Researches on Pyrolysis of Low Rank coal

Jinling Song[1, a], Lei Yang[1, b] Jiaxing Zhao[1, c] and Chuyang Tang[1, d]

[1]University of Science and Technology Liaoning, Liaoning 114051, China.

[a]astcy@126.com, [b]1049946108@qq.com, [c]z2501443131@163.com, [d]astcy@qq.com

Abstract

Coal is absolute dominance of reserves-to-production ratio terms. And direct combustion of low rank coal leads to a lot of environmental problems and causes great concerns globally. The development of clean fuels derived from co-pyrolysis of coal is beneficial to lower the emission of greenhouse gas and volatile organic chemicals. As a classical technology, pyrolysis was a reliable method to convert low rank coal through thermochemical process. In this study, the advance researches of pyrolysis coal were presented. The development tendency on pyrolytic condition was discussed further.

Keywords

Coal; Clean conversion; Pyrolysis; Fuel.

1. Introduction

Energy is a vital input for social and economic development of any nation. There has been an enormous increase in the demand for energy since the middle of the last century as a result of industrial development and population growth. Energy considerations are of paramount importance to key global concerns such as sustainable development, poverty reduction and economic growth. With the advent of industrialization and globalization, the demand for energy has increased exponentially. Apart from the phenomenal growth in population, the marvels of modern technology have enhanced the aspirations of the people for an improved quality of life. One of the indices of improved quality of life is the per capita energy consumption, which has been rising steadily for the last few decades. Fossil fuels in the form of coal, oil and natural gas comprise 80% of the world's energy use. It is predicted that if the current global energy consumption pattern continues, the world energy consumption will increase by over 50% before 2030. General agreement exists that an effective energy efficiency policy requires a combination of measures including regulatory instruments, financial incentives, information provision, and that the mix of measures needs to be adapted to the situations of each particular country. Limited growth in petroleum supply and uneven petroleum market has being brought a significant gap between supply and demand of the liquid fuel. Moreover, most air pollution results from coal combustion and coal are the source of 90% of the SO_2 emissions, 70% of the dust emissions and 67% of the NOx emissions. Due in large part to the emissions caused by burning coal. Coal, especially low rank coals such as lignite, is the most abundant and widely distributed fossil resource of the world. The effective and clean conversion process using low rank coals has recently become one of the most desired technologies to be developed worldwide, since their utilization can substantially lower the energy production cost. Pyrolysis is one of general term referring to a family of processes for producing liquid fuels from coal. Pyrolysis coal will become a viable option for the production of transportation fuels in China with cheap and abundant low-lank coals.

2. Literature Review

Coal pyrolysis is the most important aspect of coal behavior because it occurs in all major coal conversion processes. Upon pyrolysis coal is divided into a hydrogen-rich volatile fraction, consisting of gases, vapors, and tar-components, and a carbon-rich solid residue. Coal pyrolysis processes are generally classified as low temperature (<700^{o}C), medium temperature (700–900^{o}C), or high temperature (>900ºC). The pyrolysis process consists of a very complex set of reactions involving the formation of radicals. In the 1920s German Scientists discovered that it is possible to convert coal to liquids in large quantities.

2.1 Effects of product distribution during coal pyrolysis

Coal pyrolysis to produce hydrocarbons as an alternative fuel source of crude oil has been received considerable attention recently. Many excellent reviews have been published that discuss the factors affecting coal pyrolysis and product composition. These factors include temperature and heating rate, coal rank, atmosphere, pressure, catalyst, additives and so on.

The pyrolysis of coal is a good method for producing liquid fuels and other chemicals, but the yields of these products are limited because of the low hydrogen-to-carbon ratio in coal. The feasibility study on the hydromethanolysis process showed that there is enough H_2 and thermal energy to meet the consumption during the coal pyrolysis and 2/3 of total investment costs of traditional hydro-pyrolysis process could be saved. Many studies analysis the pyrolysis processes under the atmosphere of H_2, N_2, and CH_4 and so on, suggesting the existence of the synergistic effect. Some documents revealed that the conversion and oil yield of coal pyrolysis in coke oven gas and synthesis gas were higher than those from hydropyrolysis at the same H_2 partial pressure. They also concluded that the higher pressure and slower heating rate increased the pyrolysis oil yield and improved the quality when testing the pyrolysis in a pressurized fixed bed reactor. And a few of literatures clarified synergetic effect of the coke oven gas with Huolinhe lignite and the yield of tar with increasing the temperature from 570 to 660℃ in a downer reactor, while the char yield decreased.

