\frac{d\alpha_i}{dt}\right)_{exp} - \left(\frac{d\alpha_i}{dt}\right)_{model}]^2 \qquad (7)$$

$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{[\left(\frac{d\alpha_i}{dt}\right)_{exp}]_{max}}\right).100\% \qquad (8)$$

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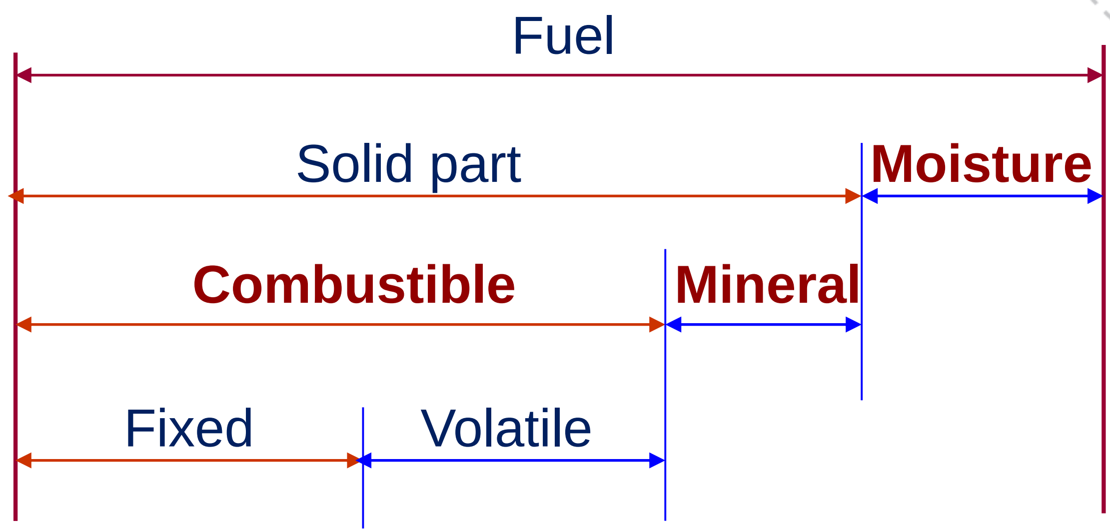
Solid fuel components



A solid fuel consists of three main components: combustible (fixed and volatile constituents), mineral (most of which becomes ash during combustion), and moisture.

Solid fuel analysis

	Anthracite	Bituminous coal	Peat	Wood
Proximate analysis (% as received)				
Combustibles	92	75	57	60
Ash	7	12	3	0.5
Mosture	1	12	40	40
Volatiles (of combustibles)	10	35	70	80
Ultimate analysis (% of combustibles)				
C	92	85	55	50
H	4	5	6	6
O	2	7	38	44
N	1	2	1	0.1
S	1	1	0.3	0

Highlights of results

Characterization of three biomass samples

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%)			
	M	VM	FC	Ash	C	H	N	O
Cassava stalk	3.12	80.77	10.36	5.75	38.60	7.22	1.00	53.18
Napier grass	3.56	64.45	14.54	17.45	35.50	6.10	1.80	56.60
Rice Straw	3.20	69.23	9.36	18.21	34.33	5.96	0.96	58.75

M = Moisture; VM= volatile matter; FC= fixed carbon.

