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Chapter 13

Pyrolysis: Pathway to Coal Clean Technologies

Andrew O. Odeh

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Abstract

Pyrolysis remains key to all coal utilisation processes such as combustion, gasification and liquefaction. Understanding the thermochemical changes accompanying these processes through pyrolysis would help in defining the technical performance of the processes. With the recent concern for the environment and renewed interest in research on clean coal technology (CCT), hydrogen from coal through the integrated gasification combined cycle has been considered for the proposed hydrogen economy.

Keywords: char, coal, pollution control, emissions, pyrolysis

1. Introduction

What is pyrolysis: pyrolysis is a thermochemical decomposition of carbonaceous materials such as biomass, plastic, tyre, coal, etc. at elevated temperatures of 200°C and above in the absence of oxygen. It is an irreversible chemical reaction in which there is a simultaneous change of chemical composition and physical phase of the matter. This reaction involves the molecular breakdown of larger molecules (polymer) into smaller molecules in the presence of heat. Pyrolysis is also referred to as thermal cracking, thermolysis, depolymerisation, etc.

What is coal pyrolysis: coal pyrolysis involves subjecting coal to high temperature of 400–450°C, in the absence of oxygen. When oxygen or steam is present, coal will start burning, and the process is no longer known as pyrolysis but rather referred as combustion and gasification. The benefits of coal pyrolysis are enormous and are listed below:

- Converts waste (char) to energy.
- The in-product can be used as fuel in existing industrial boilers and furnaces.

- The end products can also be used for generating electricity.
- It offers renewable energy source.
- Solid waste management.

Coal and coal products will continue to play an increasingly important role in fulfilling the energy needs and economies of nations. This is because of the abundant reserves of coal and its low cost [1, 2]. Coal accounts for roughly 25% of the world's energy supply and 40% of carbon emissions but even with the high percentage of emissions, it is very unlikely that any of these countries that are into coal exploration and production will turn their back on coal very soon [3]. Economic growth requires energy growth [4]. With the recent concern for the environment and renewed interest in research on alternative energy from renewable sources such as fuel cells and wind, hydrogen from coal through the integrated gasification combined cycle has been considered for the proposed hydrogen economy [5, 6]. Gasification has been tipped as the twenty-first century clean coal conversion technology than the other coal utilisation processes such as liquefaction and combustion because it is high energy efficient [7], non-polluting [8] and economical [9]. It also has the merit of going beyond the use of coal for the generation of power [10], metal processing and the production of chemicals [11], as coal could be converted to useful gases and liquids [12]. Coal is a complex carbonaceous material consisting of organic and inorganic matter [13]. During gasification, the organic and inorganic matter undergoes various chemical and physical transformations [14]. In order to maximise the gasification efficiency, there is a need to understand the mechanism of the chemical and physical transformation, as this will assist in the reduction of carbon emissions in the process especially when gasifying low rank coal [15–17]. Several options are used to control the feed rate of coal during gasification: fixed bed, fluidised bed, and entrained flow gasifiers [18]. Fluidised bed gasifiers have the potential advantage that low-grade coals rich in ash and inertinites, such that South African coals, can be processed more efficiently than in conventional pulverised coal boilers [19–21].

Therefore, the design of coal utilisation processes will require a deeper understanding of coal's intrinsic properties and the ways in which it is chemically transformed under process conditions [22, 23]. One of the ways to get this understanding is through pyrolysis which serves as an enroute to all coal utilisation processes [19]. Hence in this communication, the evaluation of six southern hemisphere coals would be used to illustrate the intermediary role played by pyrolysis in the coal utilisation processes.

2. Influence of changes in chemical and physical properties on coal performance

Currently, research efforts on the utilisation of coal and coal products are driven towards clean coal technology (CCT) [20, 24]. Previous studies on CCT for the past 30 years have been on the chemical cleaning of coal and of recent on carbon capture and storage (CCS)

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[20, 25]. Research efforts have been limited to laboratory-scale in the determination of molecular and structural parameters such as aromaticity, degree of condensation that defines the technical performance of coal during coal utilisation processes [20, 26–28]. The essence of chemical cleaning in coal is to remove or reduce the mineral content in coal as it has been reported that the mineral content in coal melts when it is subjected to heat treatment during coal conversion processes [20, 29] which results in blocking the carbon active sites [30] thereby reducing the reactivity of the coal and decreasing the emission of pollutants [20, 31].

