LIQUEFACTION OF COAL

Li Tingchen
Department of Chemical Technology for Energy Source, East China University of Science, and Technology,China

Keywords: Direct liquefaction, indirect liquefaction, thermal decomposition, hydrogenation, de-heteroatom reaction, condensation reaction, hydrogen-donor solvent, catalyst, fossil energy, Fischer-Tropsch synthesis, liquid fuel, synthetic oil, synthetic gas, hydro-liquefaction, thermal rupture, radical fragment, active hydrogen, bond scission, coke, char, catalytic hydrogenation, isomerization, dehydrogenation, intermediate product, petrographic phase, kinetic behaviour, volatility, coalification degree, peat, lignite, bituminious coal, anthracite, extraction liquefaction, preasphaltene, asphaltene, vitrain, clarain, fusain, coal slurry, carbon disposition, thermal sinister

Contents

Summary

Coal liquefaction is an industrial process in which coal as raw material, through chemical reactions, is converted into liquid hydrocarbon mixture, which, under further processing, becomes desired liquid fuels or chemical feedstock. Therefore, the main purpose of coal liquefaction lies in production of either synthetic oil as a partial substitute resource for crude oil or aromatic hydrocarbons as feedstock in organic chemical industry. Coal liquefaction, in general sense, is classified into two categories,

i.e. direct liquefaction and indirect liquefaction. Under direct liquefaction, coal undergoes thermal decomposing reactions, in the presence of solvents to form liquid mixtures that are abundant in aromatics, suitable to be refined to produce high-octane motor gasoline or be processed to aromatic feedstock. Under indirect liquefaction, synthesis gas, a mixture of carbon monoxide and hydrogen, is first produced through gasification of coal, followed by synthetic conversion of the gas mixture to liquid products, e.g., the established technology known as Fischer-Tropsch Synthesis has been employed for several decades in production of paraffin as main product, which can either be processed to high quality diesel oil or be used as feedstock for manufacture of olefins.

1. Introduction

In many countries, the long-term security of supply of liquid fuels will be strongly influenced by the ability to use hydrocarbon resources other than crude oil. At current rates of consumption, proven crude oil reserves will last an estimated 50 years. However, coal, as far as the reserves are concerned, is not only the most widely spread but also the most important source of fossil energy. With the huge coal deposits available, the world‘s energy requirements could be met for a long time to go. For this reason, in the development of modern fuel industry, much attention has been paid to the utilization of coal. People have long time interest in coal liquefaction to produce liquid fuels or chemicals. As early as in 1809, Berthelot carried out his coal liquefaction test in the presence of HI, hydrogen bromide, under atmospheric pressure at the temperatures from 270–280°C for 24 hours and finally obtained hydrocarbon oil and asphalt. Bergius preserved in his research and successfully in 1913 applied for the patent of hydro-liquefaction of coal under pressure range of 18–20 MPa, at the temperatures from 400–500°C. Because of the absence of catalysts, conversion of coal was very low.

Commercialization of liquefaction was realized when the first plant in Leuna, Germany was set up in 1927, just after I. G. Farbenindustrie invented hydrogenation catalyst in 1826. Up to the early 1940s, Germany had possessed 12 hydro-liquefaction plants with total capacity of 4 million tons per year. In those days, similar plants were also set up in several other countries as well, such as Britain, France, Italy, Korea, and China. This liquefaction technology, with its disadvantages by nature, such as high pressure (30–70MPa), high temperature (> 400°), and great consumption of hydrogen, in a word, high operation cost, lost its competitive ability with oil-based technology when many oil fields have been discovered in Middle East since World War II. The oil’s cheap price eventually led to such liquefaction plants shutting down. But energy crisis world-wide in early 1970s caused by Arab oil embargo has resulted in serious recognition of necessity and importance in diversity of energy resources and urged the industrialized countries to intensify funding of research projects in the following aspects, such as development of new types of catalysts, hydrogen-donor solvents as well as reactors, in order to mitigate severity of reaction conditions and decrease hydrogen consumption. Since the 1980s, economics of liquefaction has been strongly emphasized. Therefore, demonstration plants using newly developed technologies were set up for assessment of feasibility in commercial production scale. Despite feasibility in technologies, coal liquefaction, either direct or indirect, unfortunately, at least in mid-term can not be of competitiveness in face of cheep crude oil. Perhaps, indirect liquefaction of coal by Sasol in South Africa is a unique exception.

