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# Pyrolysis of Low-Rank Coal: From Research to Practice

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## Abstract

Low-rank coal (LRC), as a conventional fossil fuel, has wealth of reserves and a wide range of distribution around the world, and pyrolysis is thought to be an easy way for clean and efficient conversion of LRC. In this chapter, the characteristics and world's reservation of LRC are introduced. Then, the chemical reactions and product formation process during pyrolysis of LRC are described. Meanwhile, how the factors, such as temperature, minerals in coal, heating rate, particle size and atmosphere, influence the pyrolysis process are discussed. Finally, three LRC pyrolysis-based polygeneration systems are illustrated for recent developments on LRC industrial practice.

**Keywords:** low-rank coal, pyrolysis, polygeneration process

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## 1. Introduction: An overview of low-rank coal

### 1.1. Low-rank coal and its characteristics

Coal is a kind of combustible black or brownish-black sedimentary rock. The degree of change undergone by a coal as it matures from peat to anthracite—known as coalification—has an important bearing on its physical and chemical properties and is referred to as the “rank” of the coal [1]. Determined by temperature, burial pressure and the length of time during formation, coal is diverse mainly on its content of moisture, volatile matters and fixed carbon. According to “ISO 11760-2005: Classification of coals,” low-rank coal (LRC) is with bed moisture <75% and mean random vitrinite reflectance ( $\bar{R}_v$ ) <0.5%, which includes lignite (brown coal) and sub-bituminous coal. Additional subcategories of low-rank coals are listed in **Table 1**.

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Subcategory	Description
Low-rank C (Lignite C)	$\bar{R}_r < 0.4\%$ and bed moisture $>35\%$ and $<75\%$ , ash-free basis
Low-rank B (Lignite B)	$\bar{R}_r < 0.4\%$ and bed moisture , ash-free basis
Low-rank A (Sub-bituminous coal)	$0.4 \leq \bar{R}_r < 0.5\%$

**Table 1.** Subcategories of low-rank coal.

Typical LRC is a soft, friable material with a dull, earthy appearance. It is characterized by high moisture, low carbon content and low calorific value, but relatively high volatiles. As to element constitutes of organic matters, LRC has relatively high hydrogen and oxygen content. **Table 2** lists the results of proximate and ultimate analysis of some typical LRC [2–5].

The organic structure of coal is complex and compositionally heterogenetic from different coal deposits. Due to the lower degree of coalification, the organic structure in LRC generally has smaller aromatic cores, but more and longer branched chains linking to them [6–8]. Another critical characteristic of LRC is abundant oxygen-containing functional group as a part of organic matrix [9], and it consists of carbonyl, hydroxyl (including phenolic), carboxyl, methoxyl and other inactive oxygen-containing functional groups(oxygen heterocycles). It was found that oxygen in the form of hydroxyl accounted for the major fraction of the total oxygen, followed by the carbonyl oxygen [10–12], and alkali and alkaline earth metallic (AAEM) species are able to exist as ion-exchangeable cations associated with the carboxyl groups forming part of the organic coal substance. Although the accurate organic structure of LRC has not been proposed yet, compared with higher rank of coal, basic characteristics of LRC organic structure can be summarized as below:

- a. LRC has relatively less aromaticity value, less number of carbon atoms per aromatic lamellae and higher ratio of amorphous carbon.
- b. The aromatic core is not highly condensed but with a proportion of biphenyl and phenylnaphthalene skeleton structure. Each aromatic core is linked by bridged bond, such as polymethylene and ether bridged bonds.
- c. Oxygen is a predominate heteroatom in LRC. Abundant oxygen-containing functional group can directly link to the aromatic core or combine different aromatic cores.

Thus, LRC has more “incompact” macromolecule structure than other higher rank of coal. Those abundant “C–C” and “C–O” bridged linkages could play an important role on depolymerization of LRC macromolecules. Due to the characteristics of organic structure, LRC tends to have better reactivity than higher rank of coal, and it could be good material for chemical conversion, such as pyrolysis and gasification.

Categories	Source	Proximate analysis (wt%)				Ultimate analysis (wt%, dry ash-free basis)				
		M <sub>ar</sub>	A <sub>d</sub>	V <sub>d</sub>	FC <sub>d</sub> <sup>*</sup>	C	H	N	S	O <sup>*</sup>
Lignite	Western Australia	64.9	3.1	52.6	44.3	66.4	5.1	0.48	0.21	25.5
	Morwell, Australia	15.3	5.4	35.3	59.3	74.85	4.96	1.11	0.80	18.28
	Indonesia	32.70	7.56	48.83	43.60	58.09	3.39	0.46	0.17	13.90
	Schleenhain, Germany	15.5 (dried)	11.6	52.4	36.0	70.6	5.1	-	4.3	20.0 (N+O)
	Xiaolongtan, China	14.04	10.42	45.14	44.44	53.86	3.65	1.41	1.27	39.81
	Pingzhuang, China	10.91	29.08	30.56	40.36	46.24	2.78	0.68	1.20	49.1
Sub-bituminous coal	Indonesia	12.41	9.58	42.06	48.36	72.13	6.67	1.4	0.22	19.58
	Diyarbakır-Hazro, Turkey	1.32 (ad)	43.80	25.71	30.49	70.40	5.65	0.68	7.12	16.15
	India	4.57 (dried)	13.49	38.67	47.84	60.12	6.84	1.47	0.46	31.11
	Shenfu, China	5.24 (ad)	6.95	29.65	63.40	79.38	4.78	1.71	0.36	13.77
	Hongliulin, China	10.60	9.45	32.65	57.90	80.45	4.80	1.09	0.40	13.26
	Zhundong, China	8.79 (ad)	5.68	32.96	61.36	75.23	3.18	0.70	0.53	20.36

\*By difference.

**Table 2.** Proximate and ultimate analysis of some LRC.

## 1.2. Distribution and utilization around the world

At the end of 2015, the total coal reservation around the world has proved to be 891,531 million tonnes, in which LRC (sub-bituminous and lignite) is 488,332 million tonnes, accounting for 54.77% of the total. As to the distribution, above 70% of LRC reserves in United States (26.37%), Russian Federation (22.10%), China (10.71%), Germany (8.29%) and Australia (8.05%) [13].

