GASIFICATION PERFORMANCE OF PRISTINE AND THERMAL TREATED GREEK LIGNITE FUELS: THE EFFECT OF GASIFYING AGENT AND PYROLYSIS PROTOCOLS

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- The role of carbon in today’s energy mix and its prospects
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- Production of chars
- Fuels’ characterization
- Evaluation of gasification reactivity of fuels

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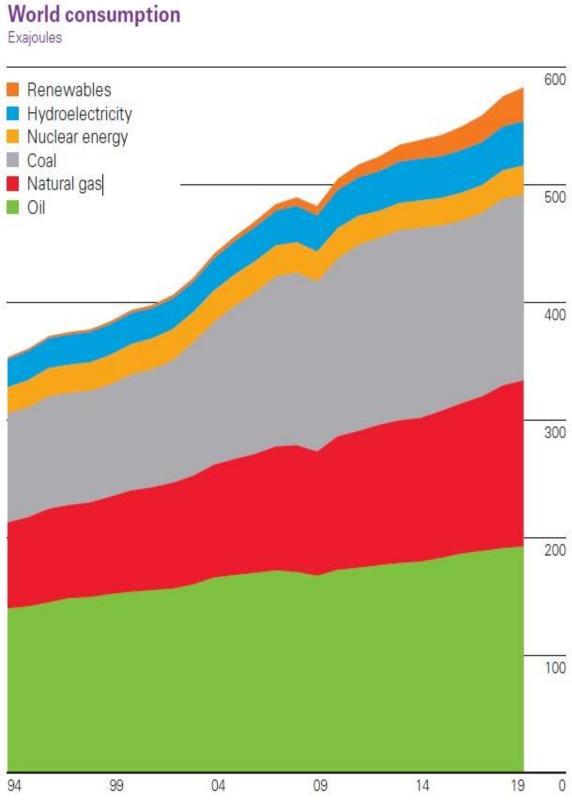
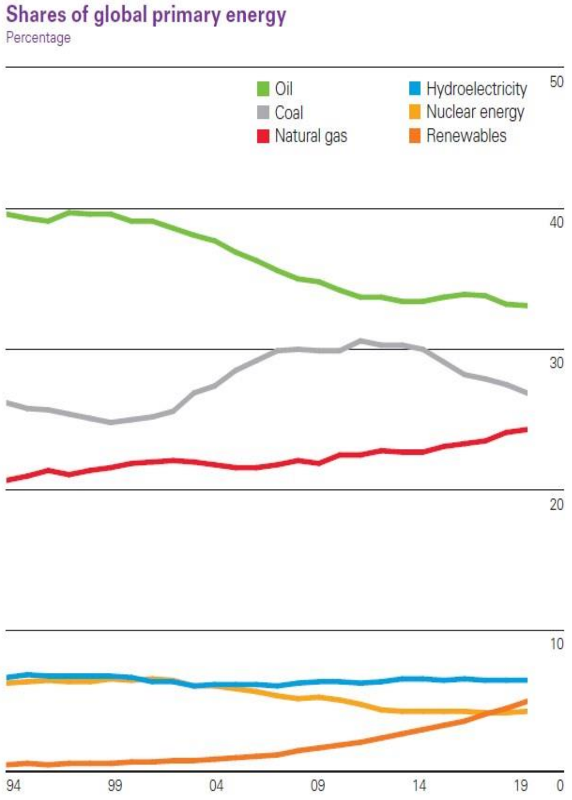
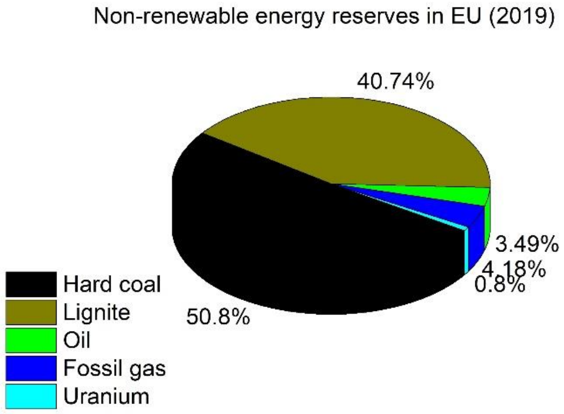
- CO_2 Gasification exps
- H_2O Gasification exps

