Combustion kinetics of char product derived from torrefaction of Miscanthus pellets with different operational conditions

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Presented at:

10th International Conference on Sustainable Solid Waste Management

Chania, Greece, 21 - 24 June 2023

OUTLINE

Background

Torrefaction & Char Product Characterisation

- Combustion characteristic
- Thermodynamic analysis

Conclusion

Background

Biomass as renewable energy to replace fossil fuel

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- Has a secure and stable supply
- Produces clean energy due to low nitrogen content which result in low undesirable emission, such as NOx

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- Biomass has high moisture content and volatile contents which lead to a low thermal quality
- Causes excessive volatilization and tar formation
- Volatility of biomass is an indication of highly reactive materials that needs to be handled cautiously which is disadvantage for energy generation purposes

Miscanthus

An energy crop that easy and quick growth

Torrefaction

As thermal pre-treatment to improve biomass properties and make biomass product less reactive.

Lower volatile content that increases the ignition temperature.

Torrefaction Experiments

Feedstock & Reactor

Fig1. Miscanthus pellets

Fig2. Medium Scale Reactor 1.9 L stainless steel reactor, 61 cm in length and 7 cm diameter, use a heating tape as heat source.

Table 1. Characteristics of Miscanthus pellets

Feedstock	MC (%)	VM (%)	AC (%)	FC (%)	C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)
Miscanthus pellet	8.77	88.87	3.10	8.04	44.47	5.60	0.27	44.30	13.42

MC= moisture content, VM= volatile matter, AC=ash content, and FC=fixed carbon; all units are in %weight.

Operational Condition

Temperatures: 175, 200, 225°C
Pellets Lengths: 1, 1.5, 2cm

Char Product Characterisation

- **Proximate analysis** – Moisture Content, Volatile Matter, Ash Content, Fixed Carbon: **Gravimetric method**
- **Elemental analysis** – Carbon, Hydrogen, Nitrogen, Oxygen : **CHNS-O Analyzer**
- **Heating value: Oxygen bomb calorimeter**

Kinetic Analysis

Thermogravimetric analysis (TGA)

The samples were heated using conditioned atmospheric air from 25 to 750°C, at a heating rate of 10, 15, and 20°C per minute.

Kinetic modelling

The kinetics parameters – activation energy and pre-exponential factor, were calculated using model-free methods, the Kissinger-Akahira-Sonuse (KAS) and Flynn wall ozawa (FWO) methods.

The isoconversional model free approach has a general equation shown below.

$$\frac{d\alpha}{dt} = \boxed{k(T)} . f(\alpha)$$

Arrhenius law

$$k(T) = Aexp\left(-\frac{E_\alpha}{RT}\right)$$

$$\boxed{G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T exp\left(-\frac{E_\alpha}{RT}\right)dt}$$

Kissinger-Akahira-Sonuse (KAS)

$$ln\beta = \ln\left(\frac{\mathrm{AE_a}}{g(\alpha)R}\right) - 5.331 - 1.052\frac{\mathrm{E_a}}{\mathrm{RT}}$$

Flynn wall ozawa (FWO)

$$\ln\frac{\beta}{T^2} = \ln\left(\frac{\mathrm{AE_a}}{\mathrm{RG(\alpha)}}\right) - \frac{\mathrm{E_a}}{\mathrm{RT}}$$