Although LRC's recoverable reserves are a lot, their high moisture content, greater tendency to combust spontaneously, high degree of weathering and the dusting characteristics restrict widespread use of such coals [14]. But for a few countries, LRC can be important in the respective national energy mix. Possible reasons are mainly on the considerations of native fossil resource endowment, security of supply, price and industry maintenance [15].

Traditionally, the major way for LRC utilization is direct burning, and its chemical energy can be converted into heat, power or electricity. Problems, such as emissions of  $\text{CO}_2$ ,  $\text{SO}_x$ ,  $\text{NO}_x$ , heavy metal and microdust, may easily be caused during such traditional utilizations of LRC. With the improvement of environmental awareness, cleaner and more efficient ways for LRC utilization are desirable. Among them, technologies based on pyrolysis are promising ways for LRC being converted into not only clean fuels but also chemicals. Since the industrial development of coal pyrolysis at early nineteenth century, people have been seeking ways for high yield and quality of pyrolytic products, and lots of views on pyrolysis mechanism or impact factors are proposed. According to these researches, new technologies and equipment are carried out as well. Recently, with the increasing pursue of cleanliness and efficiency during process, pyrolysis of LRC tends to combine with other technology forming series of polygenerative processes. And in this chapter, some new views and new technologies or ideas during recent years on LRC pyrolysis have been reviewed.

## 2. Pyrolysis of low-rank coal and its products

### 2.1. Pyrolysis of low-rank coal and its products

LRC pyrolysis is a complex process with both physical changes and chemical reactions at elevated temperatures in the absence of oxygen or in an inert atmosphere. And it is thought to be a promising and convenient method for direct generation of clean fuels and high-valuable chemicals from the abundant hydrocarbons in LRC. Pyrolysis reactions are also an important medium process for LRC conversion technologies, such as coking, combustion, gasification and direct liquefaction. Referred to different standards, LRC pyrolysis can be classified as follows [16]:

- According to the final temperature, there are low-temperature pyrolysis (450–650°C), medium-temperature pyrolysis (600–900°C), high-temperature pyrolysis (900–1200°C) and ultrahigh-temperature pyrolysis (>1200°C).

- According to heating rate, there are slow pyrolysis (1°C/s), medium-speed pyrolysis (5–100°C/s), fast pyrolysis (500–10<sup>6</sup>°C/s) and flash pyrolysis (>10<sup>6</sup>°C/s).
- According to forms, there are normal (or traditional) pyrolysis, plasma pyrolysis, hydro-pyrolysis and catalytic pyrolysis.

During pyrolysis, the organic structures in LRC are cracked by heat and amount of fragments devolatilized from the particles. Cooled by cold medium, the condensable part of volatiles forms as tar; the incondensable part forms as gas. Simultaneously, there also remain some nonvolatiles, which are solid products (coke or char).

The yields and properties of pyrolytic products are determined not only by the properties of the raw LRC but also by the operating condition of pyrolysis. As to the normal pyrolysis of LRC, temperature can be an important factor of what needs to be considered for desirable products. For example, low-temperature pyrolysis is usually for tar production, while medium-temperature pyrolysis and high-temperature pyrolysis are for char and coke production, respectively. For plasma pyrolysis, coal is heated rapidly to ultrahigh temperatures; if conditions are favorable, the emitted volatiles will consist mainly of acetylene [17]. However, for better recovery of the abundant volatiles in LRC, low-temperature pyrolysis and medium-temperature pyrolysis are preferred.

Due to the low degree of coalification, the products generated from LRC pyrolysis are also differed from the ones generated from higher rank of coal. The abundant oxygen-containing functional groups bring more moisture and oxygen-containing compounds (especially of phenols) into tars [18]. But after physical separation, tars are able to be good raw materials for production of transport fuels. On the contrary, little oxygen remains in char or coke, which elevates their calorific value and reduces the tendency to combust spontaneously. In addition, most of the pollutants (such as sulfur, volatile of organics) and heavy metals (such as mercury) are removed so that char can be much cleaner as solid fuels than the raw LRC [16]. Moreover, the developed pore structure is also a typical character of chars derived from LRC pyrolysis. With further activation methods, chars can be served as adsorbing materials or catalyst supports [19–21]. Gas products, derived from LRC pyrolysis, are full of H<sub>2</sub>, CO and CH<sub>4</sub>, which are able to be fuels or chemical synthesis after purification. However, on account of compositionally heterogeneity of LRC in different deposits, suitable ways for the development of downstream products need to be considered and tested individually.

## **2.2. Reactions during pyrolysis and the formation of products**

### *2.2.1. Reactions during LRC pyrolysis*

Chemical reactions during LRC pyrolysis are thought to be a series of complex sequential and parallel free radical reactions [22]. It involves the generations of radical fragments from the thermal decomposition of organic macromolecules and the generations of volatiles and residues (coke or char) from reactions between radical fragments [23].

In general, reactions during pyrolysis come from the thermal instability of structures. The thermostability of organic structure is much determined by the bond energy between atoms.

Generally, the thermostability of hydrocarbons is decreasing as follows: condensed aromatics > aromatics > cyclic hydrocarbons > olefins > alkanes. And this is also suitable for LRC pyrolysis [24]. Moreover, because of the conjugated structure, aromatic heteroatom (such as sulfur, nitrogen and oxygen) structures are much more thermostable than aliphatic ones. And it is also reported that the fragmentation progress of LRC is more significant than higher rank of coal [25, 26]. The instable structures in the macromolecules of LRC homolytic cleave into radicals, and small molecules are generated with stabilization of these radicals, while the stable structures associated with condensed products remain in char or coke. Due to the complexity of organic structure, there are no universal or accurate models for the description of reactions during LRC pyrolysis. But with mounts of studies, the types of pyrolysis reactions are as follows:

