EFFECT OF GREEK LIGNITE PYROLYSIS PROTOCOLS ON THE PHYSICOHEMICAL PROPERTIES AND GASIFICATION REACTIVITY OF AS-PRODUCED CHARS

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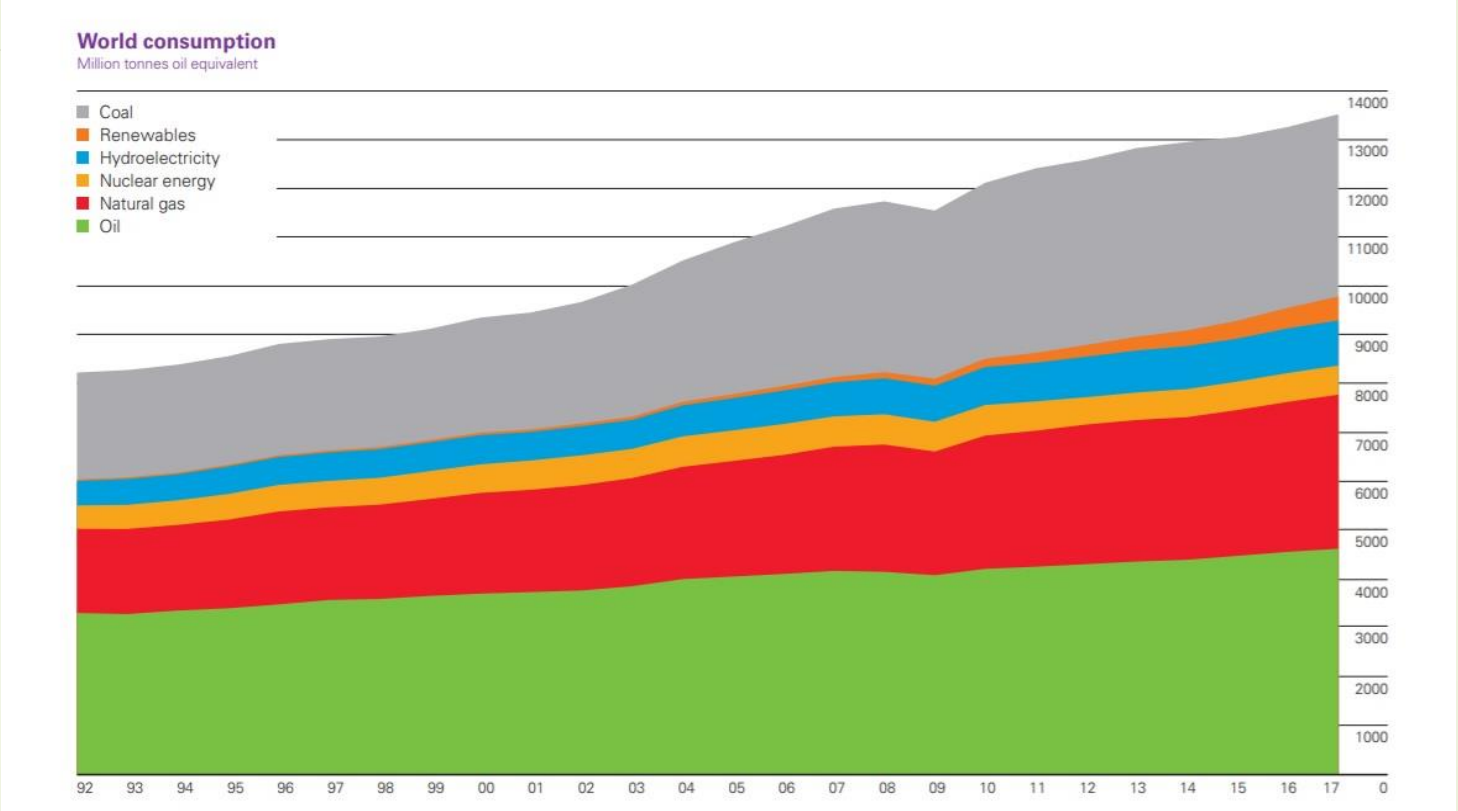
- H_2O Gasification exps

CONCLUSIONS

The Role of Carbon in Today's Energy Mix



- Coal is an abundant and cheap fossil fuel with a share of ca. 30% of world energy consumption.
- Lignite coal of low calorific values accounts for ca. 45% of the world's coal recoverable reserves (5 btn in Greece)

Conventional vs Alternative Coal Energy Conversion

- The use of Lignite coal as fuel in conventional Rankine cycle power plants is associated to various issues related to low thermal efficiency and high CO_2 emissions per produced MWh
- Pyrolysis and gasification of low rank coals are of major importance toward a smooth transition to a more efficient and cost-competitive energy future.
- Pyrolysis produces chars with better fuel characteristics compared to the pristine fuel
- Coal gasification typically occurs at 700 – 1200 °C leading to a gas mixture of H_2, CO, CO_2, CH_4 and traces of light hydrocarbons with its composition to be strongly dependent on the employed conditions (e.g. temperature, gasification agent, residence time, etc).

Aim

- To examine the effect of Lignite (LG) pyrolysis conditions on the physicochemical characteristics and gasification reactivity of as produced chars.

- To explore efficient ways to exploit Greek Lignite reserves as a short-to-medium term alternative for the transition toward a low-carbon economy.