Coal is a complex carbonaceous polymer made up of organic and inorganic substances [32, 33]. The organic materials are known as macerals, while the inorganic impurities are considered as the minerals [34]. When exposed to heat-treatment; the physical, chemical, thermal, mechanical and electrical properties of coal undergo transformation [20, 35]. One of the key parameters that are used in measuring the chemical stability of this transformation is the aromaticity [20, 36]; it gives a good representation of the maceral to char transformation, which stands as a good indicator of coal maturity due to the realignment of the carbon [20, 37].

The change in carbonaceous structure due to the modification of the organic and inorganic constituents in coal and its subsequent char is stated to be one of the main factors that affect the reactivity of coal/char in coal conversion processes [20, 38, 39]. The chemical transformation involves the change in the organic chemical structure (**Tables 1–3**) while the physical transformation involves a change in the char morphology and porosity (**Table 4**, **Figures 1–12**).

Coal	**SPL**	**SM**	**BCH**	**SSL**	**NGR**	**GER**
wt% inherent moisture (air dried)	1.5	1.0	2.1	4.2	9.6	15.4
wt% ash (air-dried)	11.2	17.3	16.2	29.1	9.0	12.4
wt% volatile matter (air-dried)	5.3	7.6	26.7	21.4	37.6	45.7
wt% fixed carbon (air-dried)	82	74.1	55.0	45.3	43.8	26.4
wt% carbon (daf)	90.2	90.4	81.6	77.5	75.6	70.5
wt% hydrogen (daf)	2.7	3.5	4.6	4.5	5.2	6.6
wt% nitrogen (daf)	2.2	2.0	2.0	2.2	1.7	0.6
wt% oxygen (daf)	2.7	3.3	10.7	15.4	16.9	18.5
wt% sulphur (daf)	2.3	0.9	1.2	0.4	0.7	3.7
Gross calorific value (MJ/kg)	29.6	28.7	26.8	20.0	24.6	21.2
H/C	0.4	0.5	0.7	0.7	0.8	1.1
f_a	0.91	0.85	0.73	0.72	0.65	0.49

Table 1. Proximate analysis, ultimate analysis, calorific values and calculated H/C and aromaticity values for untreated coal.

Coal	SPL	SM	BCH	SSL	NGR	GER
wt% inherent moisture(air dried)	2.5	2.3	2.7	1.3	1.9	1.7
wt% ash (air-dried)	1.5	1.8	1.2	3.3	2.0	0.8
wt% volatile matter (air-dried)	6.8	9.6	27.2	25.0	43.2	60.3
wt% fixed carbon (air-dried)	89.2	86.3	68.9	70.4	53.0	37.3
wt% carbon (daf)	85.6	89.0	83.4	80.9	75.1	69.2
wt% hydrogen (daf)	2.4	3.3	4.6	4.2	5.2	6.2
wt% nitrogen (daf)	2.0	1.8	2.0	2.3	1.8	0.6
wt% oxygen (daf)	7.7	5.0	9.1	12.3	17.4	20.3
wt% Sulphur (daf)	2.1	0.7	1.0	0.3	0.1	2.7
Gross calorific value (MJ/kg)	32.7	33.3	32.0	30.0	29.3	28.9
H/C	0.3	0.4	0.7	0.6	0.8	1.1
$f_{a\,(CA)}$	0.92	0.86	0.74	0.76	0.65	0.52
$f_{a\,(FTIR)}$	0.98	0.84	0.72	0.74	0.58	0.40
$f_{a\,(C\text{-}NMR)}$	0.98	0.94	0.76	0.80	0.58	0.43
$f_{a\,(XRD)}$	0.89	0.87	0.78	0.74	0.70	0.66

Table 2. Proximate analysis, ultimate analysis, calorific values and calculated H/C and aromaticity values for acid-treated coal.

