Coupling Oil Increase by Coal Liquefaction Residue Pyrolysis and Coal Pyrolysis Depolymerization Based on Big Data

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Abstract. With the continuous improvement of big data technology, my country's coal liquefaction technology has also continued to mature, maintaining a stable industrial development. Traditional coal pyrolysis technology for tar production with the purpose of increasing tar production, such as coal hydropyrolysis, has problems such as high cost of pure hydrogen atmosphere and complex process and equipment operations, which severely restrict its industrial operation process. Based on this, this paper proposes a new technology of coal pyrolysis and depolymerization coupled with oil increase by using hydrogen precipitated by the condensation polymerization reaction at relatively high temperature under big data technology to study the effect of this process on coal pyrolysis for oil production. Experiments show that at 700°C, the tar yield reaches 21.5wt.%, which is 6% and 7% higher than the pyrolysis tar yield under the same conditions under hydrogen and nitrogen atmospheres. At 600°C, the methane aromatization reaction is relatively weak, and it can be seen that the tar yield is only slightly higher than that under hydrogen and nitrogen atmospheres. As the temperature of the methane anaerobic aromatization reaction increases, the equilibrium conversion rate increases accordingly. Therefore, as the reaction temperature increases, the tar yield also begins to increase.

Keywords: Big Data, Coal Liquefaction, Residual Oil Pyrolysis, Depolymerization Coupled With Oil Increase.

1. Introduction
The destructive effect of coal on the environment in the process of production and consumption has gradually emerged and has been highly valued by people [1-2]. With the development of people’s awareness of the rational use of coal resources, the Chinese government has continuously improved environmental protection standards, improved relevant laws and regulations, and developed and utilized various new types of clean energy. However, as far as my country’s current situation is concerned, coal resources dominate the energy structure the status cannot be fundamentally changed within a period of time [3-4]. In recent years, smog has occurred frequently in many places in my country, and one of the main culprits is the burning of coal [5-6].

Coal pyrolysis technology re-entered people's vision in the 1970s, and began to systematically and extensively carry out theoretical research and technological development of coal pyrolysis [7-8]. During this period, many new coal pyrolysis processes appeared, such as the COED process in the United States, the Toscoal process, and the CSIRO process in Australia [9]. Since the 1970s, countries
have successively begun to research and develop the process of coal hydropyrolysis [10]. Coal hydropyrolysis participates in the chemical reaction process of coal pyrolysis by introducing external hydrogen to make up for its own hydrogen deficiency. In the process of generating free radical fragments of coal, the extraneous hydrogen inhibits the free radical fragments and the polymerization of the macromolecular lamella structure by combining with them in time, which increases the output of tar and the yield of light oil. The conversion rate has also been increased, as well as the effect of desulfurization and denitrification [11-12].

This article mainly introduces a new pyrolysis process that couple methane aromatization and coal pyrolysis to achieve the purpose of increasing tar yield. In this paper, the influence of different factors on the yield of tar is investigated, and the optimal process conditions for the coupling process of methane aromatization and coal pyrolysis are obtained.

2. Coupling Oil Increase by Coal Liquefaction Residue Pyrolysis and Coal Pyrolysis Depolymerization Based on Big Data

2.1 Coupling of Coal Liquefaction Residue Pyrolysis and Coal Pyrolysis Depolymerization Based on Big Data to Increase Oil

The liquefaction of coal is one of the main ways to realize the clean and efficient utilization of coal. The industrial application process of preparing clean fuels or chemical products from coal mainly includes three methods: direct coal liquefaction, indirect liquefaction and coal pyrolysis.

Direct coal liquefaction, in simple terms, is a process in which coal is placed in a reaction vessel at a certain pressure and temperature, and the coal is converted into liquid fuel through direct catalytic hydrocracking. CTL technology mainly includes the following three methods:
(1) Direct coal liquefaction technology proposed by German Friedrich Bergius in 1931. Friedrich Bergius won the Nobel Prize in Chemistry for this key technology;
(2) Indirect coal liquefaction technology proposed by Fischer-Tropsch in 1923;
(3) Convert a part of coal into main products such as liquid hydrocarbons, gaseous hydrocarbons and coke through pyrolysis.

Compared with the first two CTL methods, the direct coal liquefaction technology invented by Friedrich Bergius has a high fuel conversion rate and relatively low cost, so the technology has developed rapidly.

No country in the world has experience in industrialized coal direct liquefaction projects. my country’s Shenhua has built the world’s first direct coal liquefaction demonstration plant. With the advancement of various technologies and continuous efforts, the direct coal liquefaction process technology will be updated. Development and breakthrough.

Coal indirect liquefaction technology includes gasification unit, purification unit, FT synthesis unit, etc. The core of which is FT synthesis unit. The basic chemical reaction of FT synthesis is hydrogenation of carbon monoxide to generate saturated and unsaturated hydrocarbons. The synthesis reaction can also produce oxygen. Compounds, such as alcohols, aldehydes, ketones, etc.