Chars Production

- Pristine Fuel: Lignite from the Greek Western Macedonia basin (LG).

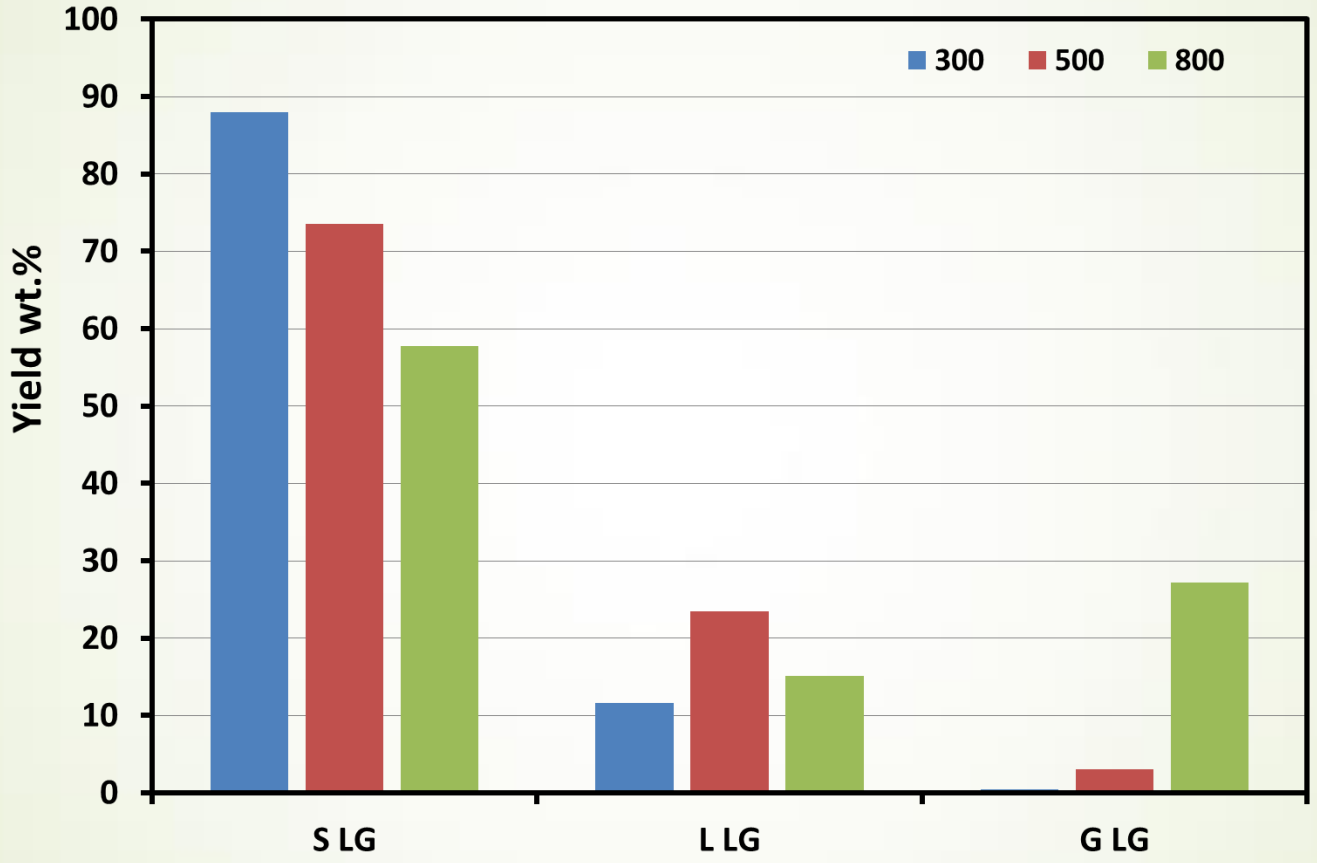
LG → Crash to particle size between 1-3 mm → Stainless steel tube (Inconel® ID = 8.5 cm & L=68 cm)- High temperature electrical furnace(Carbolite GVA 12/300)

- 300 °C torrefaction → LG300
- 500 °C mild carbonization → LG500
- 800 °C carbonization → LG800

- The thermal treatment occurred under a pure N_2 (250 cm^3/min) flow with a heating rate of 20 °C/min until the selected temperature, remained then for 1 h and cooled down naturelly.

- Prior to characterizations, all samples were dried and milled to 100 – 200 μm using an agate mortar.

