Date waste management via pyrolysis: The effect of particle size on thermokinetics and thermodynamics

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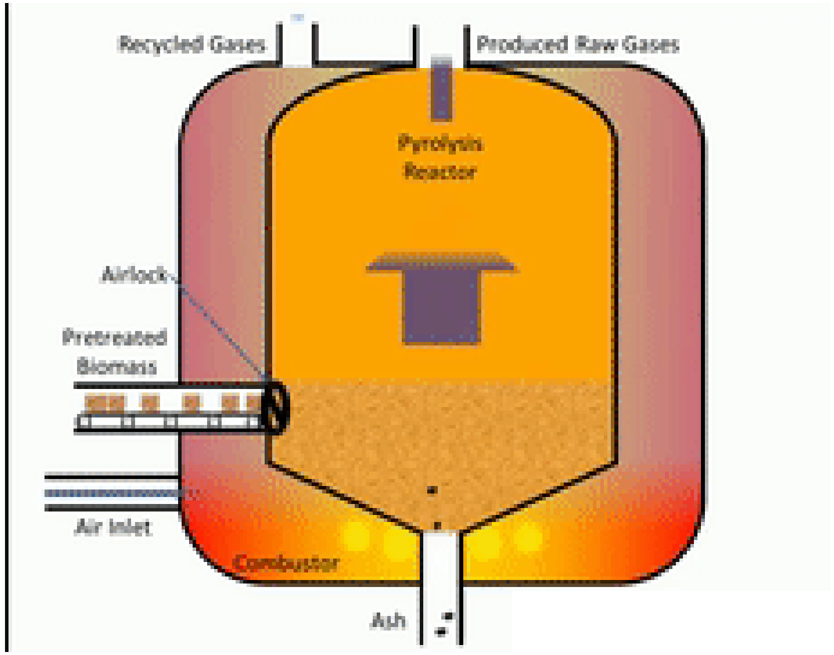
Presentation Outline

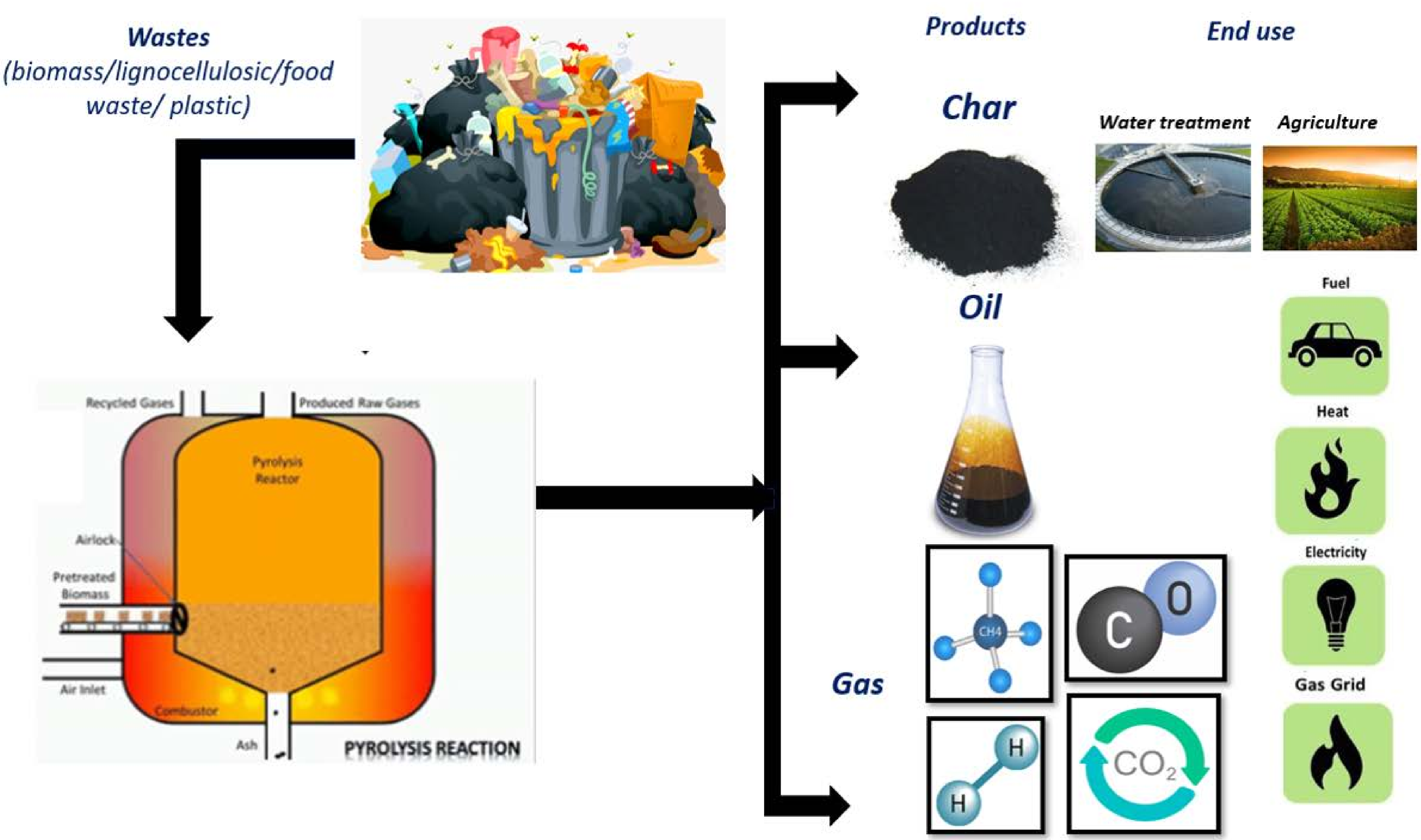
- Introduction
- Experimental Work
- Results & Discussion
- Conclusion
- References