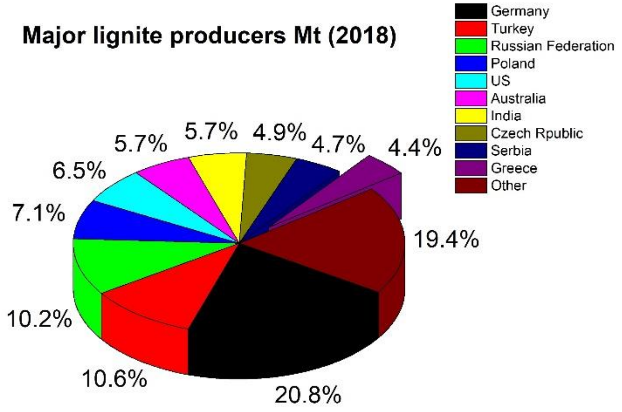
CONCLUSIONS

The Role of Carbon in Today’s Energy Mix



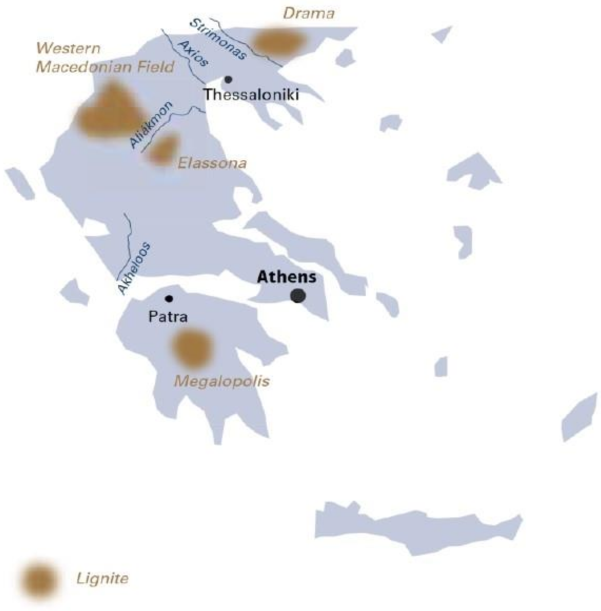


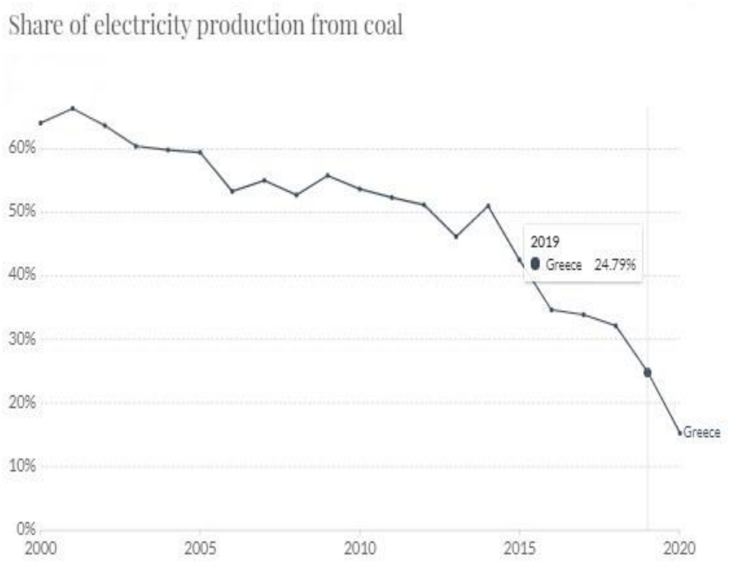


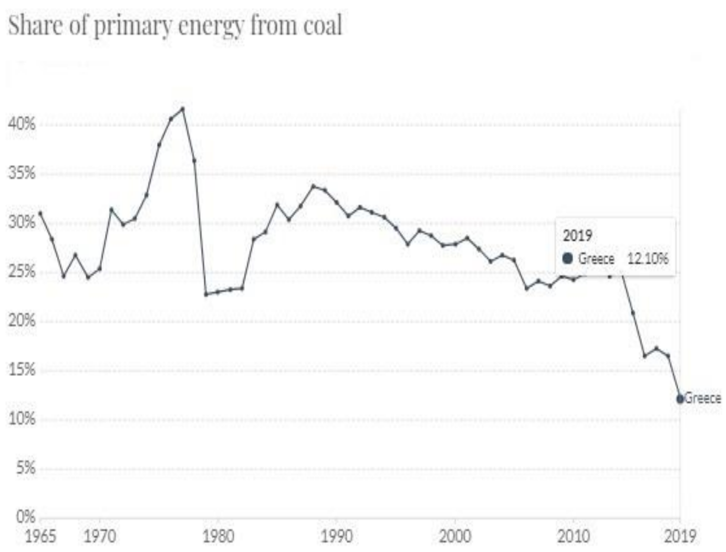


- **Coal is an abundant and cheap fossil fuel with a share of ca. 30% of world energy consumption.**
- **Lignite coal of low calorific values accounts for ca. 45% of the world’s coal recoverable reserves**

The Role of Carbon in Greek Energy Mix




Share of electricity production from coal


Share of primary energy from coal

- **Total lignite reserves ≈ 5 bt**
- **Exploitable lignite reserves ≈ 3.2 bt**
- **Based to today’s consumption rate lignite reserves could last for c.a. 50 years**
- **Lignite production ≈ 36.5 mt (2019)**

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**
- **In 2019, the European Commission announced the European Green Deal to direct the EU economy on a pathway towards climate neutrality by 2050**
- **Traditional energy sectors relying on the production and use of coal and other fossil fuels will shrink, with concomitant negative consequences on the GDP and employment of the regions in clean energy transition**
- **The countries likely to see the most coal-related job losses are *Poland, Germany, Romania, Bulgaria and Greece***

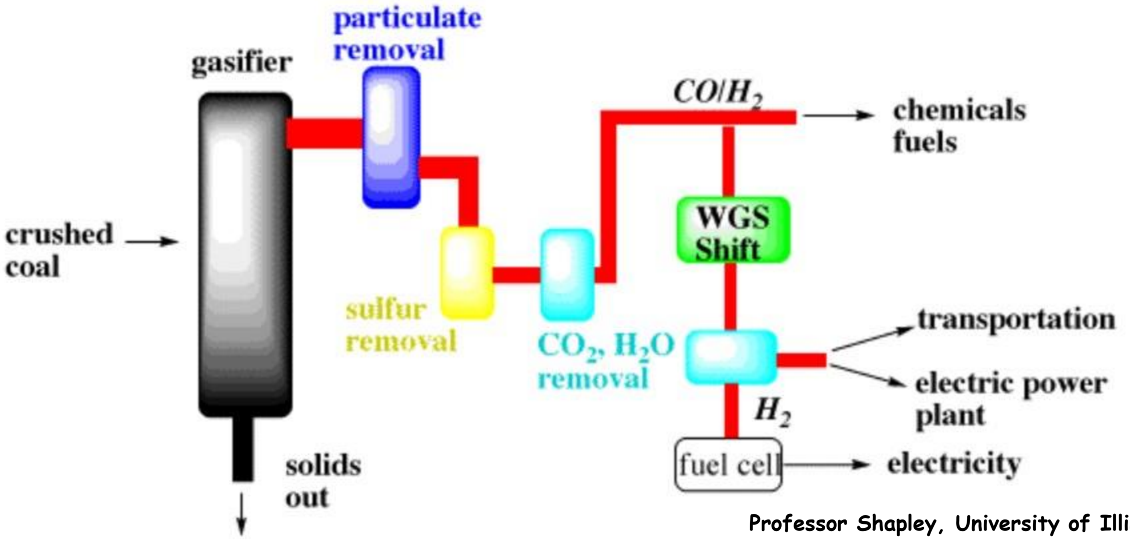
alternative strategies to diversify local economies are required to ensure that the transition will be fair and will leave no one behind

Conventional vs Alternative Coal Energy Conversion

- **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)**



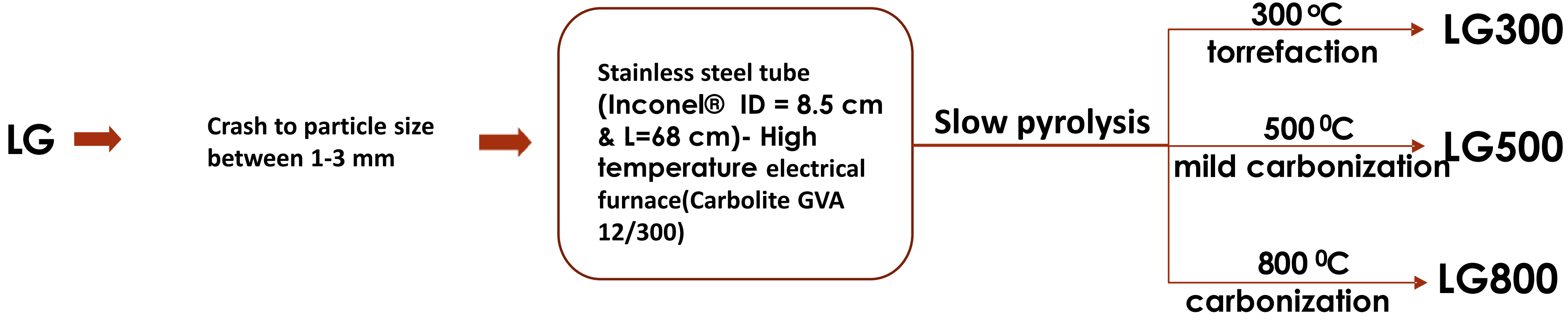
Professor Shapley, University of Illinois