Char Characteristics

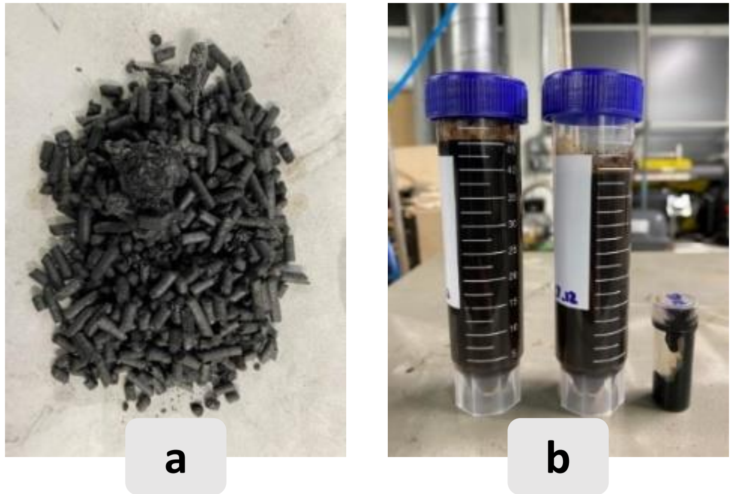

Fig3. (a) Char and (b) Aqueous Product after Torrefaction at 225°C

Table 2. Characteristics of char product

Samples	T (°C)	L (cm)	MC (%)	VM (%)	AC (%)	FC (%)	C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)
Raw	-	-	8.77	88.87	3.10	8.04	44.47	5.60	0.27	44.30	13.42
Char product	175	1.5	0.66	63.12	15.74	21.13	64.89	4.94	0.54	29.64	20.71
	200	1.5	0.76	77.52	0.75	21.73	69.44	4.20	0.62	25.75	23.86
	225	1.5	1.63	55.13	18.07	26.80	76.13	4.04	0.53	19.30	24.61
	225	1	1.88	58.73	14.97	26.29	72.78	3.69	0.53	23.01	23.12
	225	2	3.83	47.87	25.90	26.24	74.21	3.56	0.59	21.64	20.88
Coal (Rago, 2018)											
Coal	-	-	2.6	32.54	24.6	40.26	68.71	4.63	2.81	24.02	26.25

T = temperature, L = pellets length, MC= moisture content, VM= volatile matter, AC=ash content, and FC=fixed carbon