Introduction

Thermochemical processes for waste management

- Biomass/wastes→ value added products via biochemical & thermochemical conversion
- Pyrolysis -> partial or complete absence of oxygen -> 300 - 800ºC → reduces waste emission & carbon footprint
- Pyrolysis preferred over biochemical conversions → feedstock flexibility, fuel production variety, & fast reaction times
- Pyrolysis products: Oil, char & gas depending on feedstock type, heating rate, temperature, solid residence times, & particle size





Wastes
(biomass/lignocellulosic/food waste/ plastic)
Recycled Gases
Produced Raw Gases
Pyrolysis Reactor
Airlock
Pretreated Biomass
Air Inlet
Combustor
Ash
PYROLYSIS REACTION
Products
End use
Char
Water treatment
Agriculture
Oil
Fuel
Heat
Electricity
Gas Grid
Gas
CH4
C
O
H
H
CO2

Relevance to Qatar

- Qatar → average of 1.37 kg/capita/ day of MSW → 50% go to landfills, incineration and some recycling
- Ministry of Environment and Climate Change → extend its portfolio to manage waste disposal
- Qatar → co-pyrolysis of waste feedstocks to produce value added products → enhance technoeconomic feasibility

Wastes from the Date Fruit

Date palms are among the few fruits bearing trees in arid countries.

- Rich in Fe, K, Ca, Mg
- Good source of fiber
- Rich in calories
- Good alternative to refined sugar

- 120 million date palm trees globally
- 10% of the date fruit comprises date stones (DS) often thrown away.

Research Objective

- What? To understand the effect of DS particle sizes on kinetics and thermodynamics using TGA*
- Why? Particle size → impact the various process kinetics and thermodynamic parameters → pyrolysis design
- How? Coats Redfern models → reaction mechanism during thermal degradation

*Thermogravimetric analysis

Methodology

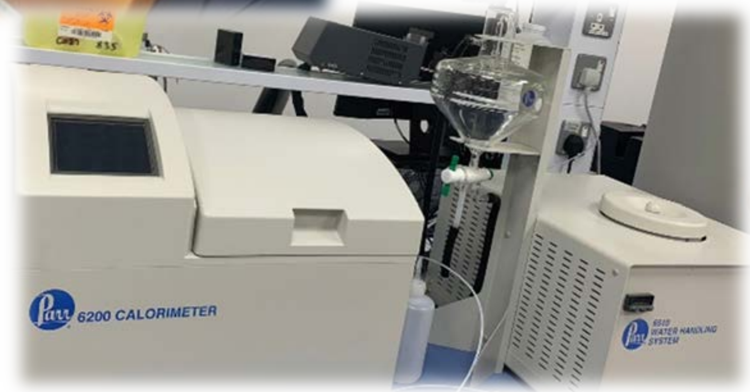
Feedstock procurement and characterisation

Dates are commercially purchased, date stones extracted, washed and grinded.

