Selection of suitable coal for liquefaction according to the various influencing factors

Seleção de carvão adequado para liquefação de acordo com os vários fatores que influenciam

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ABSTRACT
Direct coal liquefaction is a kind of clean coal technology. Its substantively is to convert solid coal into liquid oil by hydrogenation to reduce H/C ratio under certain temperature, hydrogen pressure, solvent and catalyst etc. conditions. Nitrogen, oxygen, sulfur and other heteroatoms were removed from coal at the same time. Coal liquefaction is not only conducive to improve the utilization of coal resources, but also would ease China's oil tense situation. Improve the conversion efficiency of coal is the focus of coal liquefaction research, and the influence factor on coal liquefaction rate were discussed in this paper. It mainly related to coal type, temperature, pressure, solvent, coal petrographic macerals and catalysts.

Keywords: coal liquefaction, coal type, coal petrographic constituents, catalyst.

RESUMO
A liquefação direta do carvão é uma espécie de tecnologia de carvão limpo. Sua principal finalidade é converter carvão sólido em óleo líquido por hidrogenação para reduzir a relação H/C sob certas condições de temperatura, pressão de hidrogênio, solvente e catalisador, etc. O nitrogênio, oxigênio, enxofre e outros heteroátomos foram removidos do carvão ao mesmo tempo. A liquefação do carvão não só é propícia para melhorar a utilização dos recursos carboníferos,
mas também aliviaria a situação de tensão do petróleo na China. Melhorar a eficiência de conversão do carvão é o foco da pesquisa de liquefação de carvão, e o fator de influência na taxa de liquefação do carvão foi discutido neste documento. Ele se refere principalmente ao tipo de carvão, temperatura, pressão, solvente, macerais petrográficos de carvão e catalisadores.

**Palavras-chave:** liquefação do carvão, tipo de carvão, constituintes petrográficos do carvão, catalisador.

**1 INTRODUCTION**

China’s coal consumption makes up 90% according to the statistics of 1995. This determines that coal has the dominant position in primary energy production and consumption. Yet the petroleum resources in China is relatively poor. The exploration and exploitation of petroleum is very difficult because it buried in complicated condition. The statistics in 1995 suggested that the annual petroleum yield of China was 140 to 150 million tons, only fifth in the world, and it is difficult to meet the needs of national economic and social development. In recent years, about 10 million tons of gasoline and diesel need to import.

Coal liquefaction is a cracking and hydrogenation process with the effect of catalyst and solvent under high temperature and high pressure hydrogen. The coal is converted to liquid hydrocarbon fuels such as gasoline, diesel oil, liquefied petroleum gas etc. through the process. The liquid hydrocarbon fuels can also be used to produce variety of important chemical products through separation steps.

The German scholar Bergius made liquid fuels through coal liquefaction under high temperature and high pressure, as early as 1913[1]. It laid the foundation of coal direct liquefaction technology. After that, the USA, Britain, Germany and the former Soviet union have carried out extensive research and developed a variety of mature technology. China began to research coal liquefaction since 1950s and has made remarkable headway.

Coal conversion rate and conversion speed is of great significance for coal liquefaction research. This paper investigated the coal liquefaction status at home and abroad, and it mainly includes coal type, coal petrographic constituents and coal liquefaction catalyst.
2 INFLUENCE OF COAL TYPE

Coal liquefaction property primarily depends on the molecular structure of coal, coal petrographic constituents and the minerals. Studies have shown that optimum liquefaction of coal is generally of relatively low degree of coalification, that is to say, the old lignite and the young bituminous. Roughly 60~85% carbon content, hydrogen content greater than 5%, volatile greater than 35%, ash content less than 10% and C/H less than 16\[^2,3\].

Difficulty of hydrogenation liquefaction of coal increased with increasing metamorphic grade of coal, peat < younger lignite < lignite < high volatile bituminous coal < low volatile bituminous coal. The higher H/C atomic ratio, the more weaker bond such as alkyl side chain and methylene bridge bond exists in coal and these alkyl side chain and methylene bridge bond are easier to crack in the process of liquefaction. Thus, more free radical fragments were generated \[^4,5\].

In addition, the functional groups in coal also play an important role on coal liquefaction. Oxygen-containing functional groups such as ester accelerate coal liquefaction because it can form an active centre with catalyst. Most phenolic compounds have negative effect \[^6\].