- Primary reactions: "Primary" indicates the reactions directly take place in the macromolecules of LRC. During pyrolysis, cracking reactions are the dominating primary reactions. According to the organic structures in the macromolecules of LRC, the four probable types of cracking reaction are listed below [24]:
  - (i) Cracking of bridged bond: In the organic structure of LRC, there are many bridged bonds, such as  $-\text{CH}_2-$ ,  $-\text{O}-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{S}-\text{S}-$  etc., linking to the aromatic cores. The bond energy of these "bridges" is relatively low, and they can be more easily damaged by heat or other radicals to generate new radicals. This is also the key for depolymerization of macromolecules in LRC [18]. And the thermal degradation of sulfurated and oxygenated cross-links was more substantial than that of alkyl linkages [27].
  - (ii) Cracking of aliphatic side chain: The stability of aliphatic side chain decreases with the increasing number of carbon and aromatic rings. Long side chains tend to crack to generate radicals or gaseous hydrocarbons of small molecules.
  - (iii) Cracking of aliphatics: The low molecular weight compounds with mainly aliphatic structure are melted and simultaneously cracked to generate volatiles.
  - (iv) Cracking of heteroatom functional groups: Sulfur, nitrogen and especially oxygen are the major heteroatoms in the organic structure of LRC. Aliphatic heteroatom structures are able to decompose at relative low temperature, while the temperature for decomposition of aromatic heteroatom structures needs to be 500°C or higher.
- Secondary reactions : During the process of devolatilization, high temperature in the region of both coal particles and surroundings will facilitate for secondary reactions of volatiles (primary volatiles). Major secondary reactions are listed below:
  - (i) Cracking reactions: The hydrocarbons derived from primary reactions are able to further crack at high-temperature circumstances. Consequently, more compounds with smaller molecular weight are generated.
  - (ii) Dehydrogenation reactions: Cycloalkanes can be converted into cyclenes or further into aromatics by dehydrogenation reactions Hydroaromatics can be added aromatic rings. Simultaneously, hydrogen gas is generated.

- (iii) Hydrogenation reactions: Some chemical active heteroatom-containing compounds may be attacked by hydrogen radicals. As a result, the heteroatoms are removed and form as gas molecules (such as  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ).
- (iv) Condensation reactions: Aromatics in volatiles may condense into polycyclic aromatic hydrocarbons (PAHs).
- Condensation reactions: With the increasing number of aromatic rings, the volatility of aromatics decreases. The nonvolatile parts will condense and release hydrogen gas, and it is more obvious at temperature above  $700^\circ\text{C}$ .

Besides the reactions listed above, there are also reactions, such as hydrogen transfer, rearrangements and cross-linking reactions, for final stabilization of free radicals.

### 2.2.2. Pyrolysis process and formation of products

Due to the diversity on thermostability of organic structure in LRC, the pyrolysis process is mainly determined by temperature. With the raising temperature, the extents of thermal cracking of organic macromolecules in LRC increase, and the constituents of pyrolytic products vary simultaneously.

Generally, there are few changes on the major hydrocarbon structures in LRC below  $300^\circ\text{C}$ . But noncovalent bonds in LRC dissociate and devolatilize. Saxena [28] summarized that pyrolysis reactions started with the cleavage of weak bonds. Due to the minimum amount of energy requirement for overcome the C–C bond energy, major pyrolysis reactions would not commence until the temperature was around  $400^\circ\text{C}$ . Guan [29] studied the yield and properties of the products derived from lignite (Huolinhe, China) pyrolysis at temperature below  $400^\circ\text{C}$ . It was observed that the condensate volatile was visibly colorless and transparent water with very a little value of chemical oxygen demand (COD<sub>cr</sub>), volatile phenol and ammonia nitrogen at pyrolysis temperature below  $200^\circ\text{C}$ . But when temperature is above  $250^\circ\text{C}$ , organic matters are obviously found in the condensates and the contents increase with the increasing pyrolysis temperature. The condensates derived above  $350^\circ\text{C}$  show as a mixture with oil and water layer. Analyzed by surface structure of solid residues below  $200^\circ\text{C}$ , no evident changes of phenolic hydroxyl and carboxyl groups on the surface were observed. When temperature is above  $250^\circ\text{C}$ , despite the major hydrocarbon structures are changed, some unstable functional group and side chain, such as carboxyl, aliphatic side chain and ether structure, are starting to crack and decompose. As to the organics in the condensates, alkanes, olefins, aromatics and phenols are obviously detected. Meanwhile, due to the low thermostability of carboxyl and carboxylate, it will decompose into  $\text{CO}_2$  around  $250^\circ\text{C}$ .

During the process of LRC pyrolysis, the major organic volatile-producing stage is  $350\text{--}600^\circ\text{C}$ . When temperature raises to above  $350^\circ\text{C}$ , the linkages of polymethylene or ether oxygen, side chain or heteroatom-containing functional group are obviously damaged by heat, and some hydroaromatic rings start to dehydrogenate. As a result, high-reactive fragments and radicals are generated. Then, radicals may be stabilized by hydrogen transfer, rearrangements, cross-linking reactions, condensation reactions or capturing hydrogen by colliding with other fragments or radicals. And the primary products that directly generated from the macromolecules



will be secondarily reacted during the devolatilization. Zhan et al. [30] investigated the mechanism of initial thermal decomposition associated with pyrolysis of a kind of sub-bituminous coal by molecular dynamic simulation. The calculation results showed that the primary decomposition reactions of Hatcher sub-bituminous model [27] began with intramolecular changes such as the cleavage of unstable C—C and C—O bonds. Castro-Marcano et al. [31] utilized ReaxFF reactive force field to perform pyrolysis simulations on a large-scale molecular model of coal [32]. It was found that pyrolysis mainly initiated by release of hydroxyl groups and dehydrogenation of hydroaromatic structures followed by breakage of heteroatom-containing cross-links. And further analysis of ReaxFF simulations show that aryl and alkyl C—S bonds are weaker than aryl and alkyl C—C bonds. Hence, the cleavage of the C—S bonds resulted in more extensive fragmentation leading to larger quantities of aliphatic and aromatic structures. Li et al. [33] discussed the mechanism of coal-based model compound (anisole, phenyl ethyl ether and p-methyl anisole) by detecting the reactants, radicals and products using vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry. It was found that PhO—C homolytic bond scission was the first step for the radical reaction, while  $\beta$ -H was an important factor for the nonradical reactions.