Coal	450	500	550	600	650	700
	GER					
H/C	0.5	0.4	0.3	0.3	0.2	0.1
$f_{a\,(CA)}$	0.86	0.89	0.95	0.95	0.99	1.00
$f_{a\,(FTIR)}$	0.66	0.69	0.73	0.74	0.76	0.79
$f_{a\,(XRD)}$	0.66	0.67	0.68	0.72	0.74	0.76
	NGR					
H/C	0.5	0.4	0.3	0.3	0.2	0.1
$f_{a\,(CA)}$	0.86	0.90	0.93	0.96	1.00	1.03
$f_{a\,(FTIR)}$	0.75	0.78	0.81	0.84	0.87	0.90
$f_{a\,(XRD)}$	0.67	0.69	0.70	0.74	0.78	0.80
	SSL					
H/C	0.4	0.4	0.3	0.3	0.2	0.1
$f_{a\,(CA)}$	0.87	0.91	0.93	0.96	1.00	1.05
$f_{a\,(FTIR)}$	0.84	0.88	0.90	0.93	0.97	1.00
$f_{a\,(XRD)}$	0.91	0.94	0.96	0.97	0.97	0.97
	BCH					
H/C	0.5	0.4	0.3	0.3	0.2	0.1

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Coal	450	500	550	600	650	700
$f_{a\ (CA)}$	0.86	0.89	0.92	0.95	0.98	1.03
$f_{a\ (FTIR)}$	0.83	0.86	0.89	0.92	0.95	1.00
$f_{a\ (XRD)}$	0.93	0.94	0.97	0.98	0.99	0.99
	SM					
H/C	0.4	0.4	0.3	0.3	0.2	0.1
$f_{a\ (CA)}$	0.88	0.89	0.92	0.95	0.99	1.03
$f_{a\ (FTIR)}$	0.94	0.95	0.98	1.00	1.00	1.00
$f_{a\ (XRD)}$	0.96	0.98	0.99	0.99	0.99	0.99
	SPL					
H/C	0.3	0.3	0.3	0.3	0.2	0.1
f_a	0.94	0.95	0.95	0.97	0.98	1.03
$f_{a\ (FTIR)}$	0.97	0.98	1.00	1.00	1.00	1.00
$f_{a\ (XRD)}$	0.96	0.97	0.98	0.99	0.99	0.99

Table 3. Calculated H/C and aromaticity values for heat-treated coal.

Coal	450	500	550	600	650	700
	GER					
O/C	0.132	0.103	0.092	0.073	0.064	0.056
BET surface area (m^2/g)	169.96	193.97	230.41	241.82	262.61	268.56
	NGR					
O/C	0.130	0.110	0.083	0.075	0.067	0.061
BET surface area (m^2/g)	155.78	182.61	183.19	234.10	238.14	239.74
	SSL					
O/C	0.081	0.076	0.063	0.052	0.051	0.042
BET surface area (m^2/g)	136.60	153.47	199.72	200.38	214.46	224.19
	BCH					
O/C	0.064	0.057	0.044	0.039	0.037	0.029
BET surface area (m^2/g)	130.17	158.68	183.89	206.40	215.40	224.95
	SM					
O/C	0.039	0.042	0.033	0.033	0.037	0.032
BET surface area (m^2/g)	137.94	148.17	170.35	186.54	194.60	196.99
	SPL					
O/C	0.039	0.048	0.063	0.039	0.037	0.036
BET surface area (m^2/g)	113.93	135.18	136.74	150.98	162.47	164.40

Table 4. Calculated atomic O/C and BET surface area values from SEM and ASAP 2020 for heat-treated coal.

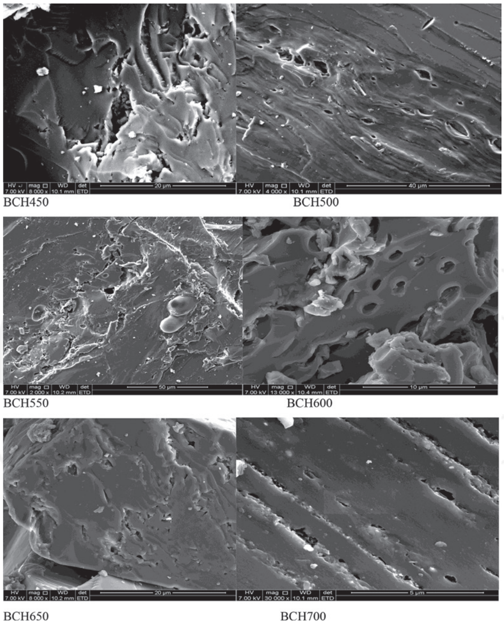

Figure 1. SEM micrographs of the transition of BCH coal to char.