3 INFLUENCE OF COAL PETROGRAPHIC COMPOSITION

Coal is a complex aggregate which formed by microscopic components. The structure of these microscopic components determines the behavior and properties of coal in the hot procedure. From the study of coal rock, people can choose easily liquefied coal, or remove not easily liquefied components in coal through appropriate coal processing. It not only can improve the coal conversion rate but also make the technological conditions of hydrogenation, such as hydrogen pressure, reaction temperature and time decreased. Coal macerals concentrate mainly includes vitrinite, exinite and inertinite.

Many scholars have carried out studies around raw coal maceral and its liquefaction property. most scholars have come to the same conclusion, namely exinite > vitrinite > inertinite \[^7-9\]. The vitrinite and exinite in the coal rock
microscopic components are the active component of coal liquefaction. The content of the two components determines difficult or easy of the coal liquefaction. The higher of the two component, the easier of the coal liquefaction. Although the liquefaction performance of inertinite is the worst in three major microscopic components, research shows that inertinite also can be liquefacted, especially those semifusinite with low reflectivity\(^{[10-12]}\). Mochida et al. found that almost all the coal semifusinite had converted in coal liquefaction only a little of them has not any change. Shiboka and Heng pointed out that the semifusinite with low reflectivity \((R < 1.0\%)\) has higher liquefaction activity.

4 INFLUENCE OF REACTION TEMPERATURE AND PRESSURE

As for reaction temperature, coal pyrolysis is the basis of coal liquefaction, only at a certain reaction temperature pyrolysis reaction will occur. In a suitable atmosphere, with the increase of reaction temperature, coal depolymerization, hydrogenation and other reactions occur. The higher the temperature, the more intense the reaction, and the oil yield gradually increases. When the temperature rises to a certain extent, the coal conversion and oil yield reach the highest value. When the temperature continues to rise, the side reactions such as coal polycondensation and isomerization are strengthened, the char yield increases and the coal conversion decreases. Therefore, there is an optimum reaction temperature for coal liquefaction, which should not be too high or too low.

As for reaction pressure, In the process of direct hydrogenation liquefaction of coal, high pressure hydrogen is beneficial to accelerate the reaction speed. Vernon\(^{[13]}\) test shows that under certain conditions, molecular hydrogen can stabilize free radicals, promote the reaction of hydrocracking reaction, and increase the yield of liquefied oil. But hydrogen too high pressure also has disadvantages. Too high operating pressure increases the requirement of equipment and investment cost.

5 INFLUENCE OF SOLVENT

The effect of solvent on coal liquefaction is divided into two aspects.
5.1 HIGH SOLUBILITY OF COAL IN SOLVENT FACILITATES CONTACT OF HYDROGEN, COAL, CATALYST

The higher solubility of solvent to coal is beneficial to the contact of hydrogen, coal, and hydrogenation reaction. At the same time, the solvent can dilute the free radical fragments of coal pyrolysis, which is beneficial to the stability of free radical fragments and reduce the occurrence of polycondensation reaction, and improve the liquefaction yield. Guin\textsuperscript{[14]} studies have shown that 1,2,3,4-Tetrahydronaphthalene has a good dispersion effect on coal particles, while coal particles are only partially dispersed in decalin, indicating that the selected solvent must be able to effectively dissolve and disperse particles. It indicates that the selected solvent must be able to effectively dissolve and disperse the particles, so that the coal can be fully mixed and contacted with hydrogen and catalyst to promote the liquefaction reaction.

5.2 SOLVENTS PLAY THE ROLE OF HYDROGEN SUPPLY AND TRANSFER IN COAL LIQUEFACTION

The role of hydrogen supply and transfer in the process of coal liquefaction, there is a complex hydrogen transfer relationship between solvent and organic matter or derivatives in coal, hydrogen supply solvent has been the focus of research. For example, 1,2,3,4-Tetrahydronaphthalene is a good hydrogen donor solvent.

The active hydrogen produced in the hydrogen donor solvent can break some strong C-C bonds in coal. 1,2,3,4-Tetrahydronaphthalene releases hydrogen to become naphthalene, and naphthalene can obtain hydrogen from the outside to become tetralin, thus circulating hydrogen to the coal liquefaction process.

In the presence of hydrogen donor solvent, the free radicals produced by coal pyrolysis are difficult to recombine. The whole process is shown in the following figure.
6 INFLUENCE OF CATALYST

The role of catalyst is adsorbed hydrogen molecules in the gas, and activated the hydrogen molecules as active hydrogen, thus the active hydrogen to be accepted by pieces of coal free radicals in the process of coal liquefaction. The catalyst can not change the reaction path, but can increase the reaction rate, which is one of the core technologies of coal liquefaction. Catalyst is the key factors affecting the rate of coal liquefaction.