Combustion Characteristics

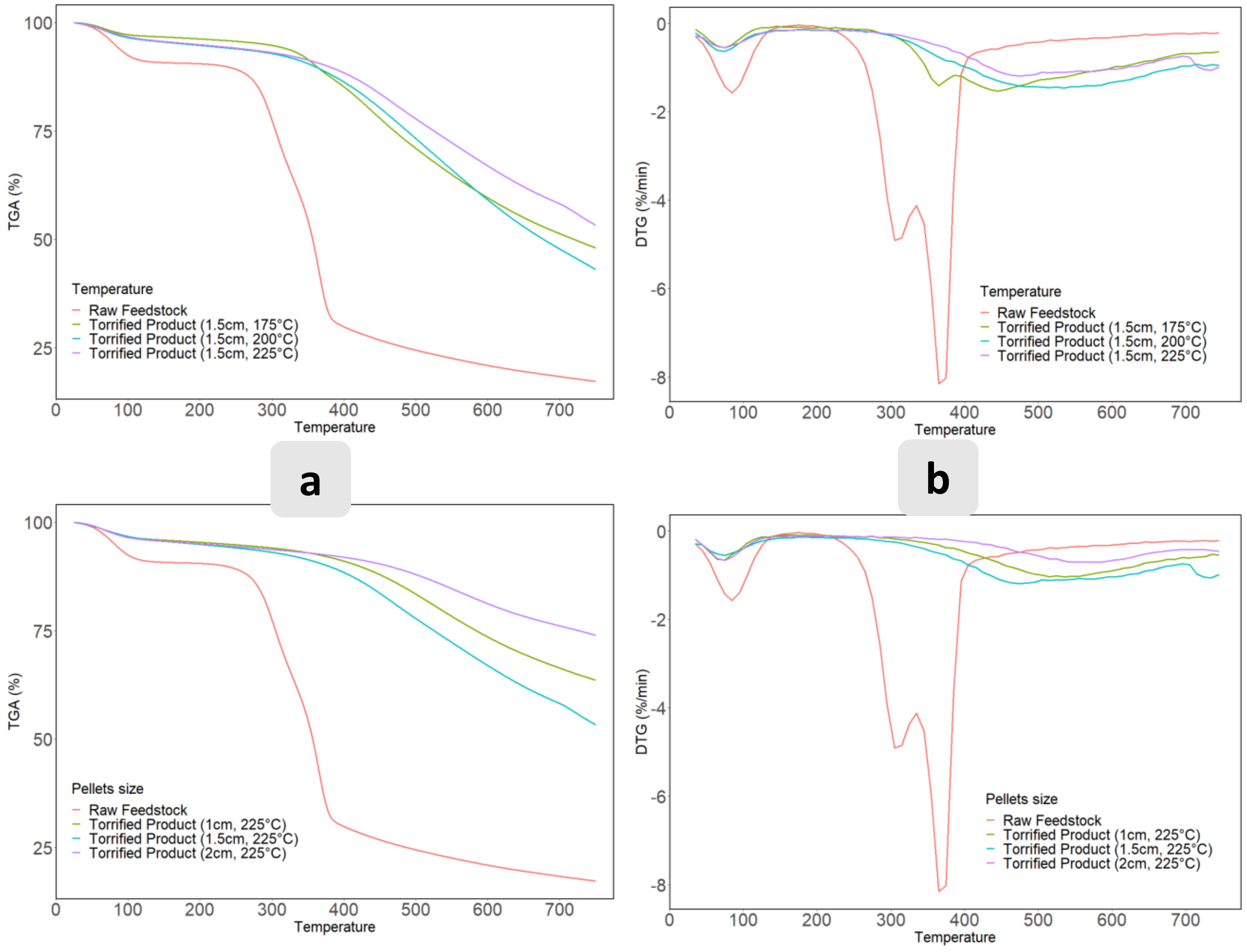

Fig4. (a) TGA graphs and (b) DTG graphs of raw miscanthus pellets and torrified miscanthus pellets

Table 3. Combustion characteristics of raw Miscanthus pellets and char products

Samples	T (°C)	L (cm)	T_v (°C)	T_i (°C)	T_p (°C)	T_b (°C)
Raw	-	-	175	299.47	365	398.33
Char product	175	1.5	150	342.33	450	563.5
	200	1.5	178.33	366.53	508.33	599.33
	225	1.5	178.33	376.95	505	560
	225	1	171.67	392.25	548.33	617.33
	225	2	188.33	398.96	575	635
Coal (Ro, 2018)	-	-	-	373	515	623

T = temperature, L = pellets length, T_v = devolatilization temperature, Ti = ignition temperature, T_p = peak temperature, T_b = burnout temperature

Kinetic Analysis

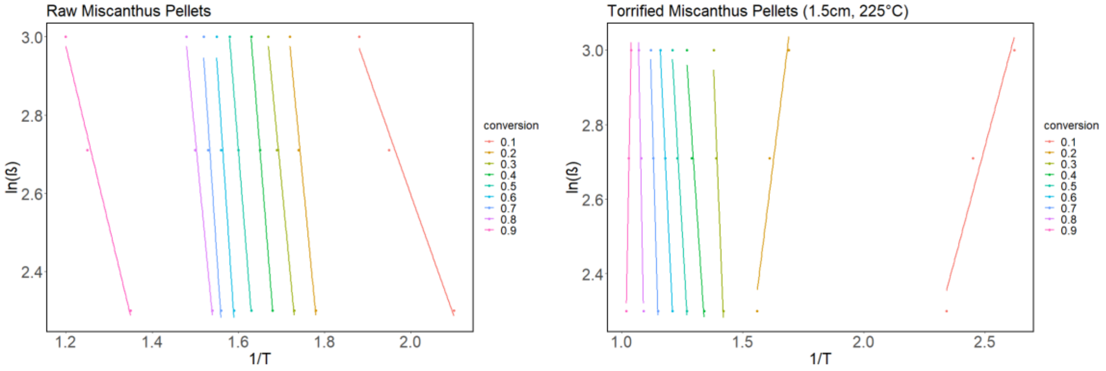

Fig5. Linear plot of KAS for (a) raw Miscanthus pellets and (b) char product derived from torrefaction at temperature of 225°C and pellet length of 1.5cm

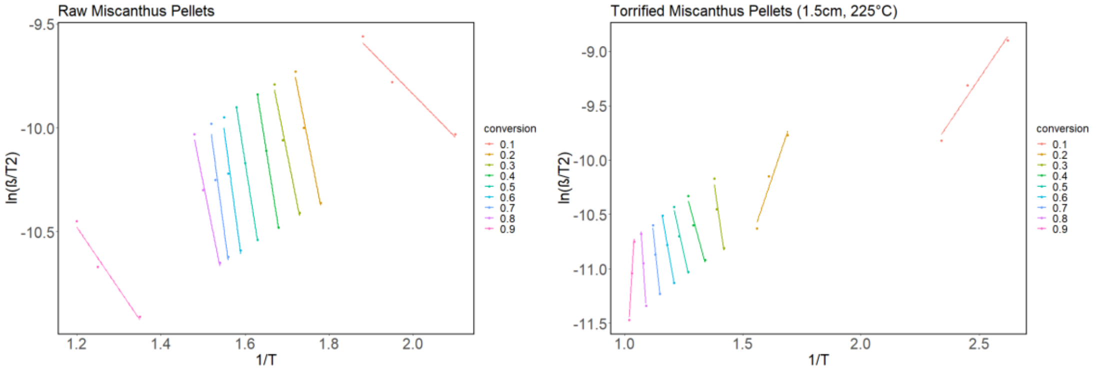

Fig6. Linear plot of FWO for (a) raw Miscanthus pellets and (b) char product derived from torrefaction at temperature of 225°C and pellet length of 1.5cm