Chars yield



- As temperature increases the yield for solids decreases
- Gas yield are increasing with temperature treatment
- The liquids are maximized at intermediate temperatures according to literature

Fuel Characterization Methods

LG
LG300
LG500
LG800

Chemical Composition	Proximate & Ultimate Analysis, XRF, EDS
Surface Area	BET
Thermal Behavior	TGA
Moephology	SEM
IR Spectroscopy	FT-IR, Raman

Proximate & Ultimate Analysis – BET

	Ultimate analysis (wt.%)					Proximate analysis (wt.%)					Heating Value (Kcal/kg)*	
	C	H	N	O	S	Moisture	Ash*	Volatile Matter*	CO_2*	Fixed Carbon*	HHV	LHV
LG	34.88	2.97	0.94	-	1.07	48.11	41.01	39.81	7.46	19.18	3054.0	2895.0
LG300	34.28	3,04	1.03	18.20	1.32	2.32	42.13	41.28	7.54	16.59	3133.9	2971.0
LG500	33.72	1,05	1.00	14.22	1.12	2.35	48.90	30.70	9.23	20.40	2894.0	2837.8
LG800	32.16	0.70	0.79	3.25	1.17	1.38	61.93	13.13	7.64	24.94	2869.0	2831.4

* dry base

Increase in Thermal Treatment

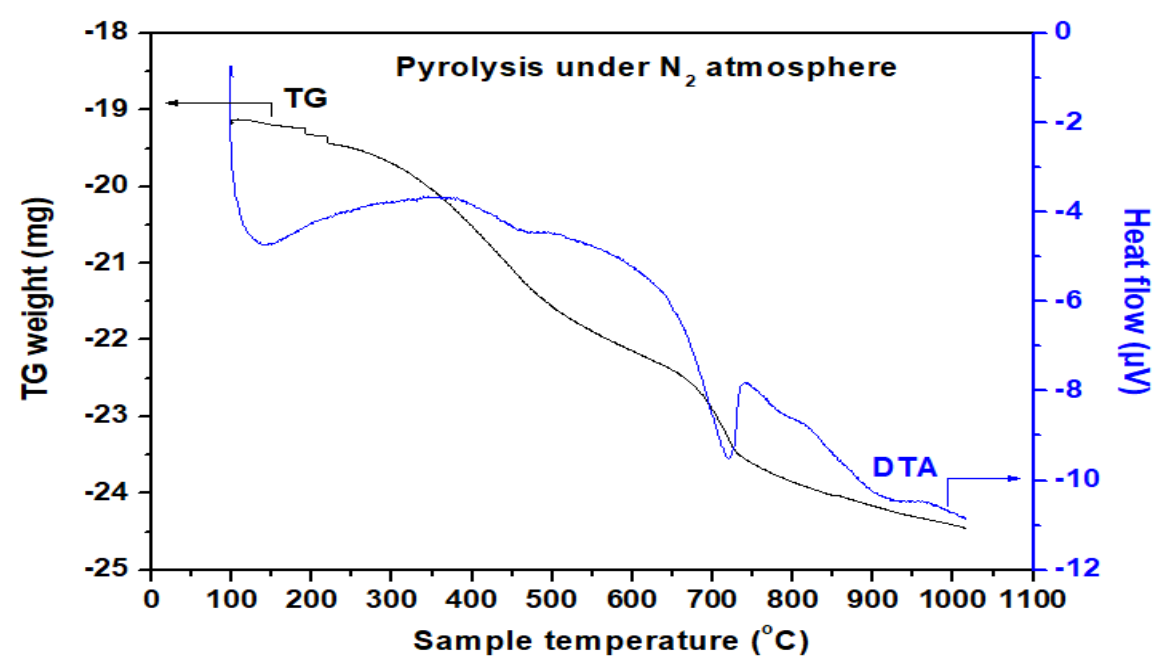
Decrease
VM, O, H_2O

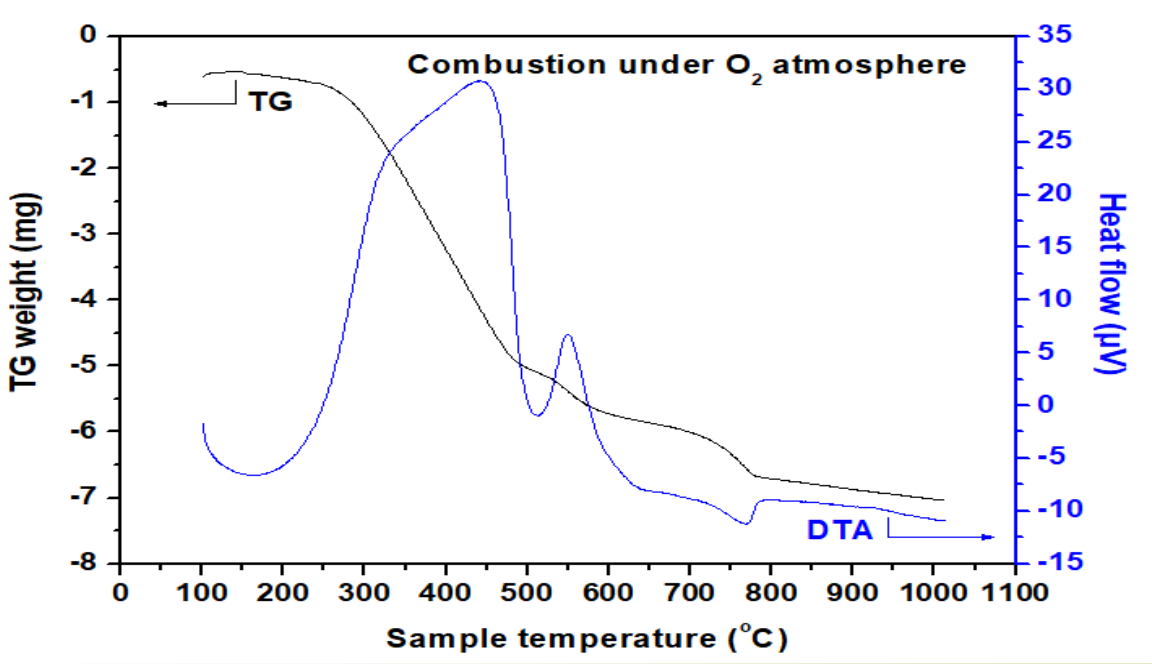
Increase
Fixed Carbon, Ash

Sample	LG	LG300	LG500	LG800
S_{BET} (m^2/g)	7.174	4.487	19.468	190.626

BET surface area increases with pyrolysis temperature

TGA Analysis



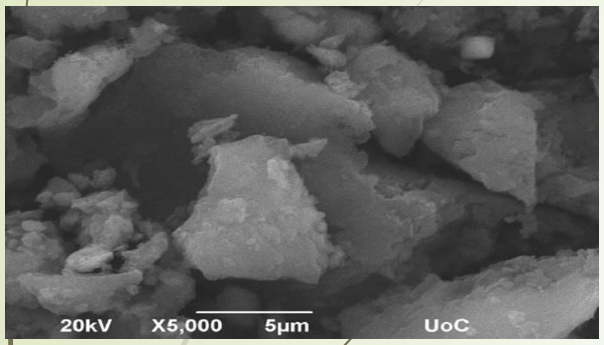


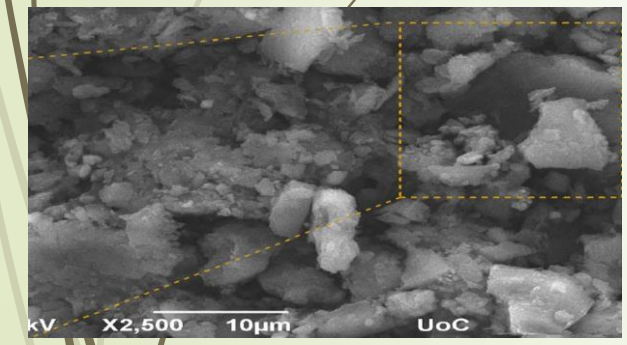
- Mass losses in the 300 – 700 °C range attributed mainly to release of loosely bound volatiles.
- A milder weight loss at > 700 °C are assigned to possible rearrangements of the carbonaceous matter.

- A sharp weight loss is observed with a broad exothermal peak at 440 °C attributed to the i) decomposition of phenol groups, ii) C=C cleavage and iii) the partial transition of carbonaceous matter into plastic state