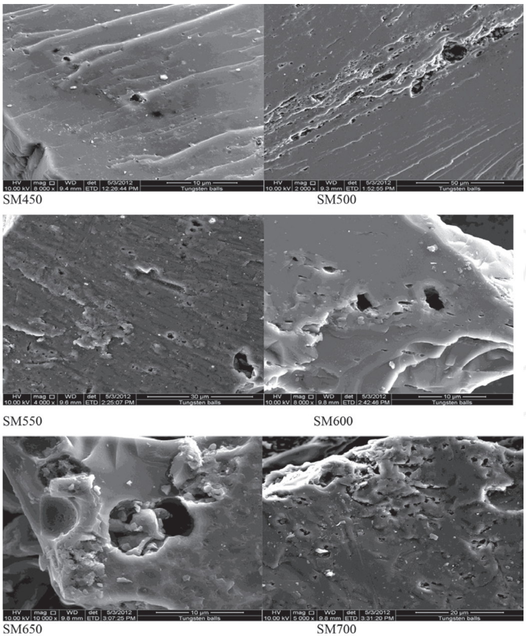

Figure 2. SEM micrographs of the transition of SM coal to char.

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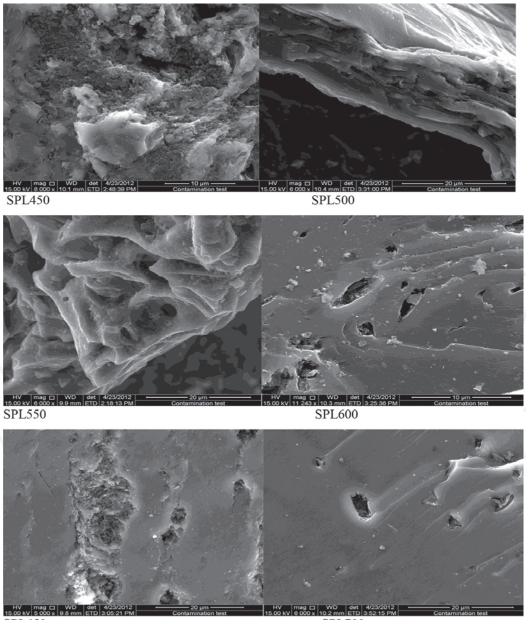

Figure 3. SEM micrographs of the transition of SPL coal to char.

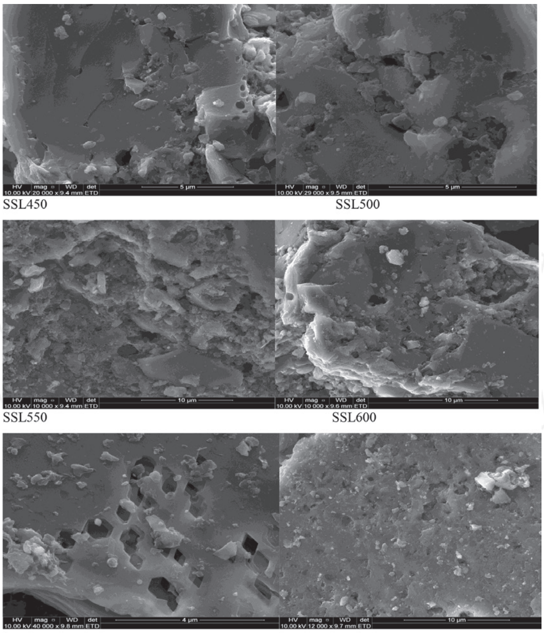

Figure 4. SEM micrographs of the transition of SSL coal to char.

