COAL TECHNOLOGY (II)

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Summary

This topic concentrates on the methods of thermal processing of coal: thermal decomposition, combustion, gasification, carbonization, and liquefaction. In essence, these processing methods are based on how to utilize the combustible, organic mass in the coal, which can proceed with two kinds of reactions, i.e. decomposition or condensation. The proceeding reactions vary with different reaction conditions. But the methods of thermal processing of coal have the following general rule. Coal, when heated, will first decompose to fragments, with different sizes of molecules, which form products of gas, liquid, and solid at room temperature. This process is termed combustion if oxygen exists, as the volatile matter of small molecules is first ignited to release heat to start combustion. The process is termed carbonization if coal is heated when isolated from air. The volatile matter comes out as gas and coal tar, while the macromolecular matter is left over under further condensation to form semi-coke. Low temperature carbonization or thermal decomposition are the terms for processes proceeding under 550℃. Bituminous coals, often processed in this manner, but at 950℃, can form coke for metallurgical purposes. For this reason, it is termed carbonization.

Thermal processing of coals always results in some amount of gaseous product, consisting of CO, H_2O, and light hydrocarbons. If these thermal processes are produced under an atmosphere of steam and oxygen, the solid macromolecule matter and light hydrocarbon will still further react with steam and oxygen to form combustible gases, such as hydrogen and carbon monoxide. So this process is termed gasification. If the process is under hydrogen pressure, activated hydrogen, transferred to the fragments, will prevent condensation, therefore, coal can be liquefied into oil. This process is termed coal liquefaction. This topic can help readers understand what the thermal processing of coal is. We can see that the history of human society is closely linked with the history of how people use energy for their own purposes. As oil resources are depleting, utilization of coal is commonly acknowledged as a bridge to new energy resources. At present, technologies of gasification, thermal decomposition, and liquefaction have already been established. The reason why some technologies, such as coal liquefaction and fast pyrolysis of coal, are not so industrialized, is that they are not competitive in economic terms with cheap-priced oil. Nevertheless, oil prices will

surely rise because of the depletion of oil. When these technologies become feasible in economic terms, they will sustain the development of human society.

1. Introduction

Being a heterogeneous mixture of inorganic and organic compounds, coal is complicated in constituents and structure. The substances composing the coal are still in the continuous process of geological chemical changes, so, at present, it is impossible to discover two lumps of coal having the same structure, with identical properties, due to the difference in original matter, biochemical action and geological factors.

Utilization of coal is referred to as the utilization of the organic constituents in the coal. Long before the Industrial Revolution, coal was extensively used to produce heat energy through combustion. Conventionally, coal is used as the primary energy source through direct combustion. The statistics data shows that nearly 47 percent of global electrical power plants use coal as fuel. Another aspect in coal utilization is carbonization of coal to produce cokes. The coke production amount is 389 million tons in 1995. Cokes are mainly used in metallurgical industry. In order to reduce production costs, many countries have set up jumbo coke-ovens. But in recent years people have been interested in the development of coal conversion technologies, including coal gasification and coal liquefaction, by which coal will be converted into clean fluid fuels as the secondary energy source. Fluid fuels (gaseous or liquid fuels) are convenient not only for shipping but also for utilization. What is more attractive is that the utilization of fluid fuels can effectively reduce environmental pollution. At present, there are several dozen technological processes, which have been developed or are under development. Some of these can be commercialized in the near future. Apart from the utilization of coal as energy-source, through carbonization, gasification or liquefaction, some chemicals can be obtained. Therefore, coal is an important feedstock source for the organic chemical industry. For example, synthesis gas, a mixture of CO and H_2, produced by coal gasification, is a feedstock for the synthesis of methane that is used to produce a variety of chemicals. A comprehensive utilization of coal can be realized by adoption of combined technological processes in different industries. These combinations are:

Coal mining—Electricity generation—Construction material—Chemical Industry
Coal mining—Electricity generation—Town Gas—Chemical Industry
Steel Industry—Coke Manufacture—Chemical Industry—Gas—Construction Material
Coke manufactures—Gas—Chemical Industry

The adoption of combination of processes is another approach to comprehensive utilization of coal. The combinations can be:

Carbonization—Gasification—Liquefaction
Thermal pyrolysis—Gasification—Electricity generation
Gasification—Synthesis

With technological development in coal conversion, we must become more aware of the importance of environmental friendship in the sustainable development of humankind.