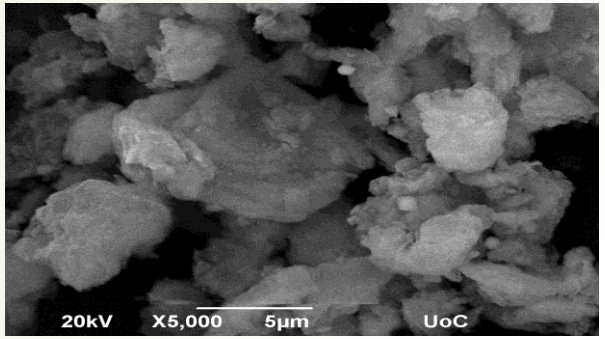
SEM Analysis

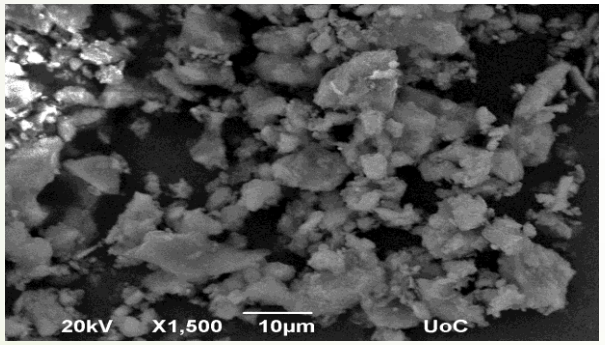
LG



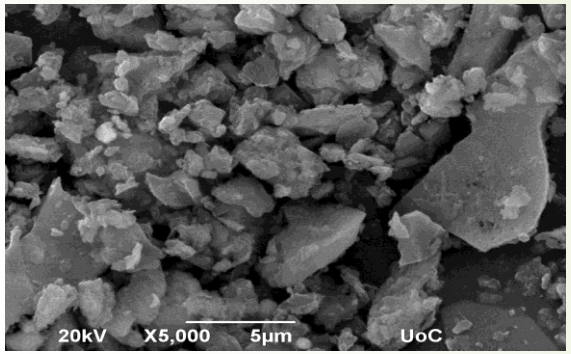


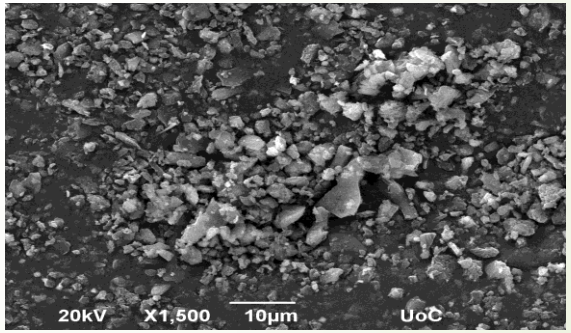
LG-300



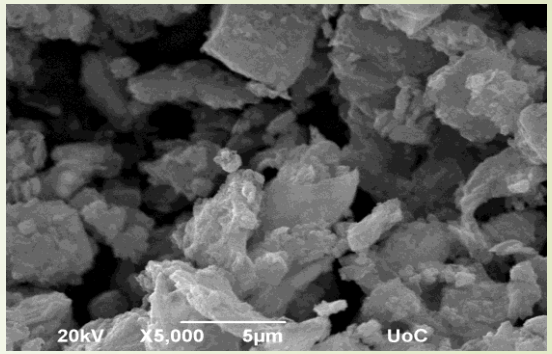


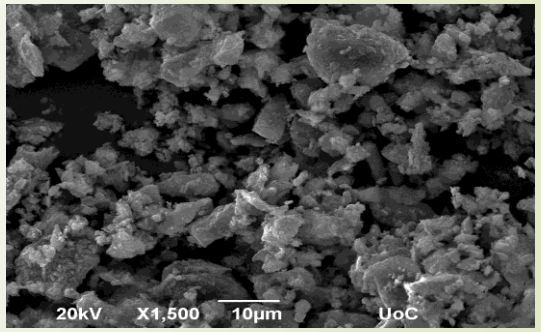
LG-500





LG-800





XRF Analysis of Ash

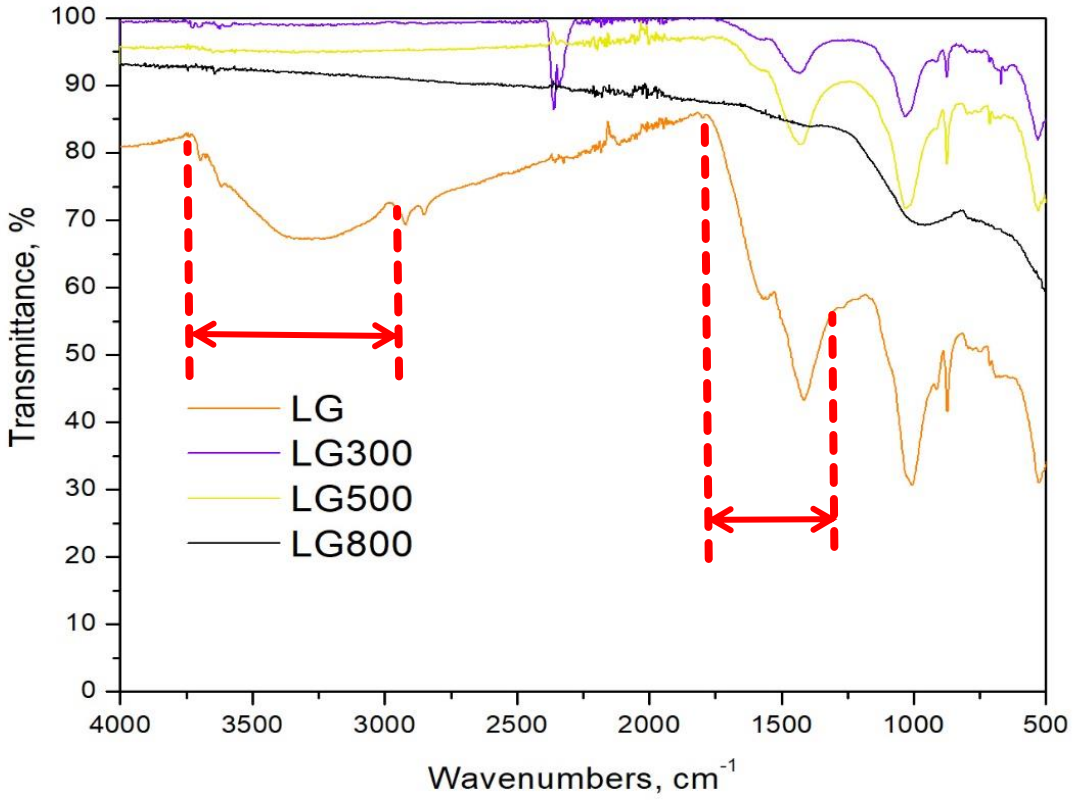
	Sample			
	LG	LG300	LG500	LG800
	Concentration (ppm) (> 100)			
Na	6630	7460	6040	7630
Mg	12750	14300	15340	20950
Al	32390	35970	39960	50090
Si	66110	73900	82180	102800
P	687.4	787.8	913.9	1130
S	9722	10470	7472	13300
Cl	< 100 (72)	114.9	142.2	169.9
K	3310	3732	4163	5430
Ca	89330	99520	114600	147900

	Sample			
	LG	LG300	LG500	LG800
	Concentration (ppm) (> 100)			
Ti	1990	2254	2504	3233
V	< 100 (79)	< 100 (89.8)	100.5	123.7
Cr	157.1	179.2	198.5	251.4
Mn	119.1	127.2	148.7	191.9
Fe	15030	16590	19330	24850
Ni	131	155.1	170.2	216.1
Sr	167	188	219.5	284.2
Zr	< 100 (63.5)	< 100 (70.8)	< 100 (93.1)	103.2
Ba	108.1	135.3	129	170.4