Themogravimetric analysis

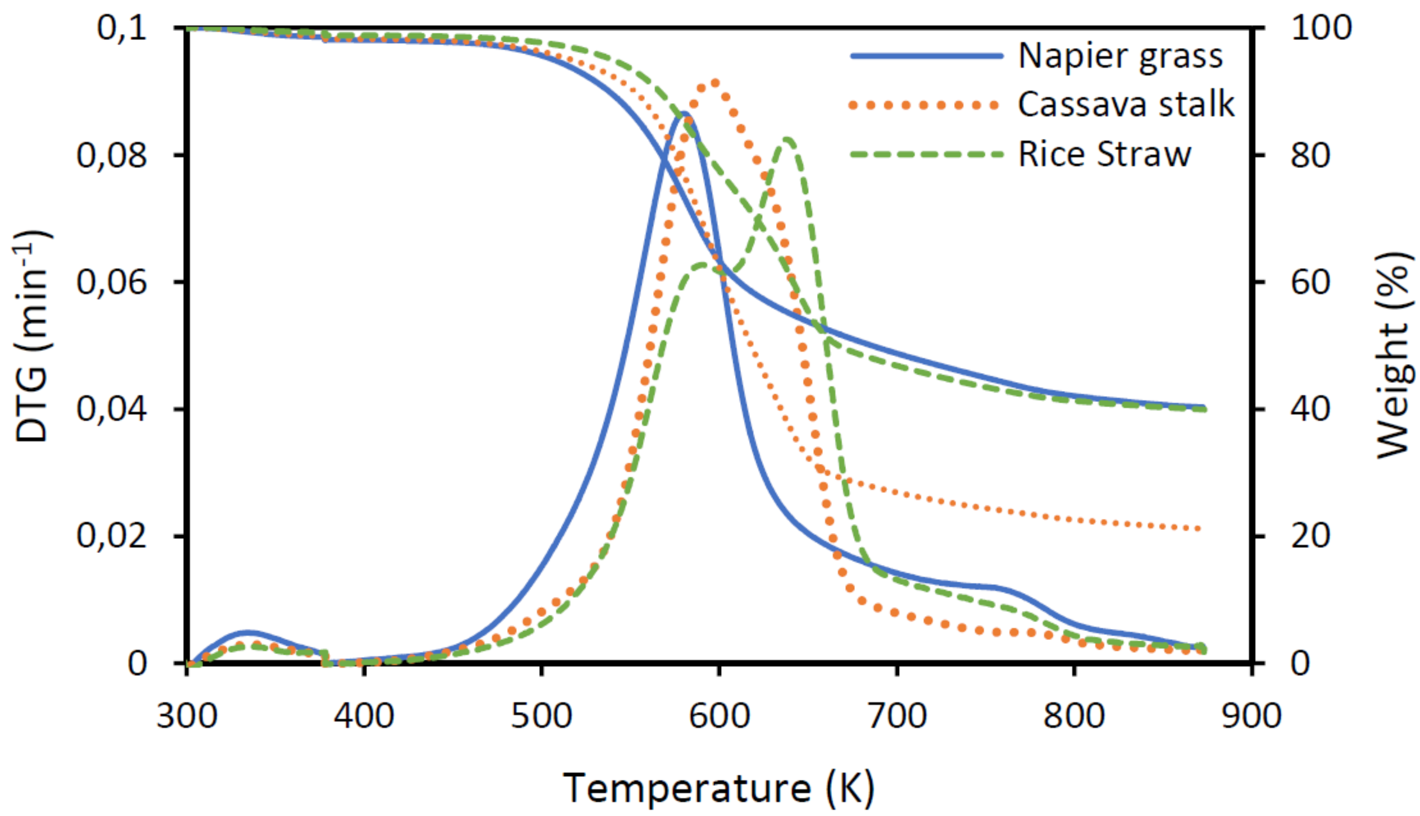


Fig. 1 TGA and DTG of the biomass samples

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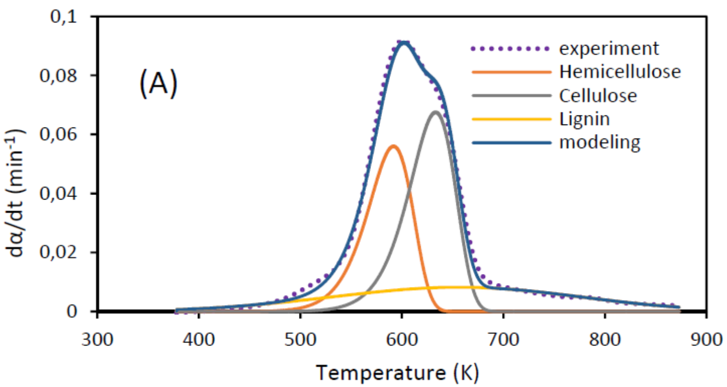
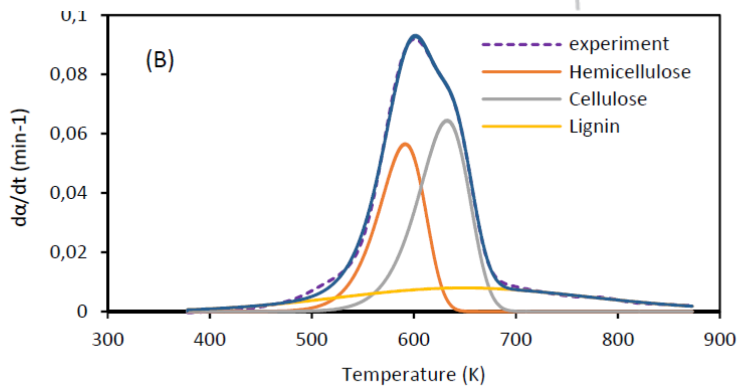
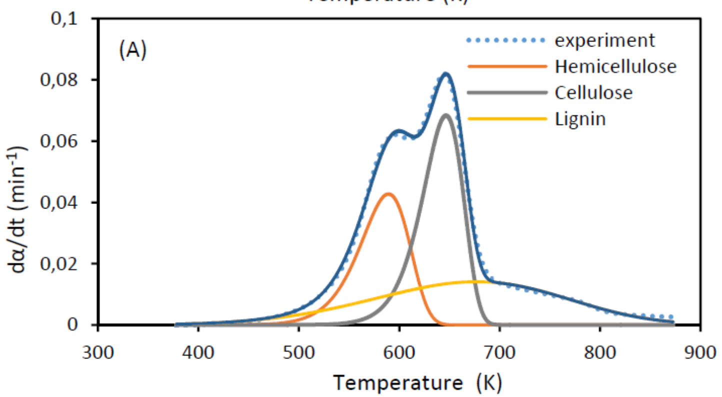
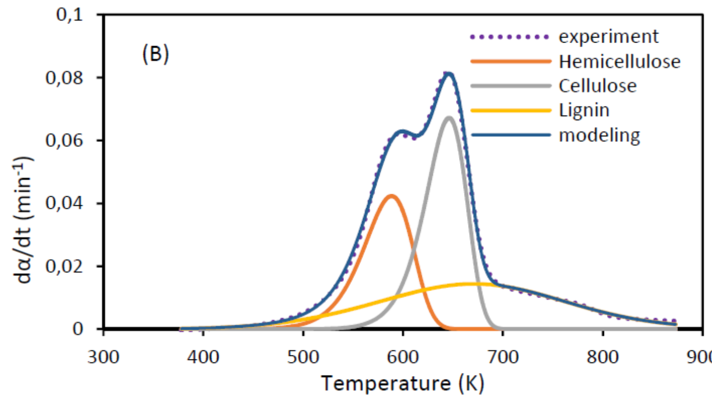
Kinetic analysis