2. Coal Combustion and Combustion Products

2.1 Fundamentals of Coal Combustion

Coal combustion is an old and most extensively employed method in the utilization of coal; it can generally be classified as either fixed bed combustion and fluidized bed combustion. The final products from combustion mainly are CO_2 and H_2O, with some amount of pollutants such as SO_2, NOx, and particles. For the reduction in SO_2 emission, coal with a low sulfur content is preferred in the combustion. If it is carried out in a cycle fluidized bed combustion, the relatively low temperatures can decrease the amount of NOx formed during combustion. But for the coal containing high sulfur content, removal of SO_2 is usually carried out in the post-combustion unit, i.e. waste gas effluent treatment.

2.1.1 The Effect of Coal Rank on Combustion

Coal rank, the degree of coalification, determines the heat value, reactivity, and major character in combustion. In general, coals of low coal rank, such as lignite and bituminous coals with high volatility, are more reactive but have lower heat value than the coals with high coal rank, such as anthracite and bituminous coals with low volatility. Anthracite is obviously more difficult to burn than bituminous coals. Coals desirable for combustion are expected to have low content of moisture and ash with high slagging temperatures, possess high reactivity and to be easily crushed.

2.1.2 Mechanisms of Combustion

The exact mechanism of coal combustion is still uncertain and it is difficult to clarify. It is, anyhow, quite certain that combustion is a process of degradation of carbon, i.e. when coal is heated, moisture and the volatile matter will first come off, meanwhile the water gas shift reaction ($CO_2 + H_2O \rightarrow CO + H_2$), produces CO and H_2. The gas combines together with the volatile matter at the start to burn over the coal particles. A simple model in describing the combustion process explains that de-volatilization is the first step, followed by ignition of the volatility; the fast combustion causes the ignition of coal particles, thus, combustion starts. It is understandable, in practice, that coal has already started to burn before de-volatilization becomes complete, and in turn, de-volatilization is accelerated, the time needed to complete de-volatilization reduces. Once the combustion starts, it can be visualized that hydrocarbons surrounding the coal particle are burning as they diffuse. On the other hand, oxygen proceeds to diffuse into the coal particles and is absorbed on the inter-surface of the coal. The complicated intermediate products are formed; the gas product desorbs and through diffusion out of carbon particles, finally returns to the bulk gas flow. Ignition of coal can occur within a very short time, and the distance from the coal surface accounts only $1\mu m(1\times10^{-6}$ meter). The formed CO will burn within the distance of 0.5–4mm from the coal surface. With the vaporization of moisture, ignition intrudes into the dried layer within the coal particle. The ignition temperature for coal varies from 600–800°C, usually dependent on coal rank. The younger the coal is, the easier the ignition becomes. In direct combustion, the elements in coal, carbon, and hydrogen are oxidized to carbon

dioxide and water respectively, and so, the chemical energy stored in coal is converted to heat energy. In combustion, many reactions can proceed simultaneously.

They are, for example, parallel reactions, consecutive reactions, and reversible reactions, which are related to the equilibrium of the system. Furthermore, the coal particle will be subject to the change in structure, both chemically and physically.

The residue from combustion is clinker, mainly containing SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO. The softening point of clinkers depends on its composition. Low softening point means the easy occurrence of slagging. Fe_2O_3, as a mineral matter in coal, under the reduction atmosphere of CO and H_2, can be reduced to FeO, consequently, in the coal fuel layer, slagging readily occurs, boiler thus is fouled. Another factor related to slagging is the content of alkaline metals. For example, the clinker is easy to remove if the content is below 5 percent by weight; otherwise, the removal of clinkers becomes difficult.

When coal is burning at high temperatures, the reaction favors the formation of CO, from consideration of chemical equilibrium; excessive air causes CO to convert into CO_2. But in practical operation, residence time of coal particles is so short and the heat transfer rate is so fast that the process in such a reaction temperature is a non-equilibrium one. The excessive amount of air needed is determined by a lot of factors, such as the highest temperature of flame, moisture content in coal, the air temperature and the complete combustion of fuel. As a rule of practice, the excessive amount of air ranges from 15 to 20 percent.

2.2 Combustion Installation

Combustion systems at present can be classified as layer combustion system and chamber combustion system. The fix-bed combustion belongs to the former system. In the chamber combustion system, combustion of coal powder is usually carried out. Coal powder can be fed into the combustor either at the top or at the bottom.