Proximate analysis - ASTM D7582-12 –moisture, volatiles, fixed carbon, and ash

Ultimate analysis - CHNS elemental analyzer → ASTM D 3176 – 8 – wt.% of carbon, hydrogen, nitrogen, oxygen, sulfur, chlorine, and ash

Calorific value - Automated Isoperibol Fixed Bomb Parr 6300 bomb calorimeter in an atmosphere of O_2



- → TGA-SDT 650
- → room to 1173.15 K
- → heating rate of 10K/min
- → inert nitrogen gas flow rate of 100 ml/min

S5- Mixed 1:1:1:1

1mm-710 μm | *710-500 μm* | *500-355 μm* | *355-125 μm*

Reaction model	$g(\propto)$
First order (F1)	-ln(1-α)
Second order (F2)	$(1-\alpha)^{-1}$ -1
Third order (F3)	[$(1-\alpha)^{-1}$ -1)]/2
One dimensional (D1)	α^2
Two dimensional (D2)	(1-α) ln(1-α) + α
Three dimensional (D3)	$1-(1-\alpha)^{1/32}$
Ginstling-Brounshtein (D4)	$[1-(2/3)\alpha] -(1-\alpha)^{2/3}$
Two-dimensional nucleation (A2)	$-\ln (1-\alpha)^{1/2}$
Three-dimensional nucleation(A3)	$-\ln (1-\alpha)^{1/3}$
Four-dimensional nucleation (A4)	$-\ln (1-\alpha)^{1/4}$
Prout-Tompkins (R1)	α
Contracting Cylinder (R2)	$1-(1-\alpha^{1/2})$
Contracting sphere (R3)	$\ln(1-(1-\alpha^{1/2})$

Power Law (P2)	$\alpha^{1/2}$
Power Law (P3)	$\alpha^{1/3}$
Power Law (P4)	$\alpha^{1/4}$
Power Law (P2/3)	$\alpha^{3/2}$

- **Linear regression formula → Activation energy (E) from slope and pre-exponential factor (A) from intercept**

- $\propto = \frac{W_0 - W_t}{W_0 - W_f}$
- W_0 weight before decomposition (kg)
- W_t is the weight at time t (kg)
- W_f is the final weight after decomposition (kg)
- R=8.314 J/mol, β is the heating rate

Thermodynamic properties

The best fitting kinetic model A and E were used to calculate change in Gibbs free energy (ΔG), enthalpy (ΔH), and in entropy (ΔS)

$$\Delta G = E + RT_m \ln(\frac{k_b T_m}{hA})$$

$$\Delta H = E - RT_m$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m}$$

T_m = Peak decomposition temperature (K)
k_b = Boltzmann constant (1.38 x 10^{-23} J/K)
R= Gas constant (8.314 J/mol K),
h = Planck constant (6.63 x 10^{-34} Js)