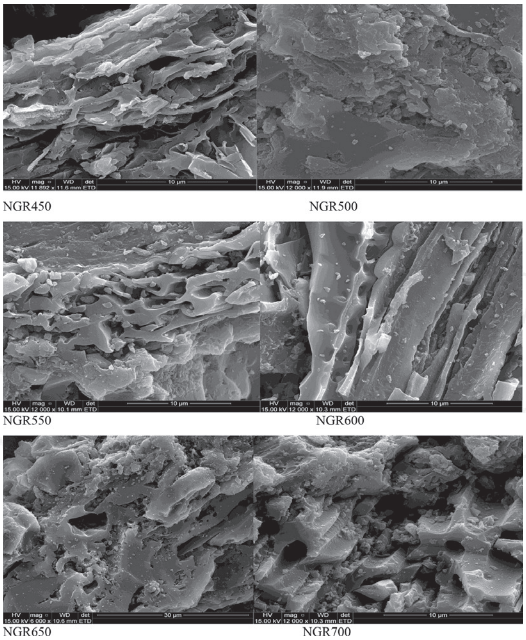

Figure 5. SEM micrographs of the transition of NGR coal to char.

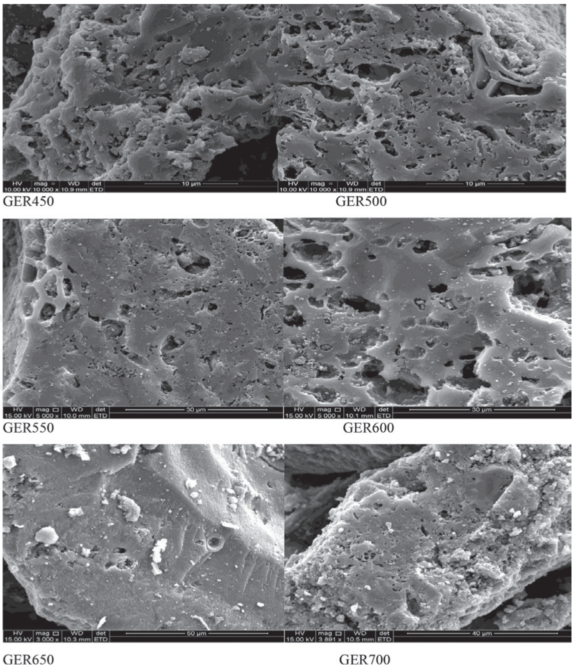

Figure 6. SEM micrographs of the transition of GER coal to char.

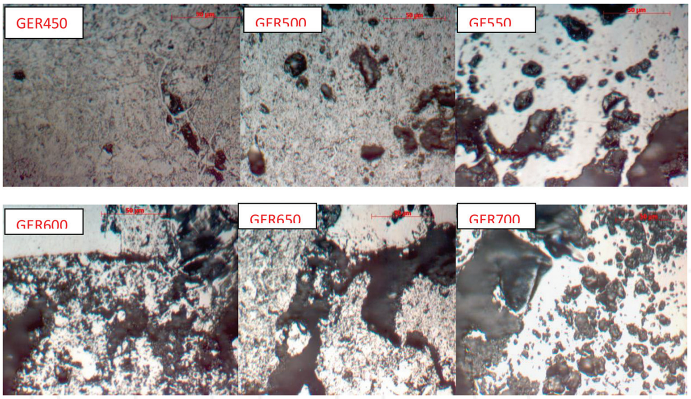

Figure 7. Petrographic pictures of the transition of coal to char for GER suites.

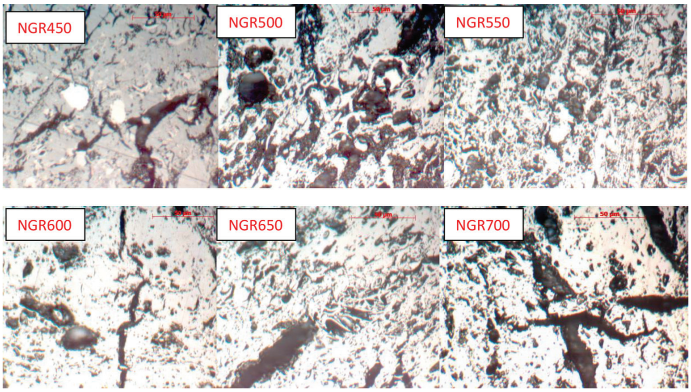

Figure 8. Petrographic pictures of the transition of coal to char for NGR suites.