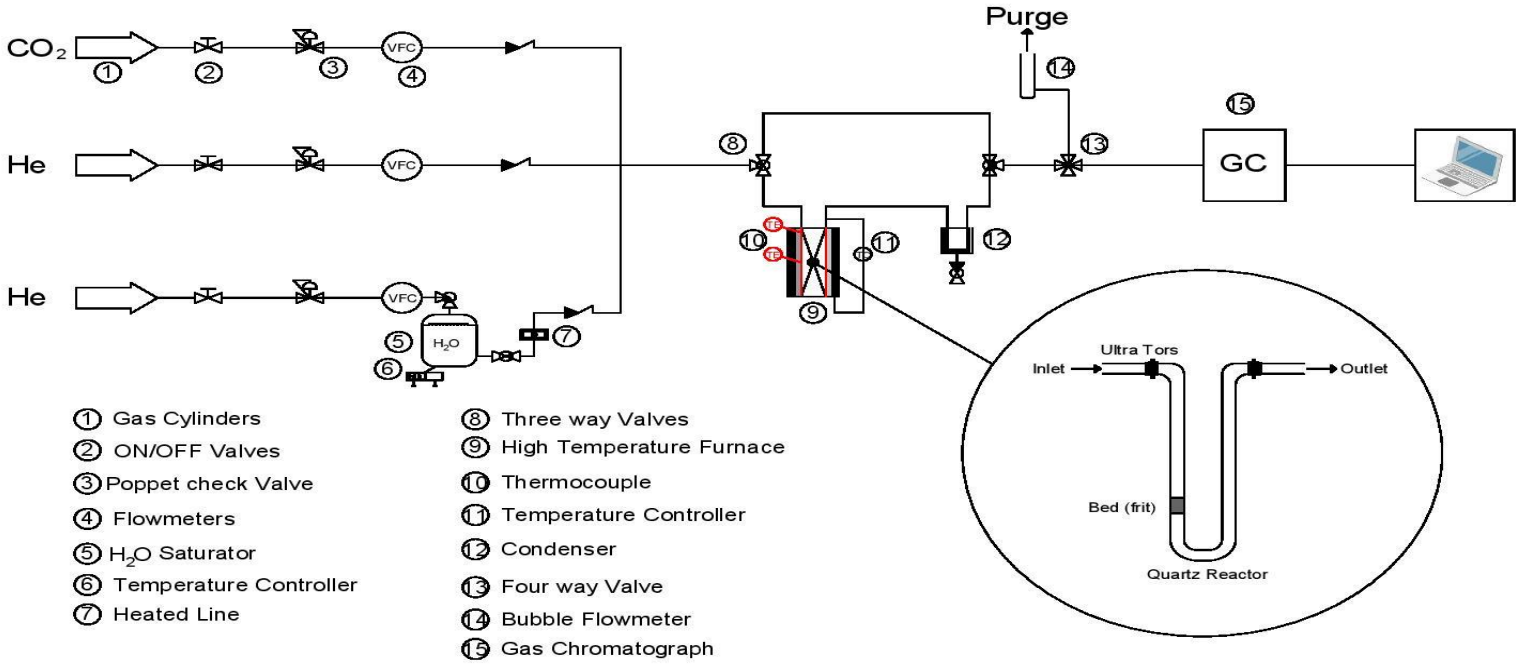
FT-IR Analysis

- In the 3700 – 3000 cm^{-1} range, LG reveals the presence of bands associated to OH groups, which are disappeared on the chars confirming their negligible moisture content.

- The peaks at 1800 – 1400 cm^{-1} are attributed to aromatic C=C, Carbonyl, Carboxyl and C=O groups decrease in intensity upon increasing LG thermal treatment, implying the coalification of produced chars.