- To examine the effect of Lignite (LG) pyrolysis conditions on the physicochemical characteristics and gasification performance 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)

Slow pyrolysis

300 ^{o}C torrefaction → **LG300**

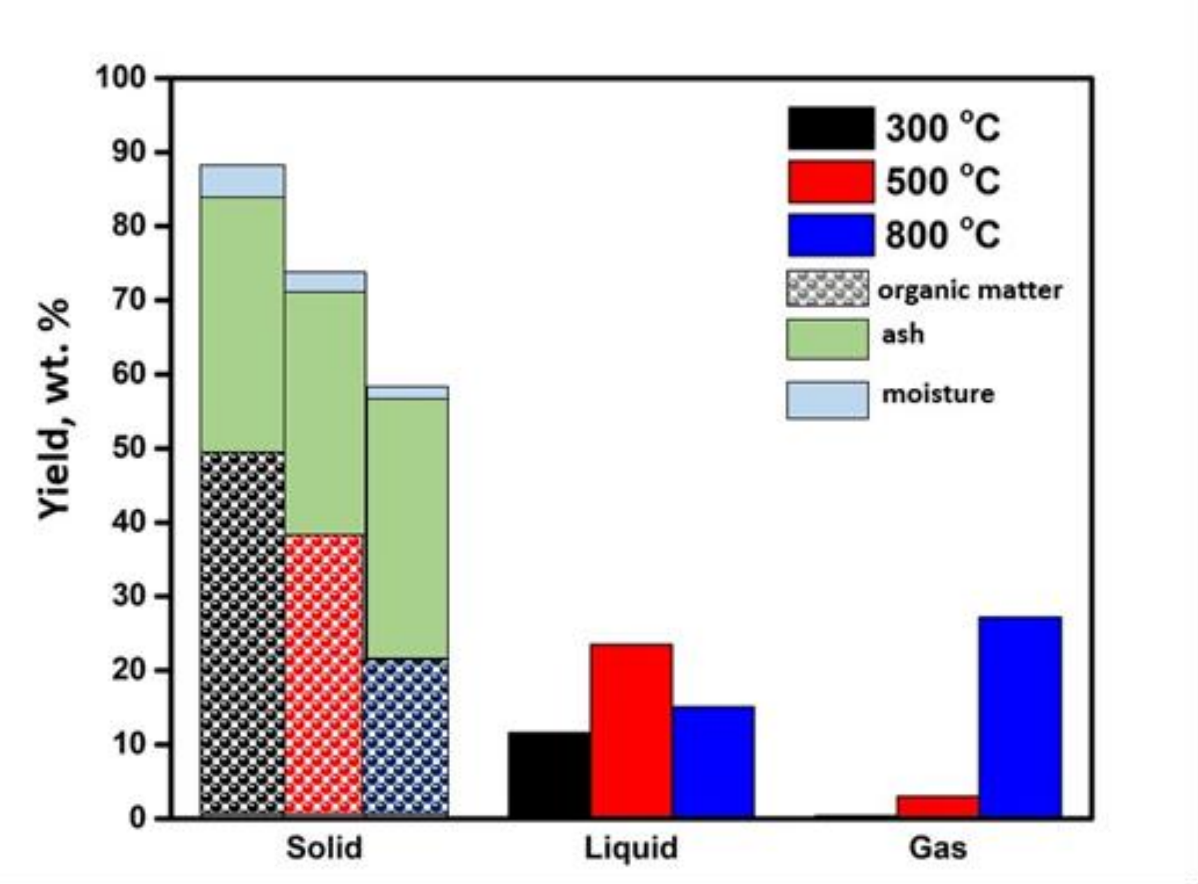
500 ^{0}C mild carbonization → **LG500**

800 ^{0}C carbonization → **LG800**

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

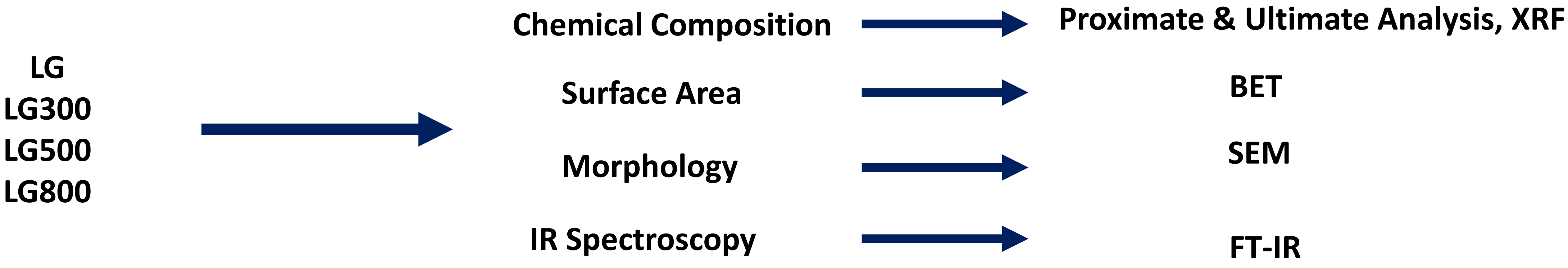
- **Prior to characterizations, all samples were dried and milled to 100 – 200 μm using an agate mortar**

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**
Surface Area → **BET**
Morphology → **SEM**
IR Spectroscopy → **FT-IR**