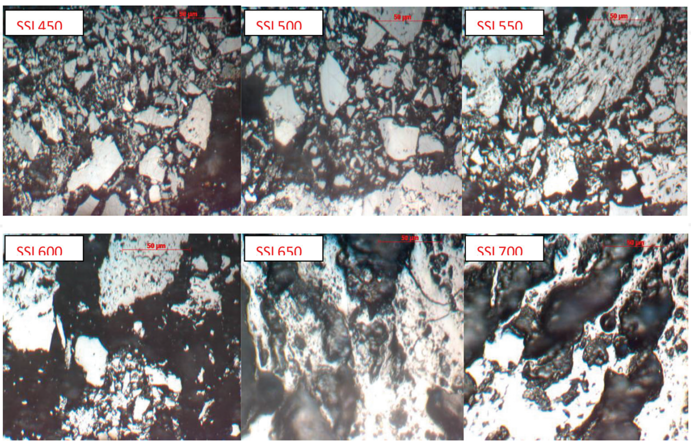

Figure 9. Petrographic pictures of the transition of coal to char for SSL suites.

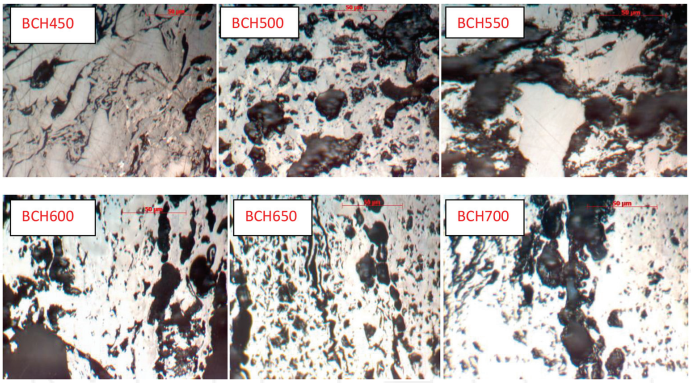

Figure 10. Petrographic pictures of the transition of coal to char for BCH suites.

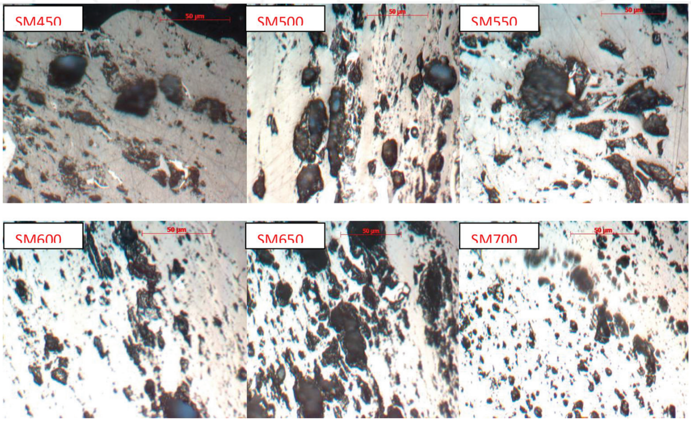

Figure 11. Petrographic pictures of the transition of coal to char for SM suites.

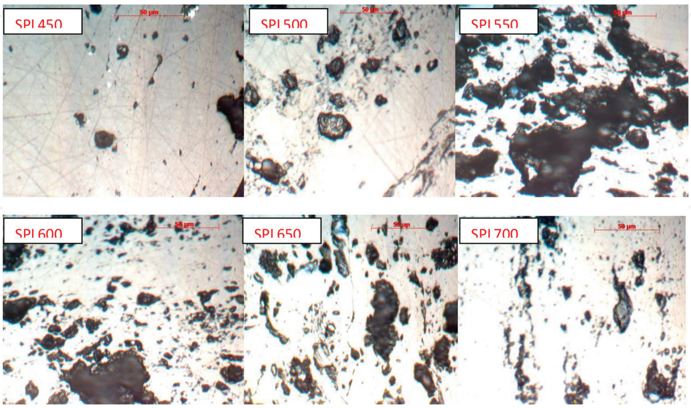

Figure 12. Petrographic pictures of the transition of coal to char for SPL suites.

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