2. Direct Liquefaction

Direct liquefaction of coal is conventionally referred to such a chemically thermal decomposition process in which coal, as raw material, at high temperature, under high hydrogen pressure, and in the presence of catalysts, is finally converted to liquid hydrocarbon mixtures as well as lesser amount of gaseous hydrocarbons meanwhile heteroatoms, e.g. nitrogen, oxygen, sulfur, etc., are chemically removed. Direct liquefaction process mainly consists of the following steps: crushing and drying of coal; preparation of coal slurry; hydroliquefaction; separation of liquid products from solid residues; purification and refine of liquid products.

2.1 Physicochemical Principles

Chemical structure of organic matter in coal, as far as we are greatly concerned with, is very complicated and varies. From most accepted concepts, coal's chemical structure, however, can be divided into five descriptive levels. Firstly, the principal part of coal is a composite of high-molecule compounds, having a three-dimension spatial configuration. In some sense, it can be regarded as a polymer formed from a variety of units, similar but not identical in structure, linked together by chemical bonds. Secondly, these structural units have condensed aromatic rings as their cores. Generally, the number of aromatic rings increases with coalification degree. Thirdly, each structural units has its peripheral parts consisting of alkyls, mainly methyl and ethylene, and functional groups, mainly phenolichydroxides and carbonyls. Fourthly, heteroatoms such as oxygen, nitrogen, and sulfur exist in chemically bonded state. Finally, a certain amount of low-molecule compounds can be found scattering in the high-molecule structures. It is no wonder why coal itself is chemically so complicated that until now there is no authorized conclusion ever made on the molecule weight of coal. Some hold the molecule weight to be 5000; some hold it to be 10 000 or even greater. Broadly speaking, coal molecules, either through cross-link by chemical bonds or non-chemical bonds in tangle, form the random spatial arrangements that determine the steric structures. Though there remain big differences in either chemical composition or molecular structure between coal and crude oil, similarity, nevertheless, exist that carbon and hydrogen are two main elements these two fossil fuels contain.

Element	Anthracite	Bituminous	Lignite	Peat	Crude Oil
C	93.1	80.3	72.7	50–70	83.87
H	2.4	5.0	4.2	5.0–6.1	11–14
O	2.4	4.1	21.3	2.5–4.5	0.3–0.9
N	0.9	1.7	1.2	0.5–1.9	0.2
S	0.6	0.8	0.6	0.1–0.5	1.0

H/C atom ratio	0.31	0.67	0.87	~1.00	1.76

Table 1. Elements content (wt. %) of coal and crude oil

The chemical objectives of coal liquefaction are to;

- Reduce the effect of chemical bonds of both the weak and the strong and through thermal rupture to separate the large units in coal structure into small ones.
- Form smaller radical fragments from thermal bond scission and stabilize the fragments through abstraction of active hydrogen.
- Increase hydrogen/carbon atomic ratio in order to avoid condensation reaction among radical fragments, and thus produce more low-molecule liquid products.

As noted above that coal itself is chemically complicated, so is the complexity reflected in the process of liquefaction that involves a series of consecutive and parallel reactions. These chemical reactions can be concluded below:

1. *Thermal Decomposition*. When coal in solvent is heated up to 400ºC, the weakest (i.e. van der Waals as well as hydrogen) bonds start to break and radical fragments appear. So heavily is the thermal decomposition dependent on temperature that, with the rise in temperature, the extent of bond scission of relatively liable bonds increases. Consequently, the amount of radical fragments increases. The continued bond rupture leads to reduction in the mean molecular size of the constituents and may cause an increase in the amount of hydrogen consumption in stabilization of newly formed radical fragments. Therefore, the yield of final products depends on the extent of bond scission, which is closely related to the distribution of molecular size.