Co-pyrolytic techniques have received much attention in recent years because they provide an attractive way to dispose of and convert additives (tar, biomass, polyamide, oil vacuum residue) and coal into higher value fuel and the specific benefits of this method potentially include: the reduction of the volume of waste; the recovery of chemicals; the reduction of the environmental impact and the replacement of fossil fuels. Both coal and biomass have complex structures containing a number of different constituents. These constituents show their inherent individual characteristics during thermal processes, and each one contributes to the apparent thermal characteristics of the feedstock. On the other hand, when coal and biomass are processed together in a process such as co-pyrolysis, some synergistic interactions may take palace, leading to significant variations in the chemical properties of the products. Some researches studied the synergetic effects in the co-pyrolysis of legume straw and Dayan lignite in a free fall reactor and at N2 atmospheres and at the temperatures of 500℃, 600℃, 700℃, respectively. Some more revealed that acid pickling is beneficial to increase the tar yield and effect on the cross-linking reaction to less resistant escaping of tar from the intra-particles of coal in the co-pyrolysis of a calcium-rich lignite coal and a high-sulfur bituminous coal on a fixed-bed reactor.

In coal chemistry, pyrolysis is the initial step in coal conversion and significantly influences the later stages. Catalyst surface modification with supported metals is an efficient way of controlling coal pyrolysis and enhancing the production of high value-added chemicals. Better understanding on the fundamentals during the catalytic pyrolysis of coal is essential in catalyst design and preparation. Some studies revealed that CoOx/HZSM-5, MoOx/HZSM-5, and HZSM-5 not only improve the evolution of CO, CH_4, and aliphatic and aromatic hydrocarbons but also prohibit the generation of the greenhouse gas CO_2 in pyrolysis of Huang Tu Miao coal. The results implied the synergistic effect of Co and Mo oxides. Some researches also showed the catalytic effect of alkali, alkaline earth and transition metals on pyrolysis of lignite and bituminous coals were investigated using TG-FTIR. The increase in gas yield is dependent on the catalysts, which are closely related to the temperature region and coal ranks. The results indicated that the orders of catalytic effects on the pyrolysis of lignite and bituminous coals were Ni ~ Fe ~ Ca ~ K and Ca ~ Fe > Ni > K, respectively.

2.2 Thermodynamics and kinetics of coal pyrolysis

Coal pyrolysis and volatilization is multiscale complex processes which involve many physical phenomena and chemical interactions. In general, two processes occur competitively when coal is pyrolyzed. One is the depolymerization process through which gas, water vapor is formed. The other is the condensation or repolymerization process, which leads to char/coke formation. Pyrolysis process of coal is greatly impacted by various factors, which includes intrinsic factors of coal and external factors. Generally, the intrinsic factors include structure, composition, particle size and rank of coal, while the external factors covers temperature, pressure, heating rate and reaction atmosphere, et al. Many researchers studied the affecting factors on the coal pyrolysis. A study researched the pyrolysis and gasification behavior of 4 typical Chinese coal samples at ambient pressure and 3MPa, respectively. The results showed that increasing pressure suppressed the primary pyrolysis, while the secondary pyrolysis of coal particles was promoted. A research investigated the pyrolysis characteristics of the coal used in the COREX process. The results showed the heating rate mainly influences the primary pyrolysis stage of the coal from 300℃ to 600℃, while the maximum weight loss rate and corresponding temperature change with increasing of heating rate. Many researchers have attempted to develop methods to quantify kinetic behavior. The most common way is to develop overall mass-change expressions for the solid and therefore for the volatiles without the knowledge on chemical changes in the solid and distribution of the volatiles especially the tar of coal pyrolysis. Tar, defined as condensable species formed during coal devolatilization, is a major volatile product, up to 50% of coal weight for bituminous coals. Tar prediction, important for several reasons, is more complex and its yield varies to a large extent depending on pyrolysis conditions.

3. Practical applications

Pyrolysis is the first step of several methods that are being developed for producing fuel from coal, which may include either direct liquefaction or indirect liquefaction. It is also considered as an effective way for clean use of coal because desulfurized char and tar can be obtained. China has a huge quantity of low-rank coal, especially lignite. The study of lignite utilization which is limited to high levels of water and ash, and low calorific value contribute to adjust energy structure and ease up the energy contradiction of supply and demand. In recent years, interest in pyrolysis was rekindled by the rising demand of oil. The pyrolysis of slow and low cheating rate is more suited to convert lignite or sub-bituminous coal with high volatile for advantage of less investment and cost. During pyrolysis, the yield of gaseous and liquid products can vary from 25% to 70% by weight, depending on a number of variables, such as coal type, type and composition of the atmosphere present, final pyrolysis temperature, time-temperature path, and pressure. Efficient utilization of all the products, solid, liquid, and gaseous, is essential if favorable economics for a pyrolysis process are to be achieved. The high aromaticity of coal pyrolysis liquids indicates that conversion to gasoline is preferred to conversion to diesel fuel. It is worth to devote attention to hydro-processing techniques, such as hydrotreating and hydrocracking in low-temperature tar processing, with the primary objectives of reducing viscosity, reducing polynuclear aromatics, and removing heteroatoms (sulfur, nitrogen, and oxygen) to produce usable fuels and chemicals. Some researches revealed that hydrogen-rich matters such as biomass supplied H2 for coal to result in improving the quality of the pyrolytic products and increasing the total yields of tar on the co-pyrolysis processes. Besides, evidence of the synergetic effects is also reported from the co-liquefaction of bituminous coal with lignin. It is accepted that synergetic effects on tar yield are observed in the co-pyrolysis of coal/biomass. However, not enough attention has been dedicated in previous studies to the influences of light oil yield in coal pyrolysis process. The study of the effect of biomass blends on the process of coal pyrolysis would contribute to increase the light oil content of coal tar.