Tromp [34] and Miura [23] believe that, as shown in **Figure 1a**, the primary devolatilization reactions are very rapid reactions, which consist of radical formation reactions, polymerization-condensation reactions, radical recombination reactions, hydrogen addition reactions, etc., and subsequent secondary gas-phase reactions are decomposition reactions of the volatile products produced through the primary reactions. And the char particles come from the polymerization and condensation reactions. But with recent researches, especially on the radicals in pyrolytic products and flash pyrolysis of LRC, it is not able to be observed the devolatilization of a whole coal particle and the absent generation of char. Wu et al. [35] measured the free radicals in some LRC pyrolytic chars at different temperatures (350–600°C) by electron paramagnetic resonance (EPR). It was found radicals also existed in chars. Liu [36] believes that a part of coal structure will be recombined simultaneously with devolatilization. During the recombination, covalent bonds still crack to generate smaller molecules and condensed as chars (as shown in **Figure 1b**). As to the tars, He et al. [37] examined the reactivity of fast pyrolysis tars and observed that tars contained high concentrations of radicals and were highly reactive at temperatures higher than 400°C to generate more radicals and form coke. Thus, the content of heavy components increased which would reduce the quality of tars.

During the process of pyrolysis and devolatilization, both physical and chemical properties of pyrolytic residues also vary with the temperature. As to LRC pyrolytic solid residues, typical changes are on the oxygen content and pore's structures. As to noncaking coal (such as lignite), they almost inherit the main skeleton structures of the raw coal during pyrolysis. Wu [38] studied the properties' evolution of Hesigewula lignite (Inner Mongolia, China) pyrolytic solid residues via temperature (75–550°C). As shown in **Figure 2a**, the content of carbon in solid residue is increasing with the increasing temperature, while oxygen content is dramatically decreasing. The decreasing oxygen content mainly comes from the decomposition of oxygen-containing functional group and crystal water of minerals. Generally, the thermostability of oxygen-containing functional group is decreasing as oxygen heterocyclic

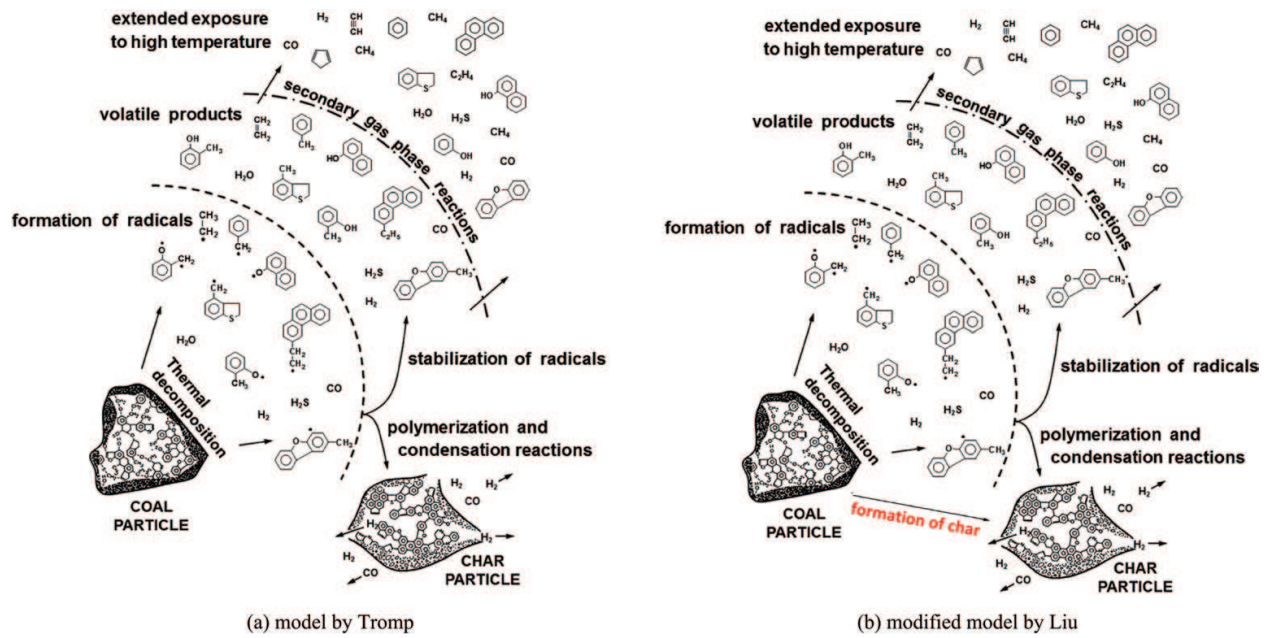


Figure 1. The mechanism model of coal pyrolysis. (a) Model by Tromp; (b) modified model by Liu.

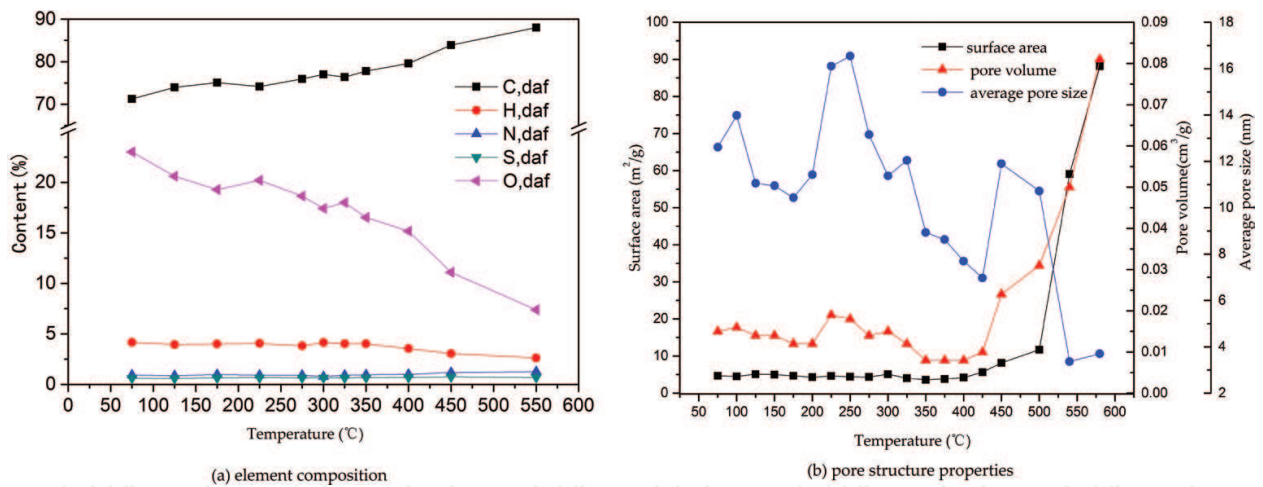


Figure 2. The evolution of element composition and pore structure properties during pyrolytic solid residue. (a) Element composition; (b) pore structure properties.