Proximate & Ultimate Analysis – BET

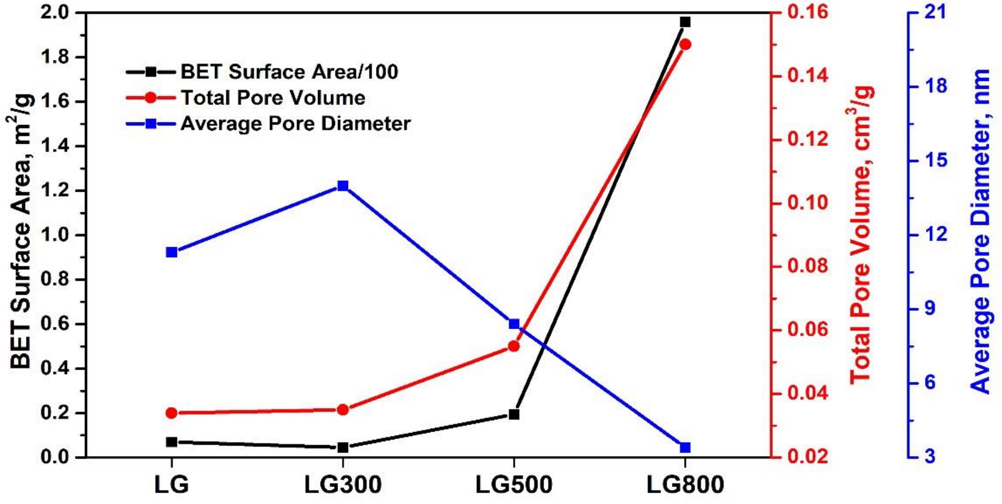
	Ultimate analysis[a] (wt.%)					Proximate analysis (wt.%)				Atomic ratios		Aromaticity factor[b]
	C	H	N	O	S	Moisture	Ash[a]	Volatile matter[a]	Fixed carbon[a]	H/C	O/C	f_a
LG	36.22	2.94	1.05	18.63	0.97	7.67	40.18	41.85	17.96	0.97	0.38	0.410
LG300	36.32	2.75	1.05	16.93	0.92	3.36	42.03	38.84	19.12	0.91	0.35	0.440
LG500	35.26	1.75	0.99	12.53	0.68	2.82	48.79	29.31	21.89	0.60	0.27	0.538
LG800	34.01	1.01	0.73	0.37	0.90	0.91	62.97	11.79	25.23	0.36	0.01	0.792

[a] on dry basis
[b] on dry and ash-free basis

Increase in Thermal Treatment Temperature

Decrease
VM, H_2O, H/C, O/C

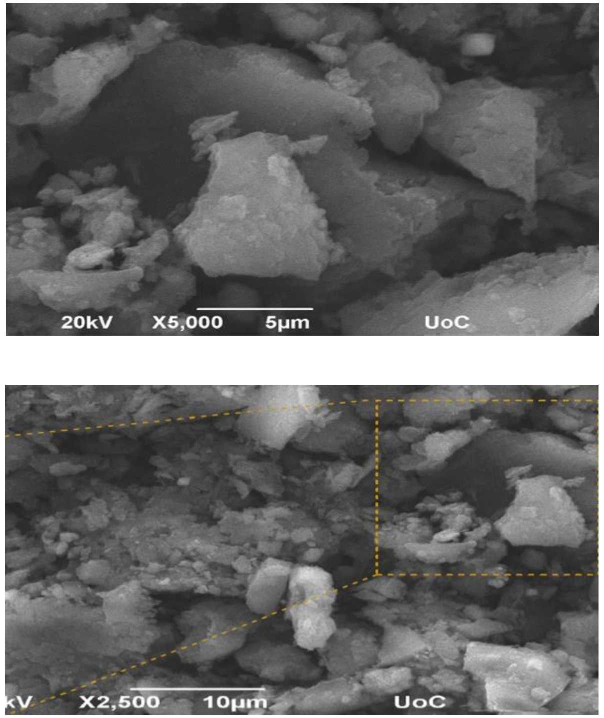
Increase
Fixed Carbon, Ash,fa



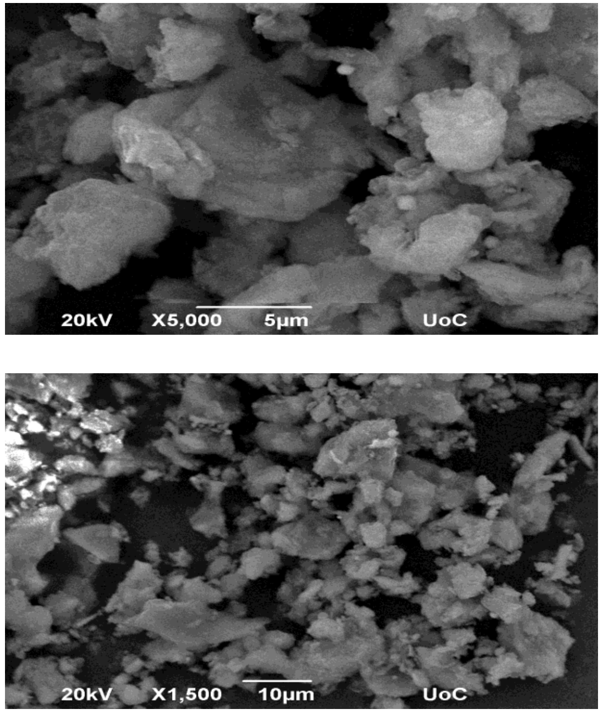
- **BET surface area and pore volume increases with pyrolysis temperature**
- **Implications that removal of the VM and tar generation during pyrolysis led to the formation of internal porosity**