Thermal decomposition occurs in the coal layer on the grate of the fixed-bed combustor, and volatile matter begins to come off. Radiation from refractory lining causes the ignition of coal. In the fixed-bed combustor, the radiation heat can only penetrate a very short distance within the fuel layer. Heat conduction is the major way for heat exchange. Reaction time can speed up for those coal particles contacting the wall. Therefore, reaction is faster for the coal particles near the wall than those away from it. The up-flow combustor is operated by feeding the primary air from under the grate and over the coal layer on the grate, by feeding the secondary air, which helps combustion. The flue is on the top of the combustor. It is so named because the flame has the same direction as the primary air. This is a combustor of the simplest structure, used either in industry or households.

Down-flow combustors are so named because air is fed from the top and products come out from the bottom; the flame has a reversed direction to the primary air. The advantage of this type of combustor is quite evident. The airflow will push back the

volatile matter from thermal decomposition to the flame zone and fuel layer, and therefore, pollutants in the emission can be reduced.

In the fluidized bed combustor, close contact between gas and solid as well as high rate of heat transfer, leads to combustion at relatively low temperatures. It is lower combustion temperatures that greatly reduce the amount of NOx formation. Besides, adoption of pressurized fluidized combustion can intensify the production capacity. One of the restraints that hinders development of fluidized combustion is entraining solid out from the bed. A high velocity of gas flow in the bed will inevitably increase the amount of solid particles entrained with effluent. This problem gives rise to a low efficiency in operation. Faced with this problem, people in the last twenty years have been developing the cycle fluidized-bed combustor. This technology recovers the entrained solid residues by cyclones and recycles them into the combustor from the bottom part. Recycle operations reduce the dust emission and unreacted particles; on the other hand, as a result from lower temperature in the bed, the concentration of NOx in emissions is also greatly reduced.

As an approach in the reduction of SO_2 formation, limestone is often blended in the coal feed. In the combustor bed, the following reaction occurs:

$$SO_2 + 1/2O_2 + CaCO_3 \rightarrow CaSO_4 + CO_2$$

An appropriate operation of a fluidized-bed combustor will not cause severe problems concerning pollution.

The entrain-bed combustor is another type of combustor belonging to the chamber system. Airflow picks up the fine coal powder and feeds the coal into the combustors. This portion of air, as the primary one, accounts for 25 percent of the total air amount needed.

The other 75 percent of air is fed as secondary air into the combustor. The temperature in an entrain-bed can reach as high as 1400 C, at which certain mineral matters become softened, volatile, and adhere to the surface of the heat-transfer unit. Adherence not only affects the efficiency of heat exchange but also speeds up the erosion of metal parts.

People learning how to use fire marked the evolution of human society from barbarism to civilization. Wood was once the main source for heat. The Industrial Revolution made it possible to replace wood with coal as the main energy source. In some countries, coal is still the most important energy source, e.g. in China, 70 percent of energy sources relies on coal.

Coal combustion is the major utilization of coal. Therefore, in many countries great effort has been made on how to improve operation efficiency and reduce environmental pollution. At the moment, the pressurized fluidized-bed combustor and the cycle fluidized-bed combustor shows what people hope to see, that other environmentally-protecting measures can be taken.

3. Thermal Decomposition of Coal

3.1 Thermal Decomposition Reactions

Coal, when heated in the condition of isolation from air, will decompose to produce gas, coal tar, and char. This process is termed pyrolysis, or thermal decomposition of coal. Based on very high temperatures, this process can fall into one of the three types: low temperature destructive distillation from 500–600°C, medium temperature distillation from 700–900°C, high temperature distillation (conventionally termed as carbonization) from 900–1100°C.

Flash pyrolysis of coal is a promising process for producing synthetic natural gas, liquid fuels, and other chemicals. This offers a third method of coal conversion in addition to gasification and liquefaction. Studies of flash de-volatilization are also important for understanding the mechanism of coal thermal conversion, such as combustion and gasification, since it is the preliminary step in these thermal conversion processes. Despite extensive research, there are generally contradictory results reported, and various views are offered as to the best approach to take, to express the kinetics of this process owing to complicated coal structure and different experiment techniques. The phenomenological models have been successful in correlating experimental data and are relatively easy to handle. Unfortunately, the kinetic parameters of those models vary with coal type and heating conditions. The chemical reactions of coal are very complex in thermal decomposition processes. Main chemical reactions of thermal decomposition are as follows:
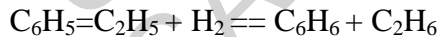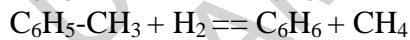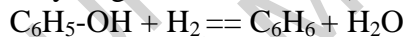
(a) Cracking reaction (700–1000°C)
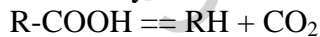 $C_2H_6 == C_2H_4 + H_2$
   $C_2H_4 == CH_4 + C$
   $R-CH_3 == R\bullet + CH_3\bullet$
   $R-CH_2-CH_3 == RH + CH_2=CH_2$
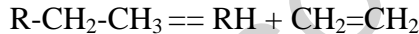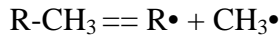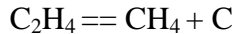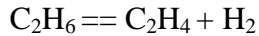
(b) Dehydrogenation reaction (700–800°C strongly)
   C_6H_{12} (cyclohexane) $== C_6H_6$ (benzene) $+ 3H_2$