ring > hydroxyl > carbonyl > carboxyl > methoxyl. The thermal decomposition of oxygen-containing functional groups generates oxygen-containing gas, such as  $H_2O$ ,  $CO$ ,  $CO_2$  and  $COS$ . And with the condensation process,  $H_2O$  will be liquefied accompany with tars. Both pyrolysis and devolatilization will strengthen the pore structures in pyrolytic solid residues. As shown in **Figure 2b**, the surface area and pore volume increase obviously after  $400^\circ C$ . Higher temperature will further facilitate dehydrogenation and condensation of aromatic cores. But as to coal with caking property, coal particles will soften and melt forming colloids together with gas-liquid-solid three-phase during the pyrolysis process. With devolatilization, colloids are swelling and finally solidifying as char or coke [39].

In general, pyrolysis of LRC could be described as a process of thermostabilization accompany with releasing thermos-unstable substances. The pyrolytic products and their source are summarized in **Table 3**.

### 2.3. The influence factors during LRC pyrolysis

As mentioned above, LRC pyrolysis and its formation of pyrolytic products are mainly concerned with chemical reactions and volatile transfer process. Although the factors that influence LRC pyrolysis are various and complex, these factors, besides the composition of raw coal itself, ultimately influence the chemical reactions and volatile transfer process. And here, some important factors and their effects on LRC pyrolysis are discussed as follows.

#### 2.3.1. Temperature

As mentioned above, thermal cleavage of covalent bonds in LRC is a single step and mainly determined by the temperature. However, the reactions of the volatiles involve multiple steps and can be influenced by many factors especially for the gas phase temperature, which is generally higher than that of the coal [40]. Generally, without effective cracking of organics at temperature higher than 400°C, desirable product yield (especially for liquid products) could not be achieved. However, higher temperature can not only promote the depolymerization of LRC macromolecules but also the secondary reactions of volatiles. Due to the competition of primary and secondary reactions on temperature, there exists a maximum yield of liquid product at a certain temperature (usually 450–550°C) according to the results of most experiments. But if the condition of volatile transfer is improved, higher yield of liquid products is also able to be achieved. For example, Zhang et al. [41] proposed and tested an indirectly

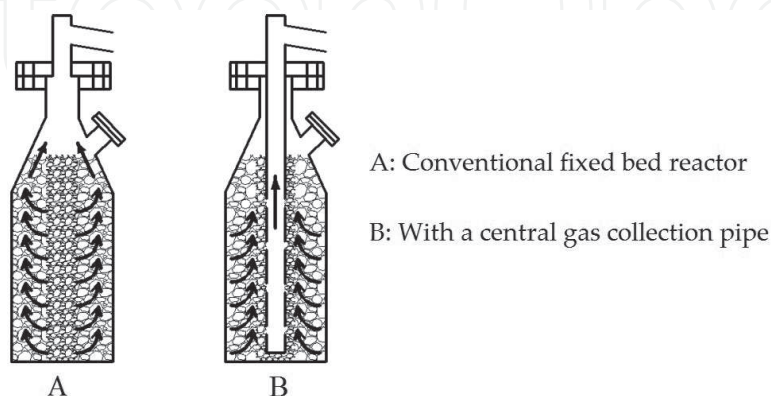
Products	Source	Process
Tar	Dissociative organics, side chains, organic units connecting by weak bonds	Distillation + pyrolysis
CO <sub>2</sub>	Carboxyl and carbonates	Decomposition of carboxyl and carbonates minerals
CO (<500°C)	Carbonyl, ether	Decarbonylation
CO (>500°C)	Oxygen heterocyclic rings	Ring-opening reactions
H <sub>2</sub> O	Moisture, hydroxyl, crystal water of minerals	Evaporation, Dehydroxylation, decomposition of minerals
CH <sub>4</sub> , C <sub>n</sub> H <sub>m</sub> (light hydrocarbons)	Aliphatic or aliphatic side chain	Dealkylation and thermocracking
H <sub>2</sub>	Hydroaromatics	Dehydrogenation and condensation
Char or coke	Solid residue and PAHs	Pyrolytic remains and condensation of PAHs

**Table 3.** The products and their major source during LRC pyrolysis.

heated fixed-bed reactor with internals to regulate the pyrolysis gas flow direction inside the reactor. As shown in **Figure 3**, the central gas collection pipe leads to the different flow patterns of the pyrolytic volatile inside the reactor, which does not only avoid deep secondary cracking from the annular layer, but also condense and capture the heavy species in volatiles by relative low-temperature core layer. As a result, the tar yield still increases from 600 to 1000°C in reactor B, while the tar yield decreases with the same temperature region in reactor A. At the tested highest temperature of 1000°C, the tar yield in reactor B was 2.23 times of that in reactor A.