SEM Analysis

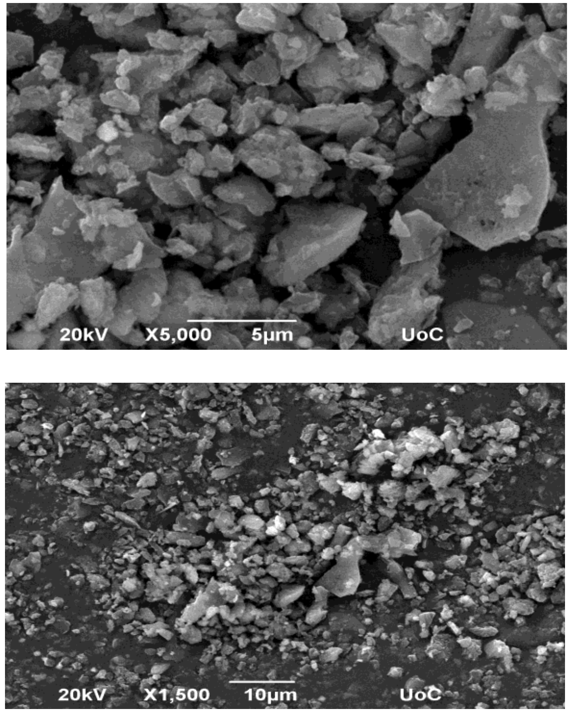
LG



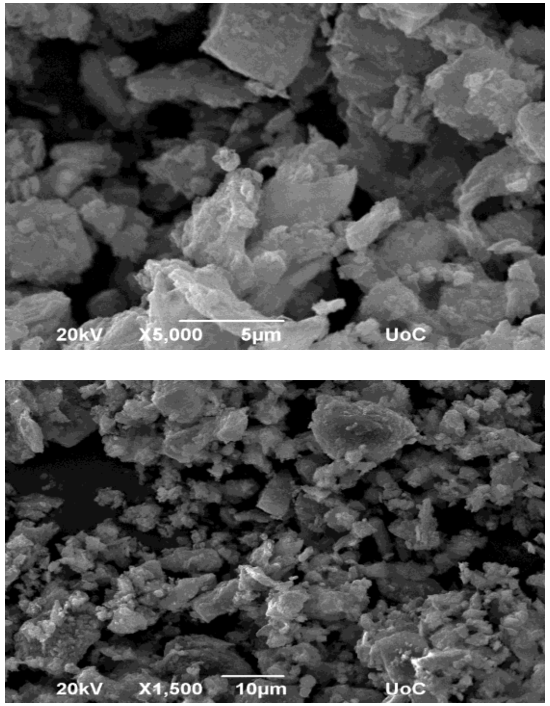
LG-300



LG-500



LG-800



- **LG reveals non-uniform particles with a size ranging from 1 to 10 µm**
- **Lignite chars is concerned, they exhibit irregular morphology with medium to high polydispersity and 0.7 to 5 µm sized particles**
- **LG300 and LG500 samples seems to possess a more compact pore structure in comparison with LG800 sample**

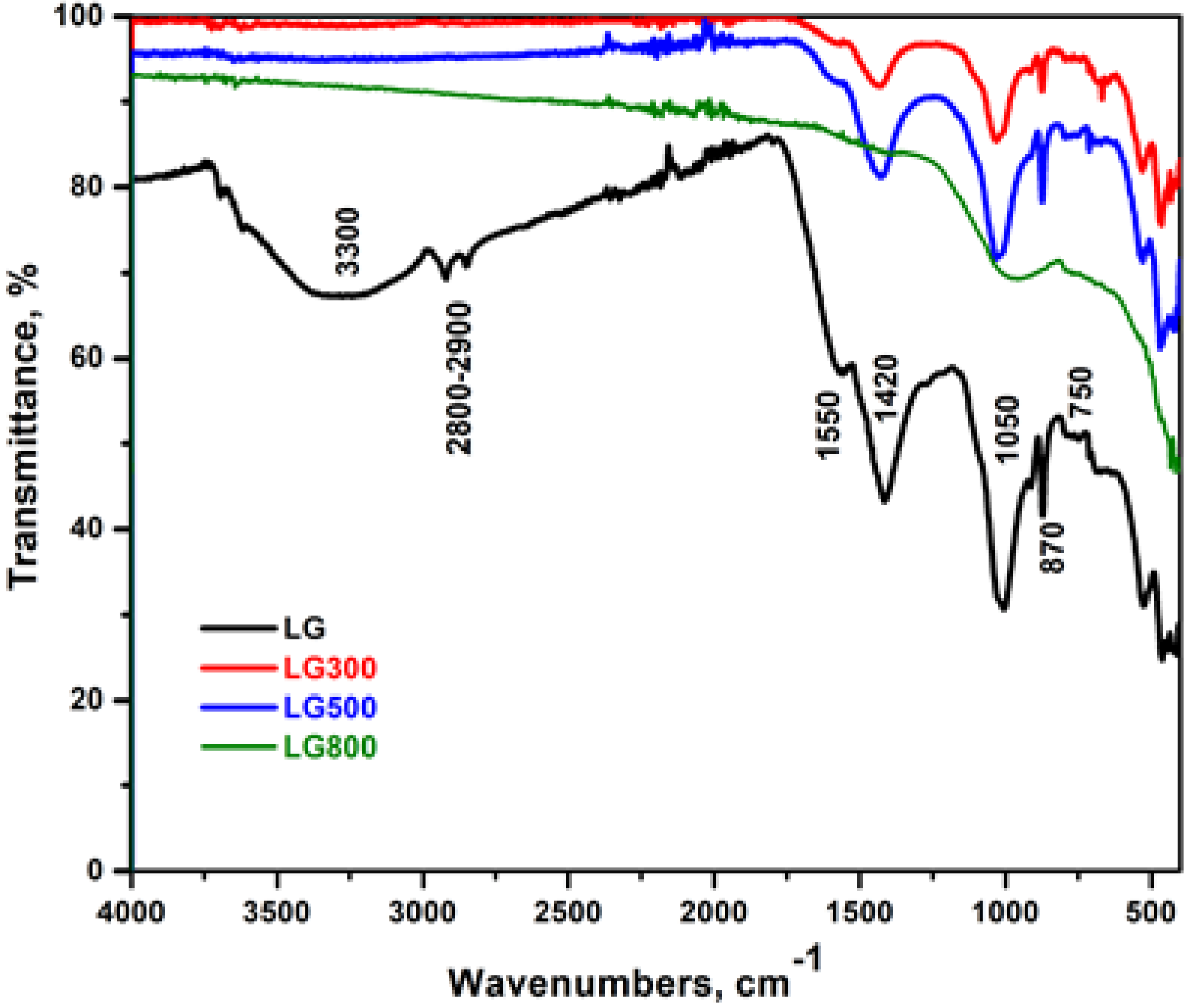
XRF Analysis of Ash

Ash composition (wt.%) and alkali index of fuel samples

Oxide	LG	LG300	LG500	LG800
Na_2O	2.16	2.18	1.61	1.58
MgO	5.11	5.15	5.04	5.33
Al_2O_3	14.79	14.76	14.96	14.51
SiO_2	34.19	34.33	34.84	33.74
P_2O_5	0.38	0.39	0.41	0.40
Cl	0.02	0.02	0.02	0.02
SO_3	5.86	5.68	3.70	5.09
K_2O	0.96	0.97	0.99	1.00
CaO	30.21	30.23	31.77	31.73
Fe_2O_3	5.19	5.15	5.48	5.45
TiO_2	0.80	0.82	0.83	0.83
Alkali Index (AI)	**31.53**	**32.99**	**38.62**	**51.73**