2. *Hydrogenation*. Coal liquefaction, in substance, is a process about how to control the extent of bond scission to the desired molecular size and, and how to promote efficiently and effectively the hydrogenation reaction. Because of low atomic ratio of hydrogen to carbon in coal constituents, adequate amount of hydrogen supplied during liquefaction is thus an important factor that can affect the yield of liquid product. In case the transfer rate of hydrogen from outside is comparatively slow, stabilization of the thermally produced radical fragments will thus turn to abstraction of hydrogen by interaction with other constituent units within the coal structure. Under the limited capacities of hydrogen donation, the free radical fragments most probably undergo recombination resulting in the formation of char or coke. Thus, the hydrogen present in coal is redistributed by hydrogen transfer within to form one fraction with hydrogen to carbon atomic ratio of ca. 1.5-1.8 and the other fraction of hydrogen-deficient solid such as char or coke.

Hydrogenation, by no means as a direct reaction between hydrogen and the coal mass, is such a reaction that the thermally produced radical fragments will abstract active hydrogen for stabilization. On this fact, coal liquefaction undergoes occasionally in hydrogen-donor solvent under high pressure of hydrogen in presence of catalysts.

3. *De-heteroatom Reaction*. Heteroatoms, such as oxygen, nitrogen, and sulfur, present in the coal structure, when they are subject to thermal rupture, will be finally removed in gas form of H_2O, CO_2, CO, H_2S and NH_3. However, the forms these heteroatoms adopt in the coal structure determine their readiness of removal. While majority of the oxygen and sulfur atoms in the coal is not located in the ring systems, this is not the case for nitrogen atoms. Thus, in the temperature range necessary for liquefaction process, heteroatoms external to the ring systems may be removed catalytically or non-catalytically. Removal of nitrogen atoms, in contrast, requires catalytic hydrogenation of ring systems in which nitrogen atoms are located, followed by the thermal rupture of the rings.

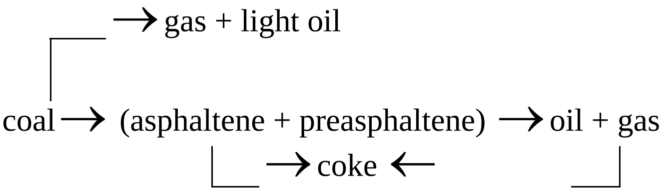
4. *Condensation*. Owing to either too high temperature range or deficiency of hydrogen, coal liquefaction will result in low yield of liquid product. The reason is that there is an occurrence of condensation between or among radical fragments and product molecules so that char or coke is formed. Simultaneously, reactions of isomerization or dehydrogenation can also contribute to the undesired result. Coal liquefaction process woven with various reactions as noted above is generally held to start with dilation of coal particles in solvent under high hydrogen pressure when heat transferred from ambient solvent cause temperature rise within the solid coal so that colloid solution is formed. The partial dissolution of organic substances brings about the destruction of coal structure. While destruction of structure accelerates with temperature rise, redistribution of hydrogen between coal structure and solvent, more often than not under the action of catalysts, becomes important. At the temperature range from 400–623ºC, preasphaltene, and asphaltene as intermediate products are formed. Further hydrogenation of the intermediate products will be intensified as temperature gradually rises. This means that thermally produced smaller fragments from preasphaltene or asphaltene, subject to hydrogenation, will finally form low-molecule substances conventionally known as oil and gas.