A (from Kissinger's equation) $= \frac{\beta E exp(\frac{E}{RT_m})}{RT_m{}^2}$

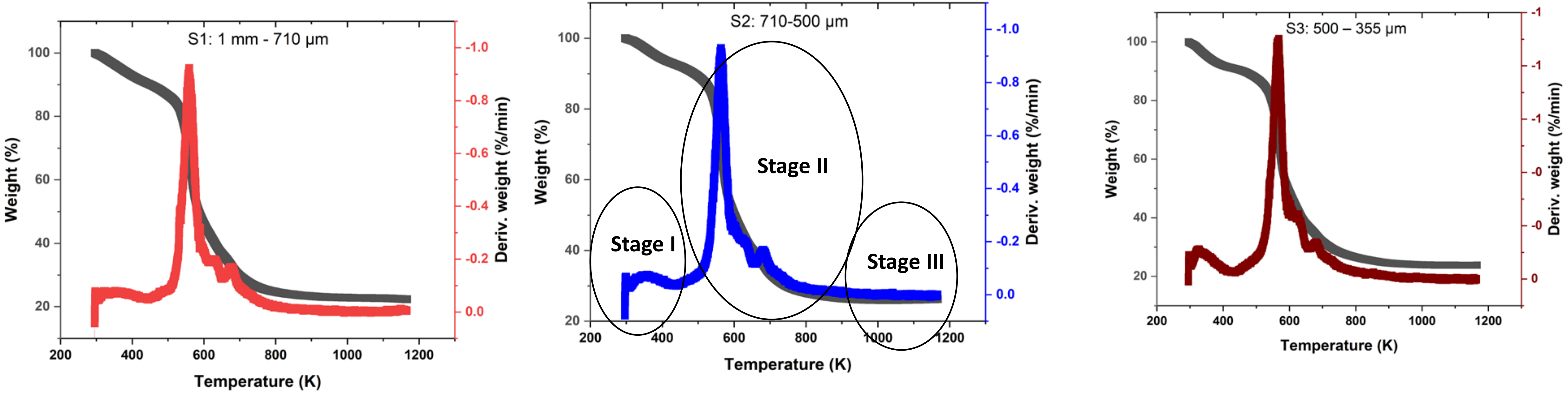
Results

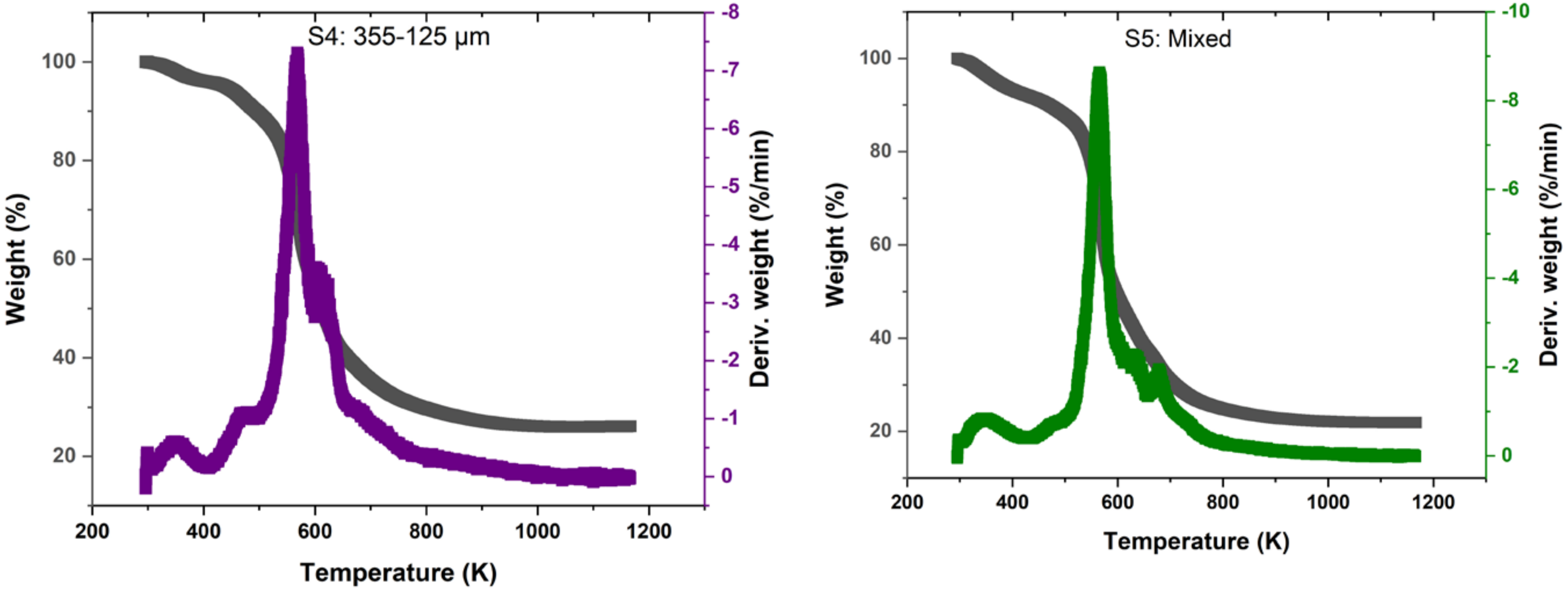
Proximate analysis (% w/w) *	
Moisture	2.63
Volatiles	63.36
Ash	12.69
Fixed carbon**	21.32
Ultimate analysis (% w/w) *	
Carbon	45.95
Hydrogen	6.20
Oxygen**	30.88
Nitrogen	4.27
Calorific value (MJ/kg)	18.25