2.1.1. Air separation unit. The air separation unit provides the required oxygen to the gasifier. The air separation unit process of the cryogenic method mainly includes air pre-cooling, air purity purification, air booster unit, air booster turbine expansion, oxygen, nitrogen rectification, etc. In the Aspen Plus modeling, the air separation plant is a complete unit composed of many unit devices and sub-machines, mainly composed of air compressors, air pre-cooling systems, molecular sieve purifiers, main heat exchangers, rectification towers, etc. Air enters the K-COMP3 module main air compressor, selects the Compr compressor, the compressed gas is air-cooled K-HEATE2 module, selects the Heater single-flow heat exchanger, and the cooled air enters the K-SEP module, selects the Sep separator Simulate the air purification system to separate impurities such as moisture and carbon dioxide. The purified air enters the main heat exchanger of the KMH1 module in three ways to exchange heat with the return product gas. The KMH1 module uses the MHeatX multi-stream heat
exchanger analog product in the heat exchange process between the air and the raw material gas, the three-way air enters the KMH1 module for heat exchange. The air K-9 stream directly exchanges heat with the main heat exchanger and then enters the lower tower. The air K-8 stream passes through the K-MCOMP1. The flat expansion increaser first pressurizes and then cools down. After defining the pressurization in the MCompr multi-stage compressor in the simulation, define the temperature for the Cooler to cool the compressed air and then enter the main heat exchanger for heat exchange, then go to the upper tower for distillation. The third air enters the K-MCOMP2 turbo-expansion booster and adopts the same definition method as the second air. After it is pressurized and then cooled, it enters the lower column for rectification.

The upper column, lower column and crude argon column are all distillation columns. The RadFrac strict rectification column is used in the simulation to simulate them. The KMH2 module of multi-stream heat exchanger is used between the upper column and the lower column to simulate the product gas The lower tower gas is reheated, and the product gas oxygen and nitrogen of the upper tower rectification are sent out as products after heat exchange with KMH2 module heat exchanger and KMH1 analog main heat exchanger.

2.2.2. Lurgi coal gasification unit. Lump coal in the Lurgi coal gasification unit is pressurized in the gasification furnace with oxygen and water oxidants to produce crude gas with carbon monoxide and hydrogen as the main components, and then sent to the gas purification unit after dust removal and cooling. The main process including pressurized gasification, ash treatment, gas cooling process. The components involved in the entire process flow are divided into conventional components and unconventional components. The ash in lump coal is divided into inert substances and does not participate in the reaction during the gasification process. The H, O, N, S, Cl is completely transformed into the gas phase, while C is not completely transformed with the change of conditions. In the Aspen Plus model of Lurgi gasifier coal gasification, the drying layer, reaction layer, and slag layer of Lurgi gasifier are simulated. The components included in the whole process are divided into conventional components and unconventional components. There are two categories. Unconventional solid components are different types of solid mixtures, including lump coal and ash. In Aspen Plus, this type of material is simplified. It is considered that it does not participate in chemical equilibrium and phase equilibrium. Only the density and enthalpy are calculated, and HCOALGEN is used. The model is used to calculate the enthalpy of coal, and the DCOALIGT model is used to calculate the true dry basis density of coal. Both the enthalpy and density of coal are calculated. Industrial analysis data and elemental analysis data are used for the characteristic data of coal; the conventional component is conventional gas the product and conventional solid components, that is, a solid with a uniform composition and a definite molecular weight.

The main module of Lurgi gasifier selects the DECOM module to crack the coal, enters the GASIFIER module and gasification agent for gasification. The DECOM module is the RYield yield reactor in the AspenPlus model, which combines complex and unconventional solid lump coal according to the composition, that is, industrial The components of analysis and elemental analysis are transformed into simple substances such as C, H, O, N, S, etc., pass through the drying layer, after drying with Q-2 thermal flow, enter the GASIFIER module, Q-2 thermal flow is after the reaction of the gasifier The heat H-6 module for high-temperature gas heat exchange, the single-flow heat exchanger in the Aspen Plus model. The gasification agent enters the Lurgi gasifier from bottom to top, and the raw coal is in countercurrent contact from top to bottom to gradually complete the conversion of coal from solid to gas. In the AspenPlus model, the heat exchanged by the crude gas and water jacket is used The heat exchanged with the ash and slag layer is used to heat the gasification agent. The heat exchanged between the crude gas and the water jacket uses the heat exchange H-3 module. The heat of the Heater single-flow heat exchanger in the AspenPlus model 9 heat flow to heat the H-4 The heat exchanged by the water and ash layer of the module uses the heat exchange H-5 module, the heat of the Heater single-flow heat exchanger in the AspenPlus model, and the heat Q-3
heat flow to heat the gasification agent oxygen and water of the H-2 module. The latter gasification agent enters the GASIFIER module to participate in the reaction.