Since various representations have been postulated for the structure of coal in spite of varying degrees of uncertainty, the route projected for explaining the liquefaction process can vary. The postulated routes put forward by many researchers, no matter how simple or complicated they are, have some points in common. Four points can be concluded as follows:

(a) Coal, if regarded as a heterogeneous mass, is composed of inorganic and organic matter. The organic matter, some constituents readily to be liquefied, some other inactive in liquefaction, can be treated as a homogenous lot, should the petrographic phase of coal be comparatively homogeneous.
(b) A small amount of gas or light oil can be produced by parallel reaction at the early stage of liquefaction; nevertheless, consecutive reaction is still dominant, whether the reaction conditions mild or severe.
(c) Preasphaltene and asphaltene are the major intermediate products from which the further thermal decomposition and hydrogenation will lead to the formation of oil and gaseous products.
(d) On condition that the liquefaction is subject to deficiency of hydrogen, too high temperature and long reaction time, the undesired condensation becomes significant when intermediate products, radical fragments and final liquid products condense

among or between themselves to form char or coke, insoluble in solvent.

From the above common points, some researchers have made out a concise and clear route to describe kinetic behaviors of liquefaction. It is the representation below.



2.2 Major Factors Pertinent to Liquefaction

2.2.1 Coal as Raw Material

Understanding the characteristics of coal pertinent to the kinetic behaviors during liquefaction can help make selection of coal type appropriate to liquefaction operation. However, heterogeneity and polytropy of coal itself make it difficult to evaluate quantitatively the reactivity of coal in liquefaction.

So far, a variety of parameters have been considered in the attempt of correlation. These parameters include carbon content, atomic ratio of hydrogen to carbon, volatility, petrographic composition, and mineral matter.

Bergius concluded that coals with carbon content lower than 85 percent by weight could be liquefied; the lower the degree of coalification, the faster the liquefaction rate. Therefore, anthracite can hardly be liquefied.

A lot of investigators have verified that coal, having a relatively high content of hydrogen and oxygen can be liquefied under relatively low hydrogen pressure but high yield of liquid product cannot always be expected.

Systematic research on liquefaction by using coals with different carbon contents has indicated, as shown in Figure 1(Relationship between carbon content and liquid yield), that yield of liquid product will increase with the increase in carbon content, in case it is lower than 81 percent.

The yield could reach the maximum values when carbon content falls in the range of 80-84 percent. However, if the carbon content is over 89 percent, the yield will become very low. Results from extraction liquefaction of 13 types of coal original in Australia, of which carbon content varies from 67 percent to 90 percent, show the tendency that the higher the atomic ratio of hydrogen to carbon, the higher the conversion of coal will be.

However, the yield of oil is not always so. It will initially increase as this atomic ratio increases.