Table 4a. Kinetic parameter of raw Miscanthus pellets and char products

Samples	T (°C)	L (cm)	α	KAS Ea (kJ/mol)	A	R^2	FWO Ea (kJ/mol)	A	R^2
Raw	-	-	0.1	17.14	1.71E+01	0.97	-24.58	2.41E+02	0.99
			0.2	85.52	6.06E+01	0.99	-90.60	1.47E+08	0.99
			0.3	84.03	4.12E+01	0.99	-90.60	1.32E+08	0.99
			0.4	106.11	2.29E+03	1.00	-110.44	6.00E+09	1.00
			0.5	106.11	1.55E+03	1.00	-110.44	4.05E+09	1.00
			0.6	125.99	4.36E+04	0.96	-131.31	1.69E+11	0.97
			0.7	125.99	3.53E+04	0.96	-131.31	1.35E+11	0.97
			0.8	84.03	2.14E+01	0.99	-90.60	6.77E+07	0.99
			0.9	24.70	7.79E+02	0.97	-36.24	2.54E+03	0.99
Average				84.403	9.29E+03		90.68	3.49E+10	
Char product	225	1.5	0.1	-26.70	1.04E+06	0.97	19.22	1.28E+00	0.95
			0.2	-53.56	3.12E+07	0.96	41.26	1.47E+01	0.95
			0.3	125.35	9.32E+02	0.96	-131.31	3.90E+09	0.97
			0.4	66.83	7.51E-02	0.96	-76.29	2.27E+05	0.98
			0.5	81.06	2.71E-01	0.98	-90.60	1.32E+06	0.99
			0.6	102.61	3.31E+00	1.00	-110.44	1.51E+07	1.00
			0.7	171.03	1.44E+04	0.99	-181.21	1.54E+11	0.99
			0.8	274.36	2.47E+09	0.99	-276.61	1.82E+16	0.99
			0.9	-299.30	5.30E+19	0.99	276.61	2.17E+13	0.99
Average				133.423	5.89E+18		133.73	2.03E+15	

Kinetic Analysis

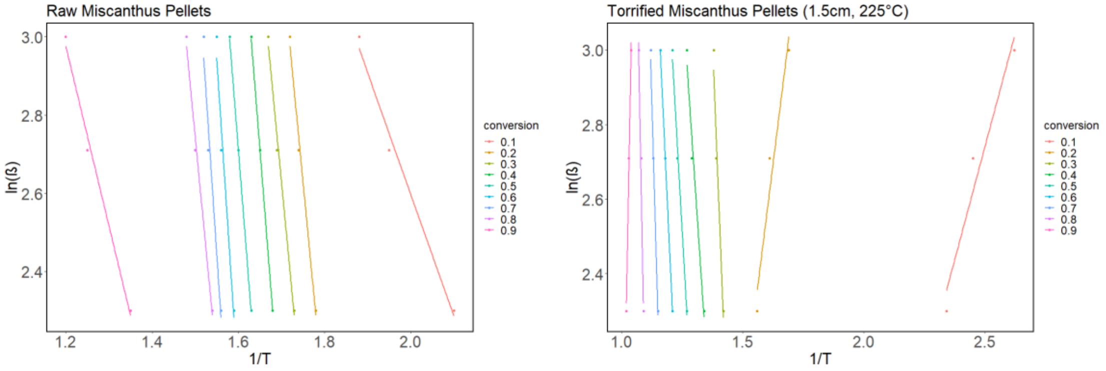

Fig5. Linear plot of KAS for (a) raw Miscanthus pellets and (b) char product derived from torrefaction at temperature of 225°C and pellet length of 1.5cm