*air-dried basis

**by difference

Characterization



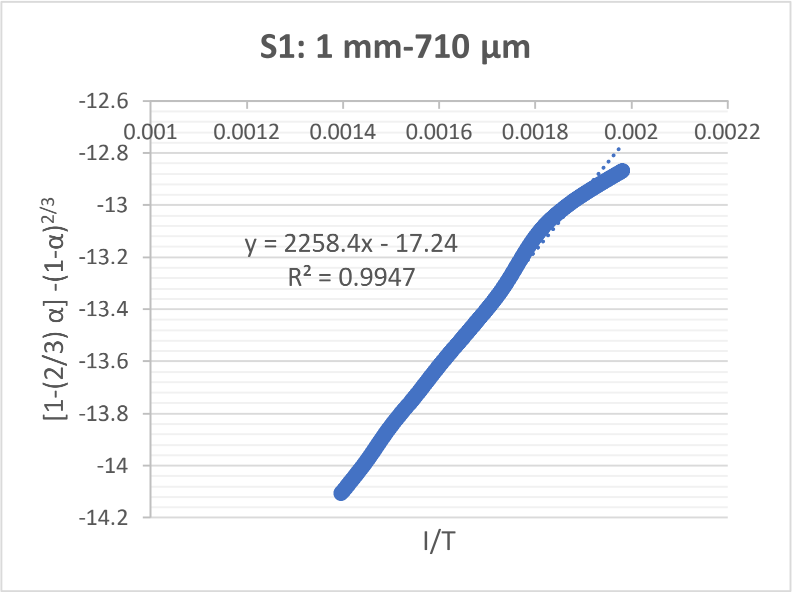


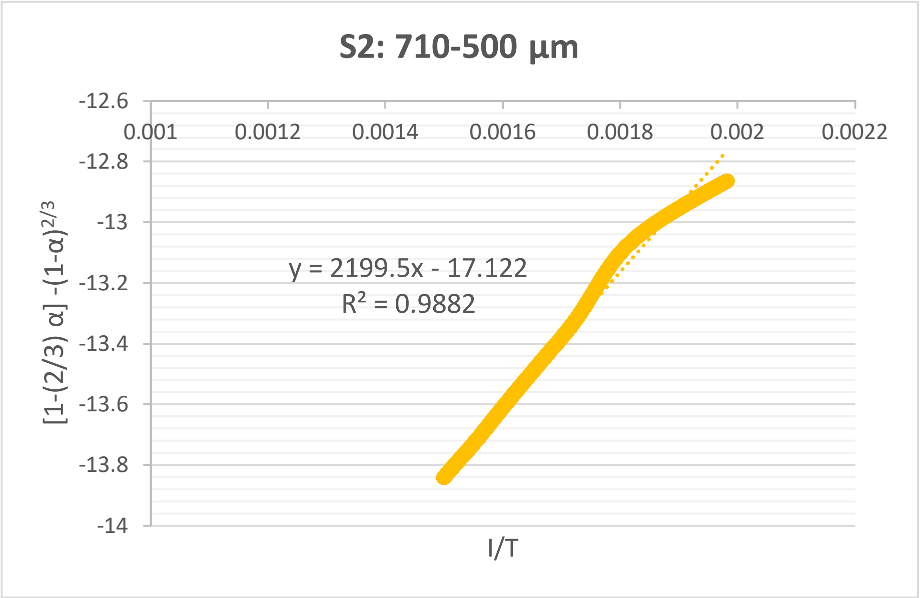
TGA & DTG curves

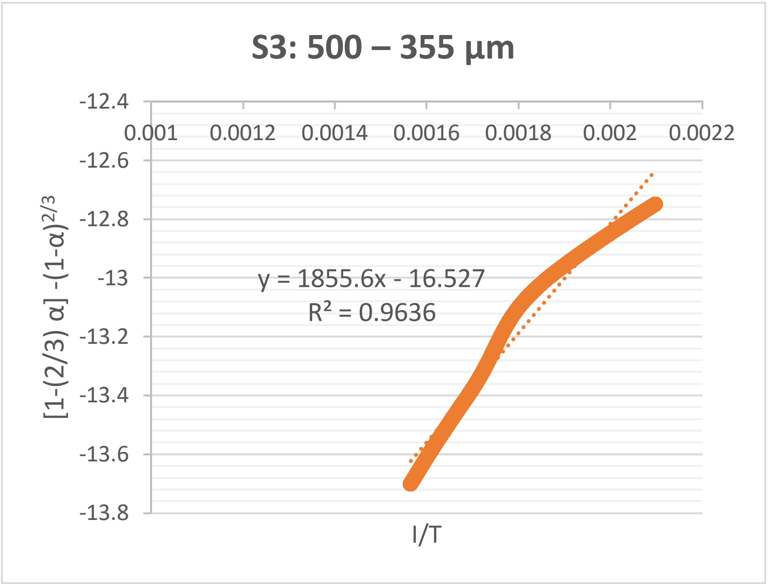
Thermal degradation behavior

	Stage I		Stage II		Stage III		Residual Char (%)	Total Weight Loss (%)
	Temp range (K)	Weight loss (%)	Temp range (K)	Weight loss (%)	Temp range (K)	Weight loss (%)		
S1	Room-504.5	13.72	504.5-715.9	57.90	715.91-1173.15	6.04	22.33	77.66