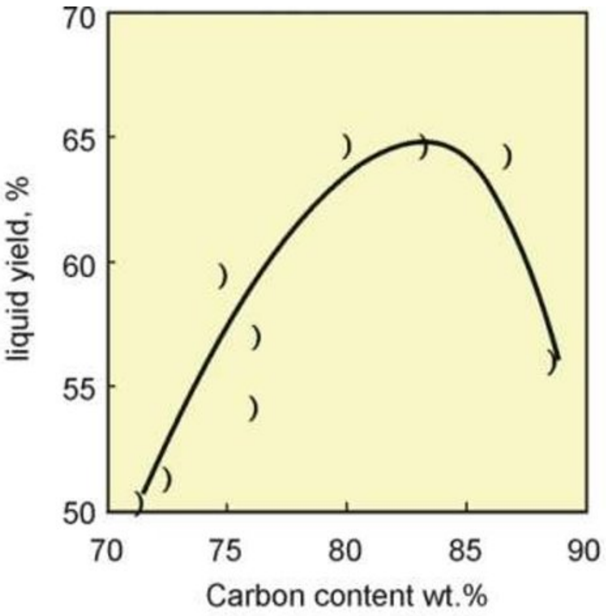


Figure 1: Relationship between Carbon Content and Liquid Yield

However, a certain value of the ratio does exits, above which the yield of oil begins to fall with the increase in the atomic ratio. The reason is that coal with high ratio of hydrogen to carbon, usually at low degree in coalification, has a high percentage of oxygen and aliphatic carbon. Therefore, through hydrogenation, gaseous product and water share a significant part of the final product; hence, liquid yield becomes low. In general, by using coal of hydrogen to carbon ratio of 0.8-0.9, high yield of oil can be obtained. However, when this ratio is below 0.6, conversion of coal is hardly over 30 percent. High yield of oil is obtainable when young bituminous coal or old lignite is used as raw material in liquefaction. Relationship between volatility and conversion or yield is closely dependent on either specific liquefaction conditions or the nature of the coal itself. However, coal with high volatility is usually comparatively reactive.

Though coals with same degree of coalification or having same element composition, it is generally recognized that petrographic composition can affect reactivity in hydroliquefaction. With regard to the influence of petrographic composition, vitrain is noted as the most reactive and soluble constituent in solvent whereas fusain is the inert and insoluble one that can hardly be liquefied. From Table 2, it can be seen that vitrain and clarain are two petrographic constituents that can be liquefied with high conversion while fusain the lowest.

Element	Anthracite	Bituminous	Lignite	Peat	Crude Oil
C	93.1	80.3	72.7	50–70	83.87
H	2.4	5.0	4.2	5.0–6.1	11–14
O	2.4	4.1	21.3	2.5–4.5	0.3–0.9

N	0.9	1.7	1.2	0.5–1.9	0.2
S	0.6	0.8	0.6	0.1–0.5	1.0
H/C atom ratio	0.31	0.67	0.87	~1.00	1.76

Table 1. Elements content (wt. %) of Coal and Crude Oil

A great variety of minerals have been reported to be present in coal. Mineral matters have been verified to have effect on liquefaction. For example, pyrite can turn to pyrrhotile, which can catalyze hydrogenation. Some mineral matters have been found detrimental to catalysts used in liquefaction. However, we still haven‘t understood quite well how minerals behave in liquefaction and to what degree they can affect the result.

In conclusion, coal as raw material; the result of liquefaction depends upon either molecular structure and chemical constituents or petrographic compositions and mineral matters. The young bituminous coal and old lignite both are suitable for liquefaction.

Bibliography

Derbyshire F. and Gray D. Coal liquefaction. In *ULLMANN'S Encyclopedia of Industrial Chemistry*, Vol. A7, pp. 197–237. ©VCH Verlagsgesellschaft mbH, D-6940 Weinheim (Federal Republic of Germany), 1986

Everett Gorin. Fundamentals of coal liquefaction. In *Chemistry of Coal Utilization.* edited by Martin A. Elliot pp.1846-1915. © 1981 by John Wiley & Sons. Inc. [These two above pieces of literatures introduce in detail the mechanism of coal liquefaction, inclusive of kinetics.]

Synthetic Fuels From Coal. Edited by Romey, P.F.M.Paul and G. Imarision © ECSC,EEC,EAEC, Brussel and Luxembourg,1987. Published by Graham& Trotman Ltd. London, UK [This book introduces indirect coal liquefaction, especially the technology of F–T Synthesis.]

Speight J. G. *The Chemistry and Technology of Coal*. Second edition, revised and expanded © 1994 by Marcel Dekker, Inc.[This book has a conceptual introduction of principles in coal liquefaction and various types of reactors used in liquefaction.]

Biographical Sketch

Li Tingchen graduated in 1982 with a BC degree in Chemical Engineering from East China University of Science and Technology (ECUST); in 1988, he was a visiting scholar at Leeds University, UK, and a fellow to the Chemical Engineering Department. Now he is associate professor at the Department of Chemical Technology for Energy Source of ECUST, working on energy conversion research in respect of hydrolysis/liquefaction of biomass and coliquefaction of biomass and coal.