6.1 ACTION FORM AND ACTION MECHANISM OF THE CATALYST

On the whole, the effect of coal liquefaction catalyst includes two aspects: promoting the pyrolysis of coal; promoting the generation of active hydrogen. The first effect has been confirmed by a number of researchers, but most researchers believe that the latter is the main function of coal liquefaction catalysts [15-16]. A large number of scholars have done detailed research on iron-based catalyst preparation and performance. According to traditional theory, the main effect of catalyst is to accelerate the transfer of molecular hydrogen to solvent, and then the molecular hydrogen shifted to coal by solvent [17-18]. In terms of catalytic mechanism, some researchers believe that the mode of action of the iron-based
catalyst is in the form of Fe$_{1-x}$S. It is the active hydrogen which provided by catalyst promoted the fracture of C - C key\textsuperscript{[19-20]}.

6.2 THE TYPES AND PREPARATION METHODS OF CATALYSTS

The role of catalysts in coal liquefaction is mainly to reduce the activation energy, accelerate the reaction, promote the molecular hydrogen dissolved in the solvent, thus makes the molecular hydrogen become the active hydrogen donor solvent. Catalyst for coal liquefaction is generally has three kinds: the first is the sulfide of metal nickel (Ni), molybdenum (Mo), cobalt (Co); the second is the metal acid catalysts, such as ZnCl$_2$ and SnCl$_2$ compounds; the third is the iron-based catalyst.

The first kind of catalyst has high catalytic activity, but this type of metal catalysts is expensive, and dropped the more serious environmental pollution. To recovering these metals from the liquefaction residue by extraction method requires a large amount investment. The second kind of catalyst has strong cracking ability, but for coal liquefaction device has strong corrosive effect. It is difficult to recovery and regeneration of these catalysts because coal liquefaction is a gas, liquid and solid material hydrogenation reaction system. A more realistic approach is to use cheaper iron containing substances as catalyst, again without recovery, therefore the third kinds of iron-based catalyst has been studied and applied widely.

Early people use cheap red mud and iron slag as a catalyst, but the catalyst particles is larger, thus the catalytic effect is poorer, and it is difficult to be used in industry. For a ideal catalyst, it must have high surface area in addition to a high activity and good bond cleavage selectivity, thus promote the mutual contact catalyst and coal, increasing the degree of interaction between them. In recent years, the ultrafine and nanoscale iron-based catalyst were adopted because of the reason.

Chadha et al.\textsuperscript{[21]} synthesized ultrafine particle of Fe$_2$S$_3$ catalyst by the way of reversed micelles method, and supported the catalyst on the surface of coal. The diameter of the catalyst particle is 40-70 nm, and has high selectivity for light
products of coal liquefaction oil. Hager et al. [22] prepared Fe$_3$C nanoparticles by the way of laser cracking method. They found that the Fe$_3$C converted to pyrrhotite in the experiment of coal liquefaction, and the liquefaction activity of pyrrhotite excessed Fe$_3$C. The Pacific northwest laboratory [23] developed a solution fast pyrolysis method to prepare varied Fe nano-catalyst for coal liquefaction. Liu et al. [24] mixed 0.01N FeCl$_3$ water solution and 0.015N Na$_2$S water solution with coal to prepared Fe$_2$S$_3$ catalyst. The Fe$_2$S$_3$ catalyst exhibited excellent coal conversion. MiKi et al. [25] dipped Fe to coal by the way of ion exchange technology under vacuum condition, and the catalyst was prepared at the existence of S. The coal conversion achieved much high only 0.25% catalyst was used.

1. Liquefaction of coal should use young coal type, that to say, coal with high H/C atomic ratio. Besides, the coal type should have high volatile, high vitrinite and exinite content, low mineral content and low levels of oxygen, nitrogen and other heteroatom.

2. The microscopic components of coal is one of the main factors affecting liquefaction. Exinite and vitrinite is the active component for coal liquefaction. Those semifusinite in inertinite has certain activity. Most of the inertinite and minerals are inert substance for liquefaction.

3. The requirement for catalyst is that it should has high activity in aromatic hydrogenation, and has strong capability of cracking C-C, C-N, C-O keys. Improvement of iron series catalyst and the development of new catalyst is the present research direction. The research of Iron series catalyst has focus on the preparation of ultrafine and highly dispersed iron-based catalyst.

4. In view of the complex influence factors of coal liquefaction, orthogonal reaction should be used to determine the most suitable reaction conditions in practice.
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