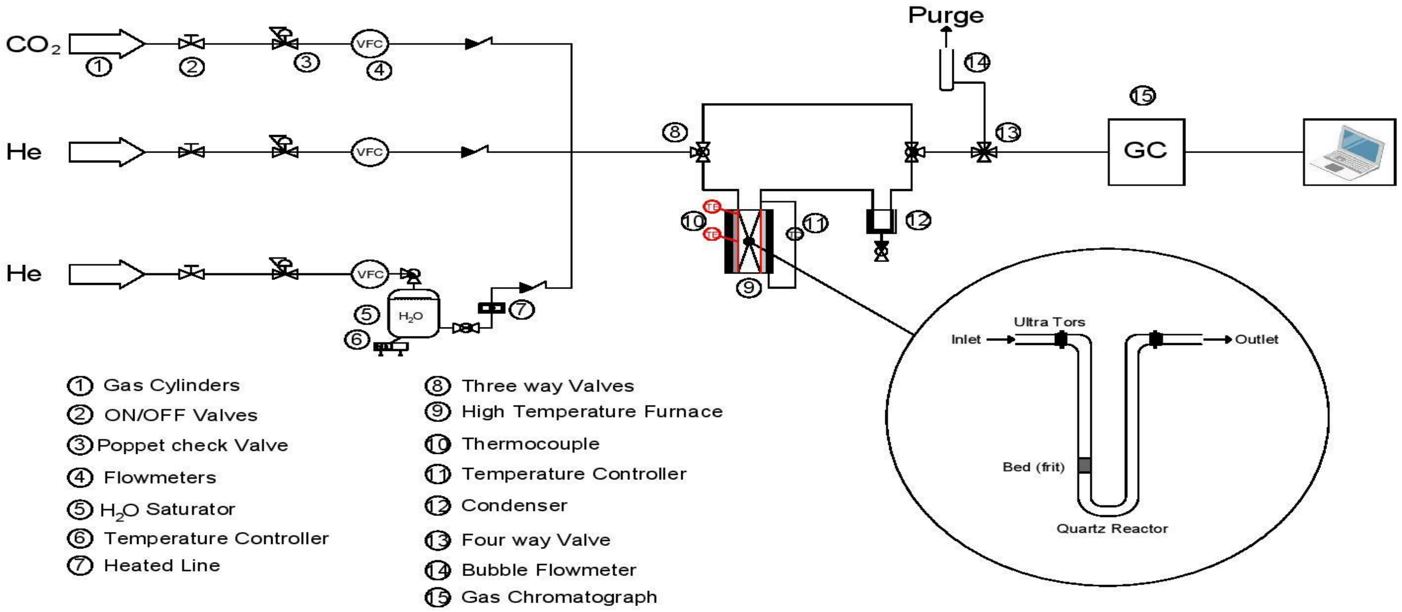
- **Alkali index follows the order: LG800 > LG500 > LG300 > LG**
- **Increase of alkali index upon thermal treatment can be associated to the increased ash content instead to the different ash composition**
- **A close relationship between the AI and the achieved gasification efficiency is obtained in the present work**

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 1600 – 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**
- **The intensity of the peak at 1000 cm^{-1} (oxygenated functional groups) is gradually decreased upon increasing the temperature of thermal treatment**
- **Bands at ca. 870 and 750 cm^{-1} (aromatic structures with isolated hydrogen atoms) are diminished in the case of LG800**

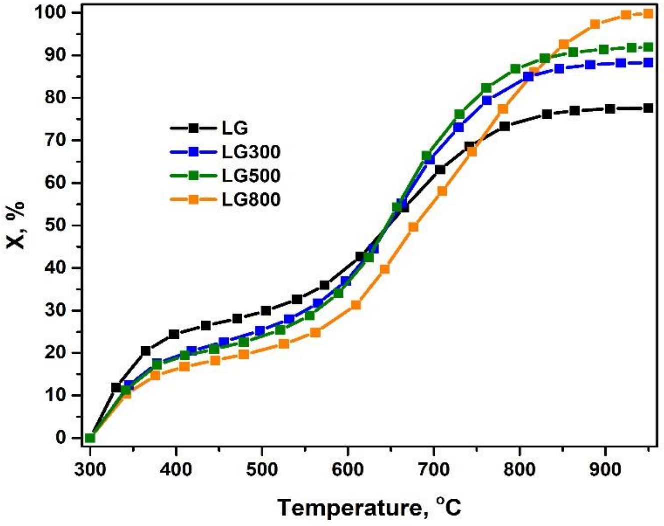
Experimental Setup - Reactor



- **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.**

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

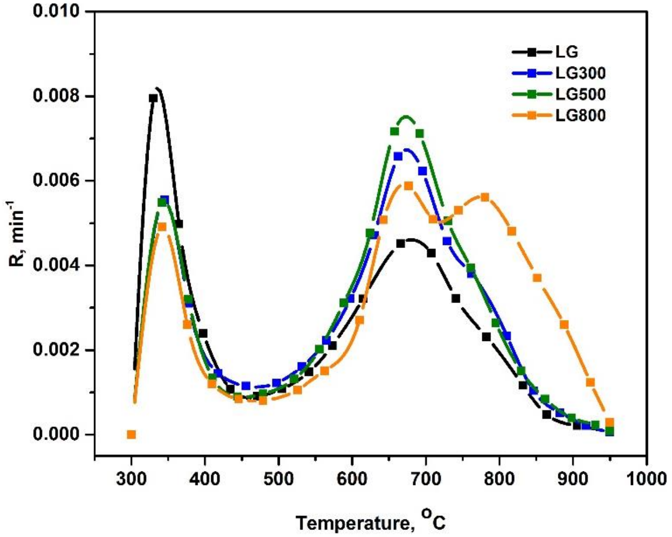
carbon-to-gas percent conversion, X (%)



$$X(\%)=\frac{\int_0^t\left[\frac{F_t\cdot\sum_i y_i}{V_M\cdot 100}\cdot MWc\right]\cdot dt}{m_0}\cdot 100 \quad i=(CO,CO_2,CH_4)$$

- **T < 450 °C ⟶ primary devol. Reactions**
  LG > LG300 > LG500 > LG800
- **450 °C < T < 700 °C ⟶ sec. devol reactions & tar cracking reactions LG500 > LG300 >LG800 >LG**
- **Above 700 °C ⟶ gasification reactions**
  LG800 > LG500 >LG300 >LG