4. Conclusion

China relies heavily on coal. However, the majority of coal is directly fired for power generation, which has low efficiency and gives rise to serious pollution. The exploration of clean coal utilization technologies has drawn much attraction in recent years. Pyrolysis is considered as an effective way for clean use of coal because desulfurized char and tar can be obtained. Moreover, high added-value chemicals, especially aromatic compounds, can be separated from tar, so it is significant to obtain high tar yield in coal pyrolysis. The existing technologies of coal pyrolysis have some disadvantages which are the low yield of tar and gas, the high asphaltene content of tar, and the low collection efficiency of dust. Inorganic matter in coal significantly influences its chemical properties and potential utilizations.

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References

[1] H.Q. Chen, X.P. Wang, L. He, et al. Chinese energy and fuels research priorities and trend: A bibliometric analysis, Renewable & Sustainable Energy Reviews, Vol. 58 (2016), p.966-975.

[2] A. KRUTOF and K. HAWBOLDT. Blends of pyrolysis oil, petroleum, and other bio-based fuels: A review, Renewable and Sustainable Energy Reviews, Vol. 59(2016)No. 4, p. 406-419.

[3] Z. GUO, Q. WANG, M. FANG, et al. Simulation of a Lignite-Based Polygeneration System Coproducing Electricity and Tar with Carbon Capture, Chemical Engineering & Technology, Vol38(2015)No. 3, p. 463–472.

[4] D. Vamvuka, E. Kakaras, E. Kastanaki, et al. Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite, Fuel, Vol. 82(2003)No. 15, p. 1949-60.

[5] G. Agarwal and B. Lattimer: Physicochemical, kinetic and energetic investigation of coal–biomass mixture pyrolysis, Fuel Processing Technology, Vol. 124(2014)No. 1, p. 174-87.

[6] Z. Wu, S. Wang, J. Zhao, et al. Thermochemical behavior and char morphology analysis of blended bituminous coal and lignocellulosic biomass model compound co-pyrolysis: Effects of cellulose and carboxymethylcellulose sodium, Fuel, Vol. 171(2016)No. 1, p. 65-73.

[7] P.H. Given, A. Marzec, W.A. Barton, et al. The concept of a mobile or molecular phase within the macromolecular network of coals: A debate, Fuel, Vol. 65(1986)No. 2, p. 155-163.

[8] H.V. Heek : Progress of coal science in the 20th century, Fuel, Vol. 79(2000)No. 1, p. 1-26.

[9] Q. Kin, S. Guo and S. Li: New concept on coal structure and new consideration for the generation mechanism of oil from coal, Chinese Science Bulletin, Vol. 43(1998)No. 24, p. 2025-2035.

[10] M.J. Ding, Z.M. Zong, Y. Zong, et al. Group separation and analysis of a carbon disulfide-soluble fraction from Shenfu coal by column chromatography, Journal of China University of Mining and Technology, Vol. 18(2008)No. 1, p. 27-32.

[11] F.J. Liu, X.Y. Wei, W.T. Li, et al. Methanolysis of extraction residue from Xianfeng lignite with NaOH and product characterizations with different spectrometries, Fuel Processing Technology, Vol. 136(2015)No. 1, p. 8-16.

[12] J. Ibarra, O.E. Mu and R. Moliner: FTIR study of the evolution of coal structure during the coalification process, Organic Geochemistry, Vol. 24(1996)No. 6, p. 725-735.

[13] S. Xun: The investigation of chemical structure of coal macerals via transmitted-light FT-IR microspectroscopy, Spectrochimica Acta Part A Molecular & Biomolecular Spectroscopy, Vol. 62(2005)No. 1, p. 557-564.

[14] B.K. Saikia, R.K. Boruah and P.K. Gogoi: FT-IR and XRD analysis of coal from Makum coalfield of Assam, Journal of Earth System Science, Vol. 116(2007)No. 6, p. 575-579.

[15] O.O. Sonibare, T. Haeger and S.F. Foley: Structural characterization of Nigerian coals by X-ray diffraction, Raman and FTIR spectroscopy, Fuel & Energy Abstracts, Vol. 35(2010)No. 12, p. 5347-5353.

[16] E.W. Hagaman and M.C. Woody: Structure Analysis of Coals by Resolution Enhanced Solid State 13C-NMR Spectroscopy, Fuel, Vol. 61(1982)No. 1, p. 53-57.

[17] A. Sharma, V. Pareek and D. Zhang: Biomass pyrolysis - A review of modelling, process parameters and catalytic studies, Renewable and Sustainable Energy Reviews, Vol. 50(2015)No. 5, p. 1081-1096.