### 2.3.2. Minerals in coal

Minerals in LRC are various. Some minerals could decompose or work catalytically, and some are inactive during pyrolysis. Many studies have been done by selective demineralization of coal with acids to investigate the effect of individual elements in coal on pyrolysis yield and distribution of products. The brown coal in the Latrobe Valley, Victoria, Australia, has a very low ash yield and contains highly dispersed alkali and alkaline earth metallic (AAEM) species, either as carboxylates forming part of its organic matter or as NaCl dissolved in its moisture [42]. Li [43] concluded that the AAEM cations in the coal substrate were able to cause decrease in the yields of tar and/or large aromatic rings. The ion-exchangeable AAEM species in coal also seem to change the aromatic/aliphatic composition of the resulting tars. Liu et al. [44] investigated the effect of mineral matter in coal on reactivity and kinetic characteristics of LRC pyrolysis, which found that inherent mineral had no evident effect on the reactivity and kinetics of pyrolysis. But CaO, K<sub>2</sub>CO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> could work catalytically during pyrolysis of LRC, and their effects were closely related to temperature region and coal types. Zeng et al. [45] studied the influence of minerals on pyrolysis yield and content of phenols. Under the same operating condition, acid-washed (demineralization) coal has higher tar yields, but lower yields of char and gas at 500°C. It was inferred that the minerals in coal had catalytic effects on the generation of CO and ethylene, and the decomposition of tar. Meanwhile, the decomposition of intermediates or the producing of final phenols during coal pyrolysis may be suppressed. However, due to the differences in composition and properties for different



**Figure 3.** Schematic of fixed reactors with and without a central gas collection pipe. (A) Conventional fixed bed reactor; (B) with a central gas collection pipe.

coals, there were discrepancies in the results obtained by different researchers for different coal samples using different methods.

### *2.3.3. Heating rate and particle size of coal*

Heat transfer is an important factor which directly influences the extent of LRC's pyrolysis reactions. Except microwave-assisted heating, the heat is transferring from the outside to the inside of the particle. It is known that, if the temperature around a pyrolyzing coal particle exceeds a threshold value (for thermal cracking reactions), external heat transfer controls the extent of pyrolysis [46]. Nevertheless, heating rate and particle size of coal can greatly influence the intensity and efficiency of heat transfer.

Heating rate mainly influences the course of temperature and time. Generally, the difference of heating rate in half order of magnitude could have tiny differences on pyrolysis yields and distribution of pyrolytic products. Thus, the comparisons of effects brought by heating rates are usually between slow, medium-speed, fast and flash pyrolysis of LRC. Higher heating rate means the coal particles are to be heated to the temperature in shorter time by the higher intensity of heat. Then the organic structures in LRC are damaged more quickly and generate mounts of volatiles in particles. Observed from the differential thermogravimetric (DTG) curves, the weight loss region during pyrolysis of LRC is shifting to the high-temperature region with increasing heating rate, and the products' evolutions are overlapped [47]. Some believe that higher heating rate increases the pressure of volatiles in particles, which provides stronger driving force for devolatilization from particles to outer space and shorten the residence time during heat transfer of fragments in particles. Therefore, the secondary reaction could be weakened and finally obtain more liquid and less gas products. But some believe that higher heating rate does not only mean higher temperature of coal particle but also the circumstances of devolatilization (in char and in outer space). Due to the opposite direction of heat and mass transfer, volatiles are heated again, which benefits for their secondary reactions [40]. The both views do make sense, while the key point is the residence time of fragments in high-temperature region. However, without a suitable residence time for secondary cracking, some active and high mass weight fragments will bring in tars which will probably lead further condensations and sacrifice the quality of liquid products [48].

Heating rate brings the intensity of heating, while particle size determines the effect of heating. In fact, the heat conductivity of LRC is poor. The particle size can greatly influence the yield and properties of pyrolytic products. The rate at which volatile matter is produced during pyrolysis is demonstrated to be controlled not at all by mass transfer, but by heat conduction to a moving reaction front inside a coal particle, provided its diameter exceeds  $\sim 3$  mm [49]. When the particle size increases, it will not only increase the time of heat transfer to the centre of the particles but also bring high tendency of secondary reactions due to the temperature difference from the surface to the centre of particles. Thus, small particles are preferable for fast heating, but the deposit of small particles in the reaction bed would possibly increase the pressure drop and hinder the devolatilization. A proper reactor is needed to be considered for pyrolysis of small particle size of LRC, while as to production of lump char, slow rate of heating is desirable of pyrolysis of lump LRC.

#### 2.3.4. Atmosphere

Generally, pyrolysis of LRC is in an inert atmosphere, such as  $N_2$ , He and Ar. But in order to increase the yields or improve the quality of pyrolytic products, lots of studies have been done on pyrolysis in reducing atmosphere (active atmosphere), such as  $H_2$ , CO and  $CH_4$ . Liu et al. [50] investigated the influence of atmosphere on pyrolysis of a sub-bituminous coal under  $N_2$ ,  $H_2$ ,  $CH_4$  and  $H_2$ -CO (2:1) atmosphere. It was found that the tar yield at different atmosphere was increasing as  $H_2 > CH_4 > H_2$ -CO  $>$   $N_2$ , and more saturates were generated in active atmosphere than in  $N_2$ . Wang et al. [51] found that higher tar yield was achieved in  $CO_2$  than  $H_2$ ,  $CH_4$  or  $N_2$ . And tars from  $CH_4$  atmosphere had relatively lower phenol content but higher cresol and  $C_2$  alkyl-substituted phenols compared with those from other atmosphere. Meanwhile, reactive atmosphere is beneficial for heteroatom removal during pyrolysis. It was found that CO promoted the pyritic sulfur to form as COS;  $CH_4$  and  $CO_2$  inhibited the evolution of sulfur-containing gases at temperatures below  $600^\circ C$ , but, respectively, promoted the formation of COS and  $H_2S$  at higher temperature; and  $H_2$  was more likely to promote the sulfur transferring to the gaseous product, especially as  $H_2S$  [52]. As to the mechanism of effects brought by active gas, many agree that active gas produces new radicals to stabilize the volatile fragments from condensations, which increases the yield and qualities of liquid products [53]. And improving the partial pressure or with the help of catalyst can facilitate the reactivity and efficiency of reactive gas. In order to improve the activity of  $CH_4$ , Hu et al. [54-57] propose a series of studies on integrated process of coal pyrolysis with  $CO_2$ /steam reforming of methane, which improves greatly of liquid yields compared with pyrolysis simply in reactive atmosphere.