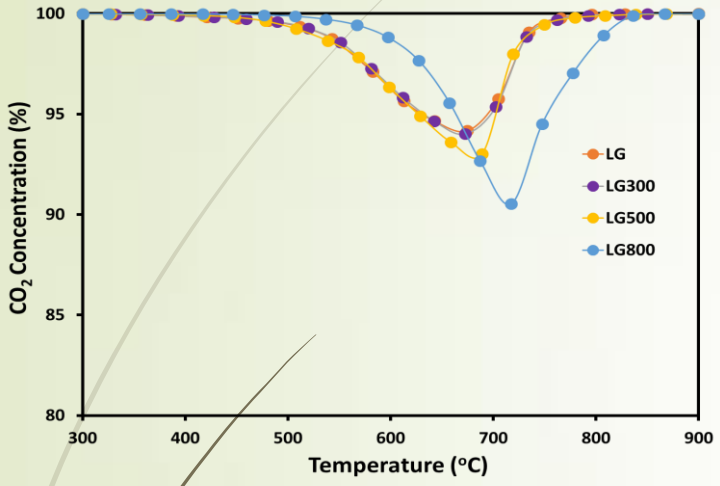


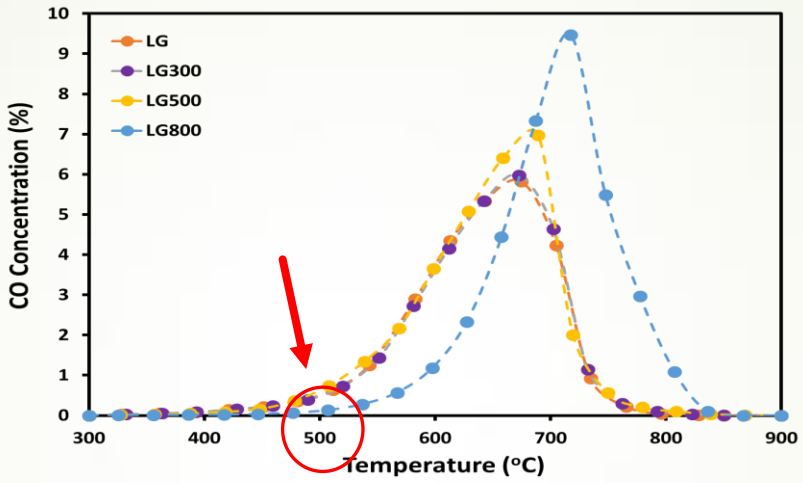
Experimental Setup - Reactor

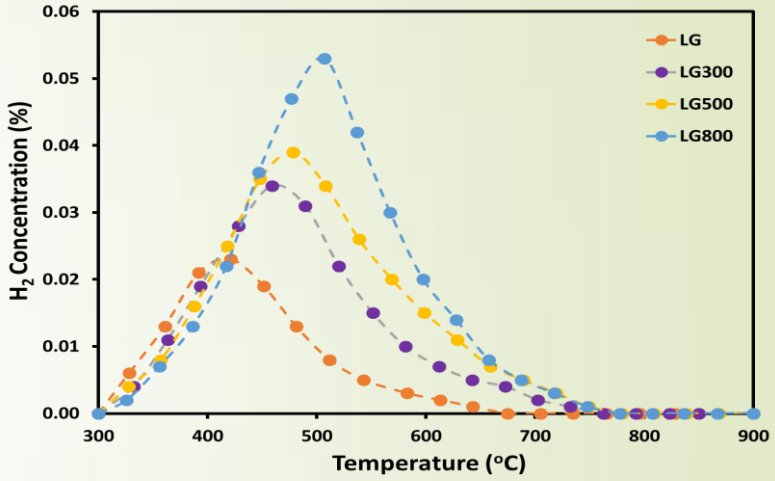


- ID = 0.8 cm – quartz U tube
- Batch operation mode
- Fuel feedstock= 100 mg
- Gasifying agents: (a) Pure CO_2 or (b) 10 v/v% H_2O/He
- Flow rate= 30 cm^3/min
- T= 300 – 950°C with a heating rate= 2 °C/min.