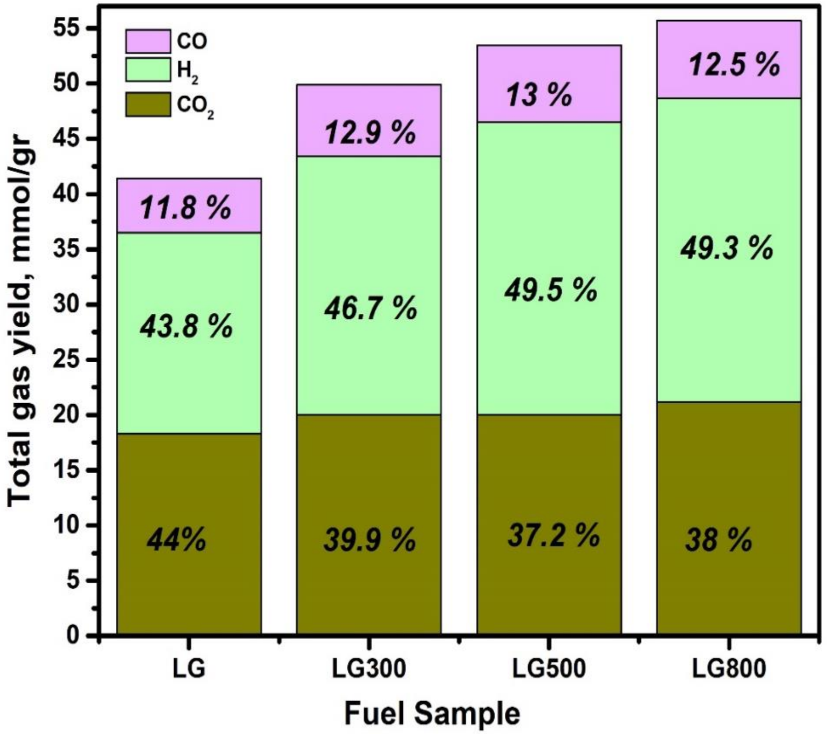
instant gasification rate, R (min^{-1})



$$R=\frac{1}{100}\cdot\frac{dX}{dt}$$

cumulative syngas products' yields, Y_i (mol)

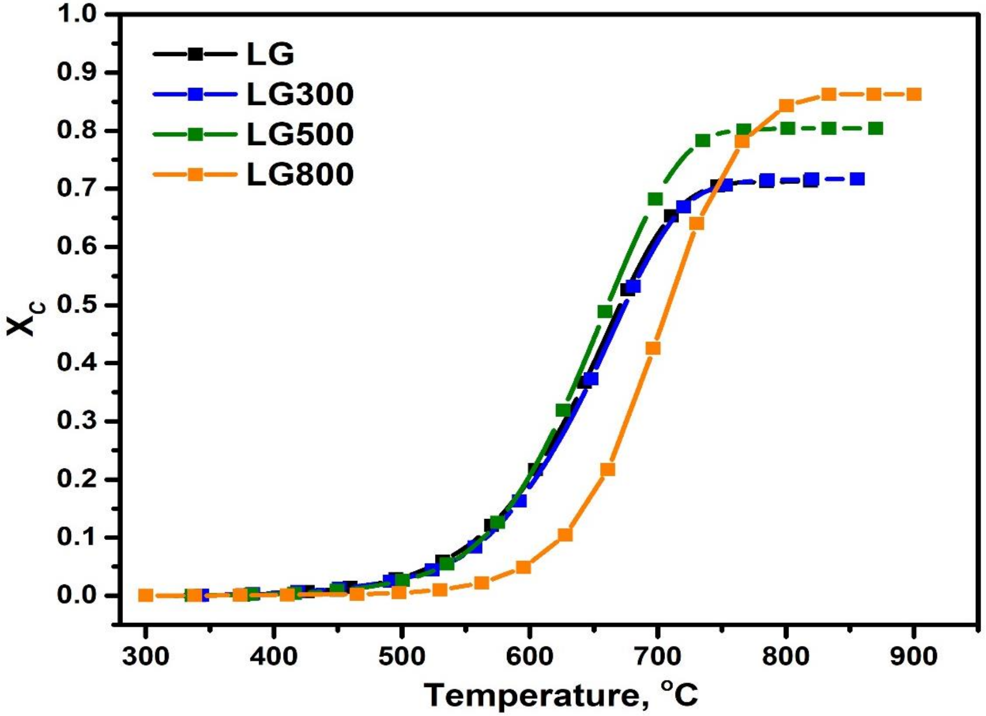
$$Y_i=\int_0^{t_f}\frac{F_t\cdot y_i}{V_M\cdot 100}\cdot dt \quad i=(H_2,CO,CO_2,CH_4)$$



↑ $T_{therm.\ Treatment}$ ⟶ ↑ H2 yield ↓ CO2 yield

CO$_2$ Gasification Reactivity with 100 v/v% CO$_2$

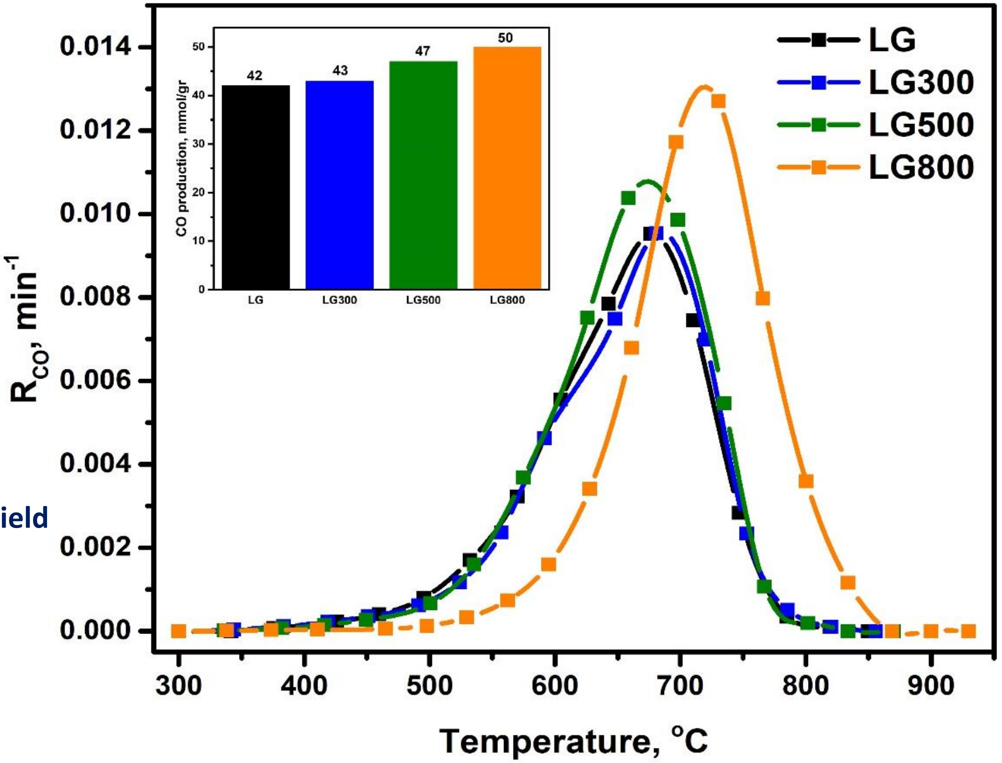
carbon-to-gas percent conversion, X$_c$ (%)



$$X_C = \frac{\sum_0^t y_{co.t}.12}{2.\, m.w_C}$$

$$R_{CO} = \frac{dX_C}{dt}$$

instant gasification rate, R (min^{-1})