S2	Room-497.05	10.51	497.05-724.87	58.43	724.87-1173.15	4.83	26.22	73.77
S3	Room-476.4	10.76	476.4-727.48	59.55	727.48-1173.15	5.87	23.81	76.18
S4	Room-406.86	3.994	406.86-871.6	68.30	871.6-1173.15	1.59	26.11	73.89
S5	Room-427.28	7.934	427.28-788.08	66.85	788.08-1173.15	3.31	21.89	78.10

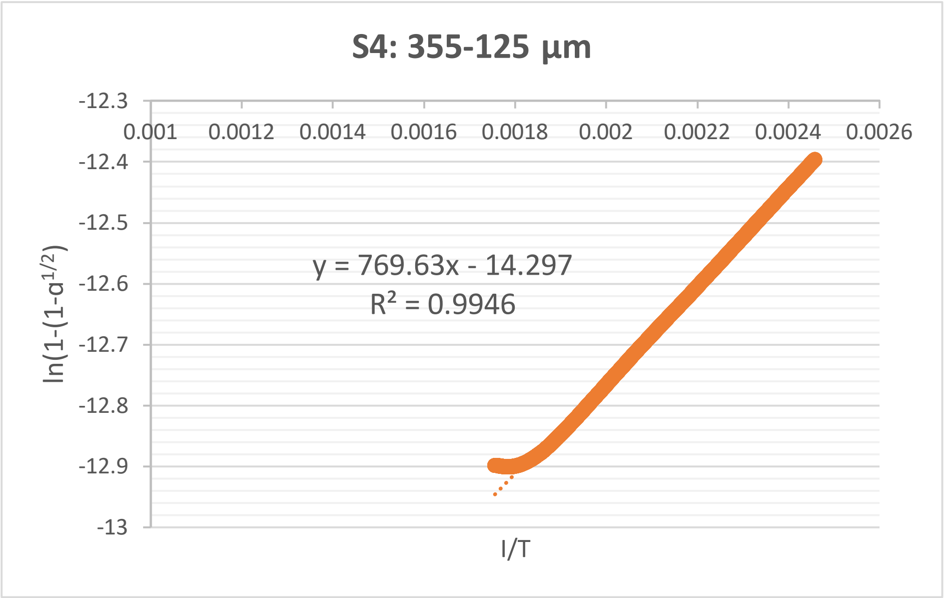
Degradation occurs over a wider temperature range, but with maximum weight loss when size is smaller and in Stage II!