(c) Hydrogenation reaction (above 650–800°C, in the present of hydrogen pressure)
   $C_6H_5-OH + H_2 == C_6H_6 + H_2O$
   $C_6H_5-CH_3 + H_2 == C_6H_6 + CH_4$
   $C_6H_5=C_2H_5 + H_2 == C_6H_6 + C_2H_6$
(d) Decarboxylation reaction
   $R-COOH == RH + CO_2$
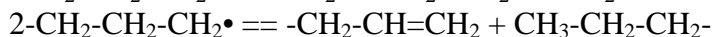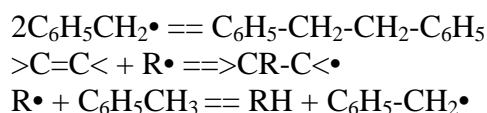
The main chemical reactions of thermal polycondensation are as follows:

(a) Radical reaction. When heated, the carbon-carbon bond or carbon-hydrogen bond in paraffin is first homolysized, and a non-paired electron in the carbon atom is formed. These non-paired electron products are then cracked to form new non-paired electron products:

   $-CH_2-CH_2-CH_2\bullet == -CH_2\bullet + CH_2=CH_2$ or $-CH_2-CH=CH_2 + H\bullet$
   $2-CH_2-CH_2-CH_2\bullet == -CH_2-CH=CH_2 + CH_3-CH_2-CH_2-$

$2C_6H_5CH_2\bullet == C_6H_5\text{-}CH_2\text{-}CH_2\text{-}C_6H_5$
$>C=C< + R\bullet ==>CR\text{-}C<\bullet$
$R\bullet + C_6H_5CH_3 == RH + C_6H_5\text{-}CH_2\bullet$

The temperature at which these radical reactions happen depends on the amount of dissociation energy within bonds. Generally radical reactions begin to take place at about 200℃, and become stronger gradually above 400℃. In a neutral atmosphere, the homolysis of single bond of carbon is carried out from 400 to 500°C, and the homolysis of the carbon-hydrogen bond that is between carbon and hydrogen in the aromatic ring takes place at about 700℃.

(b) Addition reaction. The Diels–Alder addition reaction is generally considered to play important role in the heating process of hydrocarbons, particularly in the primary heating process:

$CH_2=CH\text{-}CH=CH_2 + CH_2=CH_2 = C_6H_{10}$ (cyclohexene)
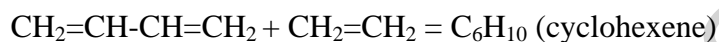
This reaction can be carried out only in heating condition, but does not require any catalyst. When a compound with an unsaturated bond is added in a conjugated diene under heating process, the cyclization reaction can easily take place in molecules. The compounds with conjugated double bonds can generally carry out additional reactions.

(c) Cyclization reaction and bridging reaction between the substituent and molecular body.

(d) Thermal polycondensaion reaction of condensed aromatics.

(e) Bridging reaction of aromatics.

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Biographical Sketch

Yan Yongjie was born on March 13 in 1943 and graduated from the Department of Fuel Chemical Technology at East China Institute of Chemical Technology (since 1993 renamed as East China University of Science and Technology). He was a visiting scientist at the Massachusetts Institute of Technology, USA, during 1982–1984, and visiting professor at Nagoya Institute of Technology, Japan, during 1988–1989. He was appointed as professor at ECUST in 1992. Professor Yan has worked in researching and teaching at ECUST for over 30 years, and is in charge of national research projects in the field of Energy Conversion. More than 90 scientific papers have been published in journals and at international conferences, some of which have been in English. He has obtained 2 scientific and technological progress awards from ministries in China. Professor Yan also acts as a member of several scientific and technical societies and sits on the editorial boards of various journals.