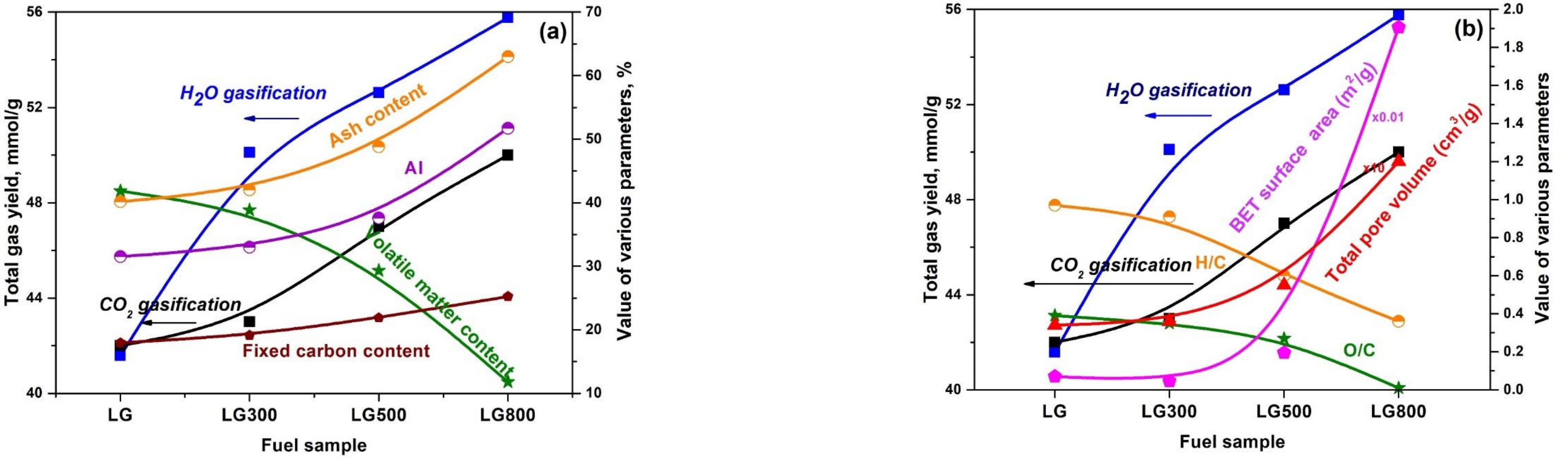


- T < 700 °C → devol. and tar cracking reactions
  LG500 > LG300 > LG > LG800

↑ T$_{\text{therm. Treatment}}$ → ↑ CO yield

- Above 700 °C → gasification reactions
  LG800 > LG500 >LG300 >LG

Conclusions



- **The increase on thermal treatment leads to more reactive fuels in terms of syngas production**
- **During CO_2 gasification, CO was the main product with the samples following the gasification reactivity order of: LG800> LG500> LG300> LG**
- **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, AI index, BET surface area and total pore volume**
- **Although LG800 exhibits the best behavior in terms of syngas production, further techno-economic assessment is required; solid yields and energy consumption during char production at different temperature levels should be taken into account towards the optimum fuel choice for practical applications**

Acknowledgements

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Abstract

Coal is the cheapest and most abundant fossil fuel worldwide, accounting for ca. 30% of global primary energy consumption, still leading the electricity generation sector. Although lignite accounts for 45% of the world’s coal recoverable reserves (5 billion tones in Greece), its applicability is limited due to its rich moisture and ash contents, low calorific value, chemical reactivity, and flammability. Therefore, the use of lignite for power generation evolves a series of problems, associated to its low thermal efficiency and high CO_2 emissions per produced MWh. Accordingly, alternative ways to utilize the existing lignite reserves such as pyrolysis and gasification are of major importance to retain lignite role in the energy mix at least until complete decarbonization is realized.

Coal gasification typically occurs at temperatures 700 - 1200 °C and leads to a gas mixture of H_2, CO, CO_2 and CH_4 with traces of light hydrocarbons, where its composition is strongly dependent on the employed conditions (i.e., temperature, gasifying agent, residence time, etc). CO_2 gasification results almost exclusively to CO and can be regarded as a potential way to utilize captured CO_2 emissions, while steam gasification enhances H_2 formation, producing syngas mixtures at various H_2/CO molar ratios, that can be employed either for power generation in solid oxide fuel cells or as raw material for high added value chemicals.

Char is the solid product which is yielded by carbon pyrolysis, where the carbohydrate fraction splits into three products, namely: char (solid), condensable vapors (liquid) and non-condensable gases. The thermal treatment of low rank coals results in chars with better fuel characteristics compared to pristine samples.

In the present work the effect of lignite pyrolysis protocol (torrefaction and carbonization) on the physicochemical properties and CO_2 or/and H_2O gasification performance of as produced chars is examined. A lignite coal from the Greek Western Macedonia basin was selected as fuel. Fuel samples were characterized by a variety of

methods including ultimate and proximate analysis, XRF, XRD, BET, SEM, TGA, infrared and Raman spectroscopy. A close relationship between the solid state properties and syngas generation of lignite fuel samples was disclosed. The lignite treated sample at 800 ^{o}C showed the optimum behavior attributed mainly to its higher BET surface area and higher fixed carbon content. Upon CO_2 gasification, CO was the primary product followed by minor quantities of H_2 and CH_4 generated at lower temperatures (< 550 ^{o}C) due to the released volatile matter. When H_2O was employed as gasifying agent, a gas mixture consisting mainly of H_2, CO_2, CO and CH_4 was produced, with the CO_2 molar fraction being higher compared to CO. A positive effect of CO_2 and H_2O feed concentrations on syngas production rates was revealed without observing any substantial modifications on products' distribution.

Acknowledgements

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