#### 2.4. Further research and interest on LRC pyrolysis

In general, the process of product formation during LRC pyrolysis is complex. It includes both chemical reactions and heat/mass transfer process. Although thousands of studies have been done on pyrolysis, there are still many problems need to be further considered:

- Pyrolysis reactions: Due to the influence of secondary reactions and complexity of coal macromolecules, it is also difficult for observing the primary reactions during pyrolysis. Recent strategies for LRC pyrolysis mechanism and process are to study the relatively simple coal-based compounds or use in situ analysis methods.
- Dynamics, heat/mass transfer: As discussed above, it is a comprehensive process with lots of factors for the final yields and properties of pyrolytic productions. However, pyrolysis dynamics of LRC is developed generally according to the thermogravimetric results. It only represents the dynamics of devolatilization, but some reactions remain in the solid (such as formation of char). It may be not beneficial for the design of pyrolysis reactor. Thus, more accurate dynamic models need to be established [36]. The heat and mass transfer process also dramatically influence the pyrolysis process. Better understanding of the two processes will also greatly help for better designing the reactors or their internals.
- Catalyst: Pyrolysis of LRC is a direct liquefaction process. Volatiles generated from pyrolysis are firstly cooled to obtain liquid products. But the liquid products are complex, high moisture and relative poor quality. Traditionally, the liquid products need to be heated for

further conversion. If the volatiles could be in situ converted during pyrolysis, it would be great efficient for the whole process. Thus, proper catalysts are the key points for in situ catalytic conversions of volatiles. Together with active atmosphere, integrated process of coal pyrolysis with catalytic conversion could be an important method for utilization of LRC.

### 3. Pyrolysis and its polygeneration technology

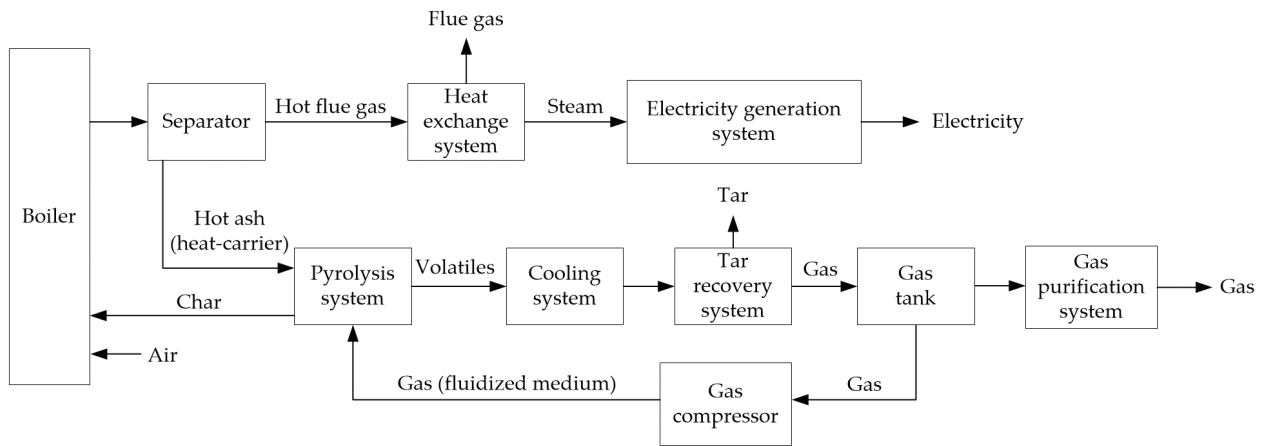
In order to meet the needs of continuous operation for industrial applications, various technologies on pyrolysis of LRC are proposed and tested. According to the motion state of coal particles, pyrolysis reactor can be designed as moving bed, fluidized bed or entrained bed. As to heating method, there are internal heating (coal contact directly with the heating source), external heating or hybrid heating. And for heat carrier, it may be solid, gas or the both.

Since nineteenth century, pyrolysis of LRC has been industrially applied for fuels or chemicals production. During 1910–1950s, the low-temperature pyrolysis of LRC was quickly and well developed in Germany, typically producing liquid fuels by lignite pyrolysis in three-stage Lurgi. Whereafter, with the development of petroleum chemical industry, large-scale industrial production temporarily was interrupted. But due to strategic needs, a series of fundamental studies and industrial tests have been carried out. Typical technologies of LRC pyrolysis developed during this period are COED (multistage fluidized bed, USA), Toscoal (horizontal rotary kiln, ceramic ball as heat carrier, USA), Garret (entrained flow bed, char as heat carrier, USA), L-R (moving bed, char as heat carrier, Germany), CSIRO (double fluidized bed, char as heat carrier, Australia), DG (moving bed, char as heat carrier, China), etc. From 1990s, the increasing price of crude promoted a new round of researches and development of LRC pyrolysis around the world. But large scale of industrial tests were mainly reported in China, such as continuous vertical retorts (SH series, SJ series and ZNZL series), rotary kiln technology (by China Coal Research Institute), Guofu retorts (by Beijing Guodianfutong Science and Development Co., Ltd. China), BT technology (by Institute of Process Engineering, Chinese Academy of Science, PR China), etc. Other typical technologies are LFC (Bluegrass Coal Development Company, USA) and CCI (Covert Coal Company, USA).

Recently, with the increasing concern on environment and efficiency, cleaner and more efficient technologies of LRC pyrolysis are required. Due to the best use of chemical resources in LRC, polygeneration system based on pyrolysis is a good way to meet the requirements. According to properties of the raw coal and market demands, lots of conceptions have been carried out [58, 59]. The major concept is for clean fuels and chemicals or materials of high added value. However, minority of them is applied or industrial tested. Here, three application examples of LRC-pyrolysis-based polygeneration technologies are briefly introduced.

#### 3.1. Heat-electricity-gas-tar polygeneration system

Heat-electricity-gas-tar polygeneration system is designed by Zhejiang University, China. As shown in **Figure 4**, LRC is heated to around 600°C by hot ash in a circulating fluidized bed



**Figure 4.** Circulating fluidized bed polygeneration system.

reactor. The produced volatiles sequentially go through cooling system and tar recovery system to obtain tar and gas. A part of gas is conveyed by gas compressor to the pyrolysis system as fluidized medium. And the rest part of gas is used for methanol synthesis after purification by purification system. The produced char is moved into the boiler and burns. And the high-temperature ash and hot flue gas are separated in separator. A part of hot ash goes into pyrolysis system as solid heat carrier. And the energy of hot flue gas is recovered by producing steam in heat exchange system. The produced steam is used for electricity generation. Recently, the system has developed 12 and 25 MW circulating fluidized bed polygeneration system and constructed a 75 t/h testing apparatus [60].