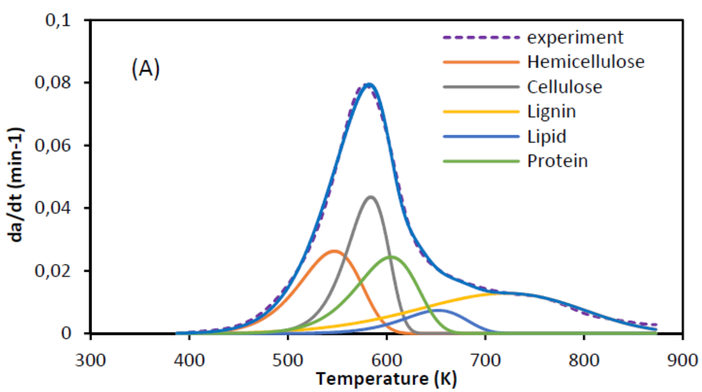


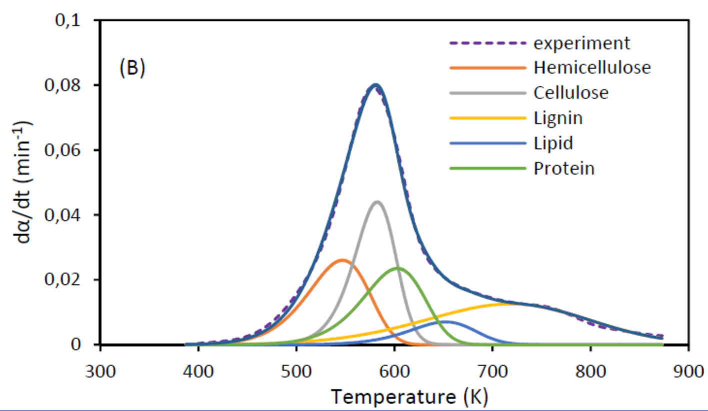
Cassava stalk,
(A) n=1; (B) n≠1





Rice straw,
(A) n=1; (B) n≠1





Napier grass,
(A) n=1; (B) n≠1

Extracted kinetic data

Sample		n=1					n≠1					
		A (min-1)	Eo (kJ/mol)	σ (kJ/mol)	c	Fit (%)	A (min-1)	Eo (kJ/mol)	σ (kJ/mol)	c	n	Fit (%)
Napier grass	H	7.52E+06	100.64	18.04	0.20	98.70	4.91E+06	98.04	17.58	0.20	1.02	98.93
	C	2.78E+11	171.05	30.66	0.24		2.79E+12	184.81	33.13	0.24	1.20	
	L	2.75E+02	61.10	10.95	0.26		4.47E+02	64.41	11.55	0.26	1.16	
	Ld	1.15E+08	147.14	22.34	0.11		1.57E+08	148.01	22.96	0.11	1.32	
	P	4.75E+07	123.08	22.06	0.19		5.94E+07	124.22	22.26	0.19	1.07	
Cassava stalk	H	9.00E+10	166.61	29.86	0.32	98.41	1.11E+11	167.85	30.09	0.33	1.05	99.00
	C	2.39E+11	187.02	32.57	0.44		5.66E+10	176.21	31.24	0.43	1.06	
	L	5.88E+00	31.60	5.68	0.24		7.98E+00	33.24	5.97	0.24	1.18	
Rice Straw	H	5.14E+09	149.21	26.32	0.29	98.85	7.33E+09	151.27	26.65	0.29	1.04	99.15
	C	1.53E+13	223.37	36.95	0.48		1.60E+13	223.53	36.98	0.48	1.04	
	L	4.16E+01	41.57	9.13	0.23		9.63E+01	46.08	10.24	0.23	1.20	

Concluding remarks

- The thermal pyrolysis of Napier grass, cassava stalk and rice straw was analyzed by means of a thermogravimetric analyzer, operated non-isothermally in nitrogen environment.
- The assumed DAEM model was found to be suitable to describe the experimental data.
- The extracted kinetic parameters from simulation and curve fitting were in good agreement with the reported values.
- The obtained kinetic data were not considerably different for both cases of $n=1$ and $n\neq1$.

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Thanks for listening!

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