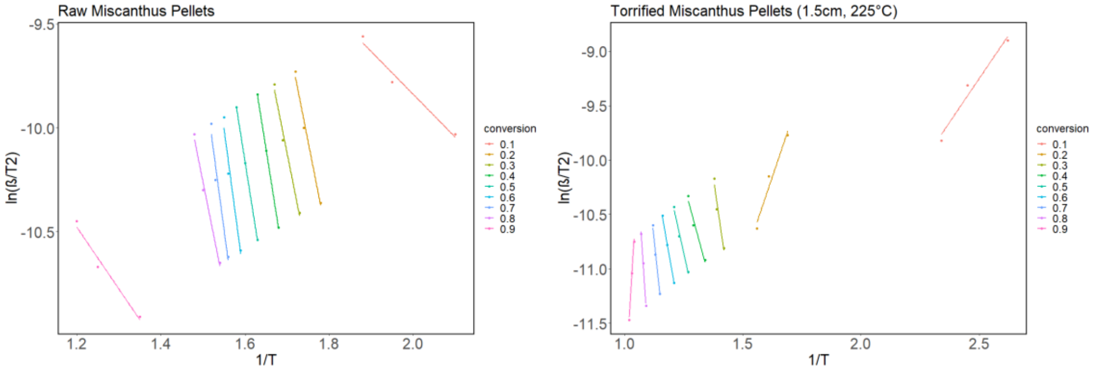

Fig6. Linear plot of FWO for (a) raw Miscanthus pellets and (b) char product derived from torrefaction at temperature of 225°C and pellet length of 1.5cm

Table 4b. Kinetic parameter of raw Miscanthus pellets and char products

Samples	T (°C)	L (cm)	KAS		FWO	
			Ea (kJ/mol)	A	Ea (kJ/mol)	A
Raw	-	-	84.403	9.29E+03	90.68	3.49E+10
Char product	175	1.5	118.853	1.30E+09	123.93	1.37E+16
	200	1.5	200.051	1.93E+19	188.01	7.56E+19
	225	1.5	133.423	5.89E+18	133.73	2.03E+15
	225	1	183.530	7.14E+12	185.37	4.66E+19
	225	2	159.011	8.70E+08	166.23	1.6E+16

Thermodynamic analysis

Thermodynamic analysis can provide information regarding the equilibrium conditions for char product derived from the torrefaction process. The thermodynamic parameters, change in Gibbs free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS).

$$\Delta H = \mathrm{E_a} - RT$$

$$\Delta G = \mathrm{E_a} + R \cdot \mathrm{T}_m . \ln\left(\frac{\mathrm{K}_B \cdot \mathrm{T}_m}{\mathrm{h} \cdot \mathrm{A}}\right)$$

$$\Delta S = \frac{\Delta H - \Delta G}{\mathrm{T}_m}$$

Table 5. Thermodynamic properties of raw Miscanthus pellets and char products

Samples	T (°C)	L (cm)	KAS			FWO		
			ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/mol.K)
Raw	-	-	79.10	211.35	-207.25	85.37	153.75	-107.15
Char product	175	1.5	112.84	255.33	-197.04	117.92	193.18	-104.08
	200	1.5	193.55	200.32	-8.65	181.51	218.08	-46.79
	225	1.5	126.95	249.79	-157.85	127.26	214.14	-111.66
	225	1	176.70	281.00	-126.96	178.54	200.30	-26.49
	225	2	151.96	294.48	-168.04	159.18	203.85	-52.67

Conclusion

- Torrified products have better combustion characteristics than raw Miscanthus in terms of its low reactivity and volatility.
- The char derived from torrefaction at 225°C has a higher ignition temperature than coal, as the char started to burn around temperatures of 376 – 398°C.
- The lower reactivity of the char products was also confirmed by a higher overall activation energy as a less reactive product required more energy to start the reaction.
- Regarding pellets sizes, char product from 1cm length pellets have a higher activation energy at 183.53 kJ/mol, compared to char products from 1.5 and 2cm length pellets with lower values at 133.42 kJ/mol and 159.01 kJ/mol.
- The torrefied products have positive values of ΔG and ΔH, as well as negative value of ΔS, as an indication of a non-spontaneous process and lower thermal decomposition reactivity. Therefore, an external energy source is required to provide extra heat to generate the activated complex.
- Less reactive products demonstrated better fuel properties that result in better thermal efficiency and release less pollutants when used as biofuel.

THANK YOU!