### 3.2. Clean solid-liquid fuels polygeneration system

Based on DG process, Dalian University of Technology (China), Shenmu Fuyou Energy Technology Co., Ltd. (China) and China National Chemical Engineering Co., Ltd. design and construct a  $60 \times 10^4$  t/a LRC pyrolysis and  $12 \times 10^4$  t/a medium/low-temperature tar processing polygeneration system [61]. As shown in **Figure 5**, the raw coal (sub-bituminous coal, particle size  $< 6$  mm) is firstly dried by the hot flue gas and mixed with hot char fed into the moving bed pyrolysis reactor (around  $500^\circ\text{C}$ ). A part of produced char is moved into char heating and lifting system and partial combusted to be heat carrier ( $750\text{--}800^\circ\text{C}$ ). And the hot flue gas is cooled to around  $500^\circ\text{C}$  for the desiccation of raw coal. Another part of char is going to shaping system to generate char balls, which are clean solid fuels for civil use. The produced volatiles sequentially go through purification system and cooling and recovery system to obtain tar, gas and water. Gas fraction is used to generate  $\text{H}_2$  by pressure swing adsorption (PSA) process. And  $\text{H}_2$  is utilized for hydrogenation and refining of tar by a total fraction hydrogenation technology. Finally, clean liquid fuels can be generated.

### 3.3. Coal to calcium carbide/acetylene polygeneration system

Coal to acetylene polygeneration system is proposed by Shenwu Environmental Technology Co., Ltd. (China). Traditional calcium carbide production is using char or coke as carbon



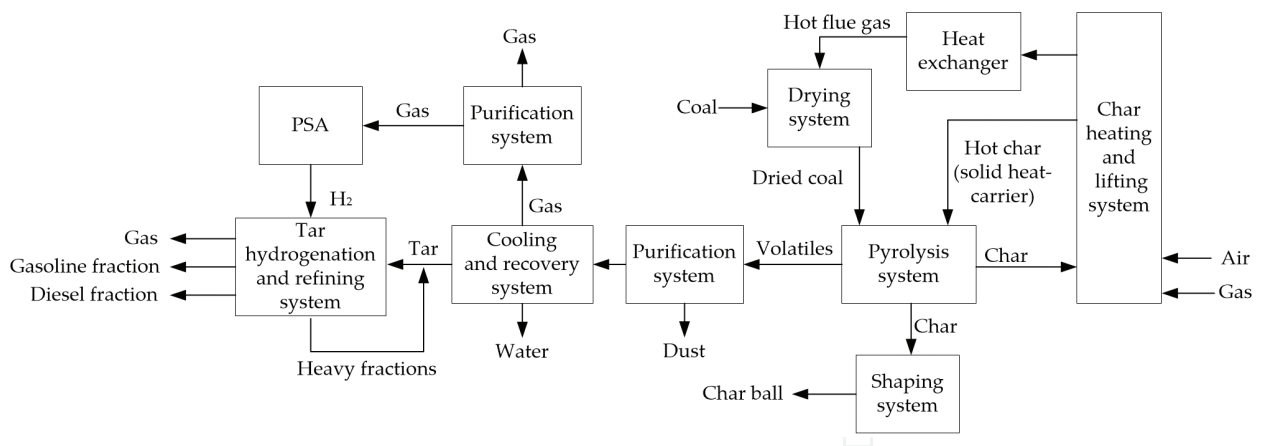


Figure 5. Clean solid-liquid fuels polygeneration system.

source [62]. In this system (Figure 6), lower price of LRC is firstly mixed with quick lime and proportionally shaped as calcium-coal ball. Then, calcium-coal balls are conveyed into a rotary hearth furnace for pyrolysis. The generated volatiles are going to tar and gas recovery system to obtain tar and gas. The produced calcium-char balls are conveyed in thermal state to calcium carbide production system. And the exhaust produced by calcium carbide furnace is used for calcining the limestone after purification. Moreover, the calcium carbide can be generated acetylene with water. Recently, based on the system, an  $80 \times 10^4$  t/a polyethylene project is under construction in Baotou, China. Besides polyethylene, liquefied natural gas, tar and polybutylene are also by-produced. But due to the high content of CO in exhaust produced by calcium carbide furnace, it can be used for glycol synthesis with H<sub>2</sub> from gas produced by pyrolysis in the future.

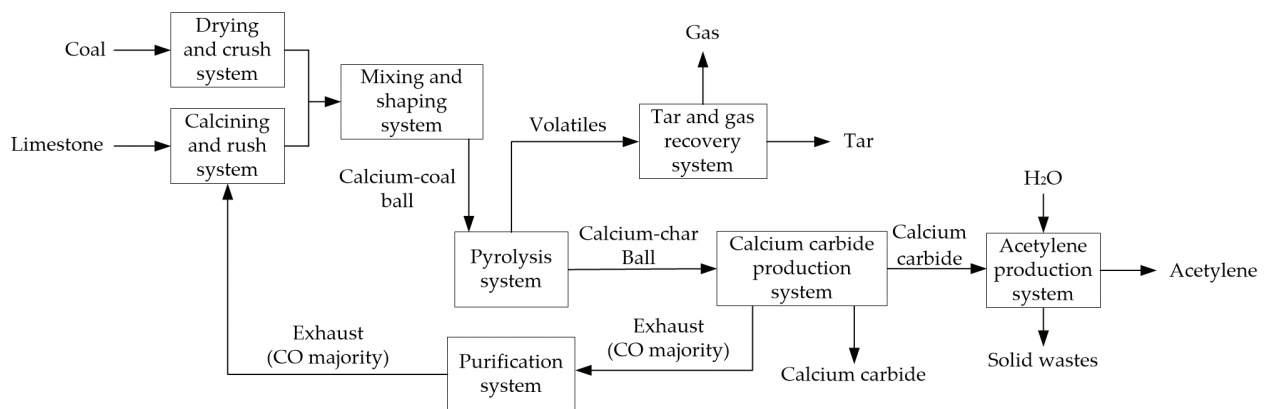


Figure 6. Coal to calcium carbide/acetylene polygeneration system.

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