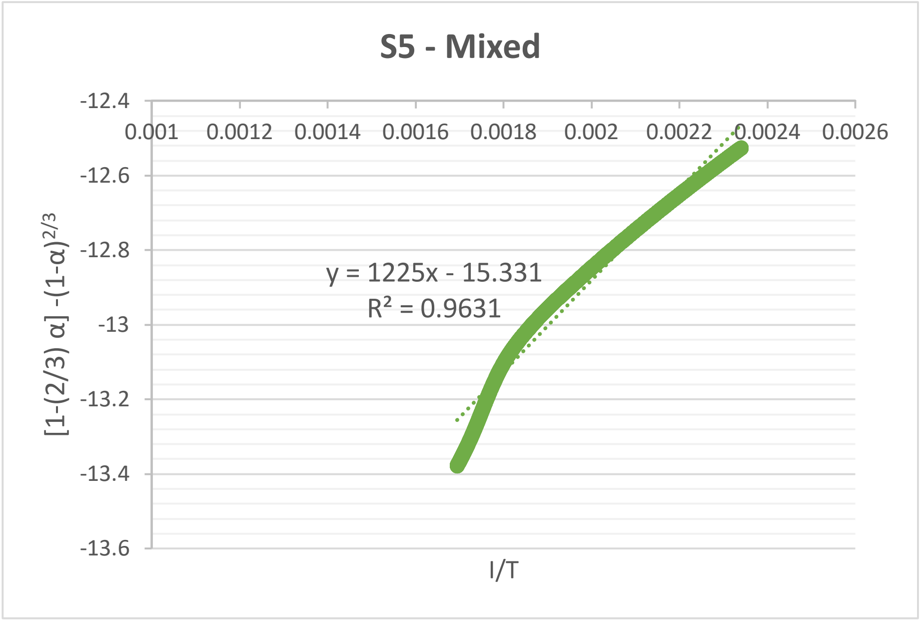






Best fit
kinetic models
R^2 > 0.9630 for Stage II





Results

Sample	CR model	E (kJ/mol)	A (s^{-1})	ΔH kJ/mol	ΔG (kJ/mol)	ΔS (kJ/mol K)
S1	D4	18.78	1.16E+10	14.09	51.23	-0.0658
S2	D4	18.29	1.00E+10	14.00	51.61	-0.0671
S3	D4	15.43	4.65E+09	10.70	52.43	-0.0735
S4	R3	6.40	2.08E+08	1.67	58.13	-0.0993
S5	D4	10.18	9.29E+08	5.48	54.59	-0.0869

Comparison

	Particle size	Ea (kJ/mol)	A (s^{-1})	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol K)
Date stones	1 mm - 125 µm	93.42-4.80	1.73×10^{3} – 1.16×10^{10}	-0.90 – 49.25	51.23 - 183.94	-0.065-0.196
Date palm surface fibres	N. R	166.91-0.598	3.18×10^{-6} – 2.2×10^{11}	-4.05 – 162.25	53.29 - 367.98	-0.14 – - 0.47
Date stones	N. R	671.26-12.75	6.69×10^{-3} – 2.03×10^{34}	7.94 – 113.51	166.48 – 195.40	-0.092 - 0.3 -
Date palm leaflets	<2mm	226.28 – 1.94	2.4916×10^{-5} – 4.4×10^{11}	N. S	N. S	N. S

N.S: not studied

Our study found values in the range of published date-based studies.

Conclusion

- Results show particle size of date stones affects the degradation, kinetic and thermodynamic properties during pyrolysis.
- The onset degradation temperature, activation energy, enthalpy change, and entropy decreases with lowering particle sizes.
- The mixed and lower particle-sized date stones are preferred due to the lower activation energies.

Current and future studies

- Kinetics and thermodynamics effect in lab scale tube furnace studies for products generation of different biomass
- ASPEN Plus process flow, technoeconomic studies
- Co-pyrolysis with plastics, and major chunks of MSW
- Pyrolysis studies of existing landfill wastes
- Pilot scale studies

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thanks for listening!