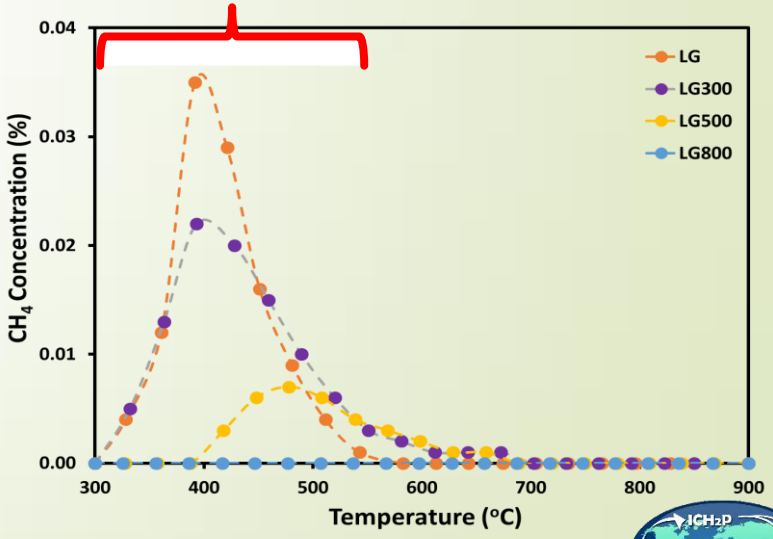
CO_2 Gasification Reactivity



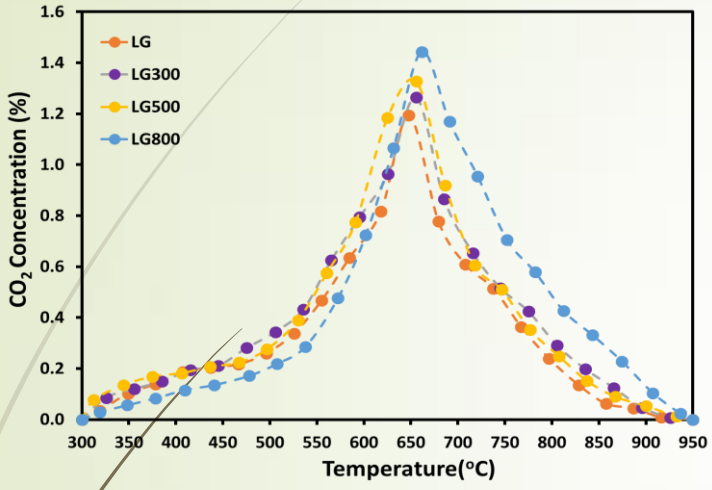


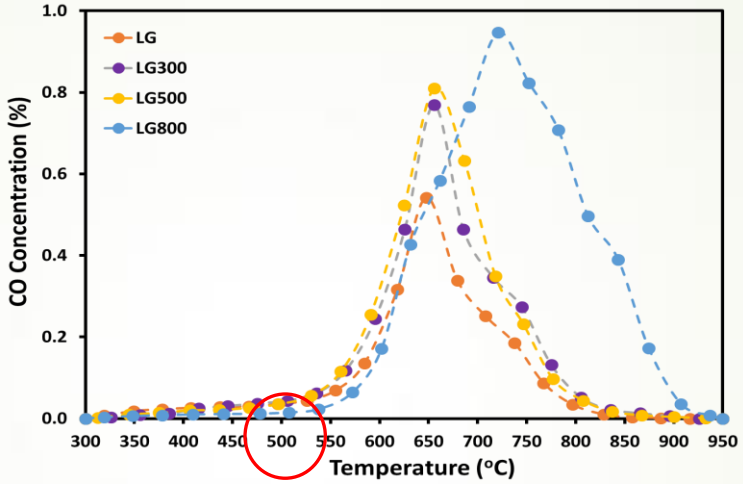


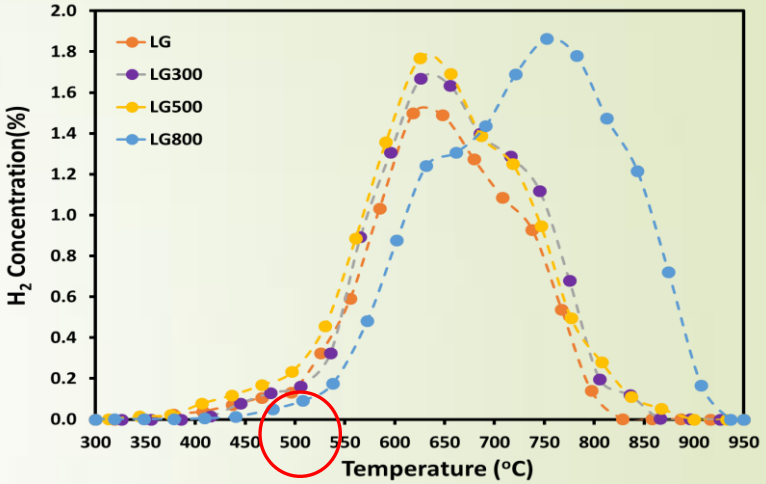
FUEL	CO (mmol)	H_2 (mmol)	CH_4 (mmol)
LG	5.09	0.021	0.020
LG300	5.11	0.037	0.019
LG500	5.55	0.046	0.006
LG800	6.54	0.056	0.000



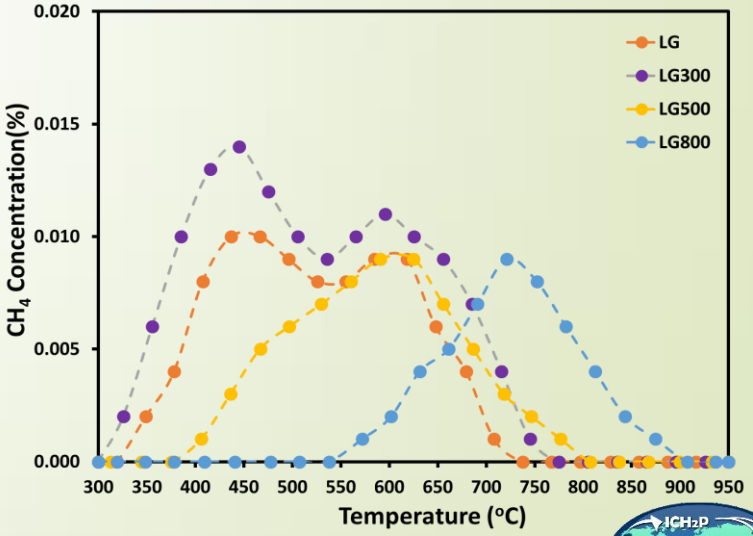
H_2O Gasification Reactivity with 10 v/v% H_2O/He







	CO_2 (mmol)	CO (mmol)	H_2 (mmol)	CH_4 (mmol)
LG	1.36	0.44	1.73	0.016
LG300	1.58	0.58	2.03	0.024
LG500	1.61	0.62	2.16	0.013
LG800	1.74	1.06	2.73	0.001



Conclusions

- In the present work the impact of lignite thermal treatment on the physicochemical properties and gasification reactivity of as-produced chars was investigated.
- The increase on thermal treatment leads to more reactive fuels.
- During CO_2 gasification, CO was the main product with the samples following the gasification reactivity order of: LG800> LG500> LG300> LG. Apart from CO, minor quantities of H_2 and CH_4 were also observed at lower temperatures associated to the released volatiles and gas phase reactions.
- When H_2O was employed as gasifying agent the reactivity of fuel samples follows the same order as in the case of CO_2 gasification experiments. The produced gas mixture is consisting mainly of H_2, CO_2 due to the WGS reaction, following by CO and minor quantities of CH_4 with a $[H_2 / (CO + CO_2)]$ molar ratio equal to unity.
- LG800 sample exhibited the optimum gasification performance, attributed mainly to its enhanced textural characteristics, higher fixed carbon content and absence of aromatic bonds (C=C, C=O και C=N).

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