2.2.3. FT synthesis unit. F-T synthesis technology is an effective measure to alleviate the oil crisis. It adopts the iron-based slurry-bed F-T synthetic oil technology with my country's independent intellectual property rights. The main process route is the process of synthesis gas hydrogen and carbon monoxide through the Fischer-Tropsch synthesis reaction to generate hydrocarbon products. The slurry-bed Fischer-Tropsch synthesis reaction is the core technology of the indirect coal liquefaction process. The synthesis feed gas enters the slurry-bed reactor at a certain pressure and temperature, and the Fischer-Tropsch synthesis reaction occurs under the action of the catalyst to produce light distillate and heavy oil. A series of products such as distillate oil, heavy wax, water and oxygenated compounds. After the Fischer-Tropsch reaction, most of the synthetic products and tail gas after heat exchange, separation and collection are directly recycled through the pressurized cycle machine.

The raw material gas from the low-temperature methanol washing device is first mixed with the circulating gas, and then heated to enter the reactor for synthesis reaction to produce light oil, heavy oil, heavy wax, synthetic water and other products; light oil, heavy oil and synthesis The oil is pumped out from the top of the reactor in the form of gas phase. After cooling, heavy oil is separated. After the gas phase continues to be cooled, light oil and synthetic water are separated out. The gas phase continues to enter the compressor to be pressurized and used as circulating gas. The heavy wax is extracted from the middle of the reactor, and the released gas is separated and sent to the oil processing unit together with light oil and heavy oil. The oil processing unit is hydrocracked to obtain the final products naphtha and diesel. The Fischer-Tropsch synthesis reaction process is established in AspenPlus, which mainly includes Fischer-Tropsch synthesis reaction, heavy wax separation process, heavy oil and light oil separation process, and the separated crude oil enters the oil processing unit for processing into products.

The pyrolysis of coal is the basis of coal thermal conversion processes such as coal gasification, liquefaction and combustion. The study of coal pyrolysis is closely related to coal thermal processing technology, and has a guiding role in the thermal processing of other coals.

2.2 Data Problems Faced by Coal Companies

With the in-depth integration of automation and informatization of coal enterprises, large coal enterprises now have 20 or 30 large and small information systems. These production management and monitoring systems generate a large amount of data every day. However, these data are not only used for basic daily addition to statistical analysis, there is a lack of centralized management and deep mining of data. The specific problems are manifested in the following three aspects:

(1) The amount of data is large. Large coal companies manually record and automatically generate more than 10,000 pieces of data every day, and the information department requires a large amount of work and a long time to collect, copy, and analyze millions of pieces of data generated each year.

(2) The data is scattered. Because large coal companies are usually geographically dispersed, and systems are built separately according to business needs, there is a lack of connection between systems that have been built successively, and the problem of "information islands" between systems is obvious. The databases of each system are independent of each other, so the data of the entire enterprise is in a state of decentralized storage, and there is less correlation between each other.

(3) The data format is not uniform. Since the development and design of the system did not follow a unified data standard, the current data format of the various systems of coal enterprises was not uniform, which made the internal system integration, data integration and data analysis more difficult.
2.3 Design Ideas for Visualized Management of Big Data in Coal Enterprises

In response to the above-mentioned problems, this article introduces the concept and technology of big data management into the data management of coal enterprises, through data integration, data mining and visualization to show the "three-step" strategy, and build a coal mine big data visualization management platform based on data mining, to realize the comprehensive integration and unified management of data in coal enterprises, and fully explore the intrinsic value of data. The overall construction ideas of the coal mine big data visualization management platform are as follows:

(1) Data integration. Based on the data association model, carry out the unified data collection and comprehensive integration of the coal mine comprehensive automation system, logically form a data warehouse, and solve the problems of data islands, dispersion, and heterogeneity.

(2) Data mining. On the basis of this data integration, conduct data mining according to themes, discover the internal laws and potential value of the data, and provide preliminary preparations for the realization of platform functions.

(3) Visual display. According to the cognitive habits of managers, optimize the design of the visualization platform, present the data mining results to users in an intuitive form, and provide data support for corporate management decisions.

2.4 Product Yield Calculation

The focus of the investigation of pyrolysis products includes tar, semi-coke, water and so on.

Tar yield $Y_{\text{tar}}$

$$Y_{\text{tar}} = \frac{W_{\text{tar}}}{W_o \times (1 - A - M)} \times 100\%$$ (1)

Aquatic yield $Y_{\text{water}}$

$$Y_{\text{water}} = \frac{W_{\text{water}} - W_o \times M}{W_o \times (1 - A - M)} \times 100\%$$ (2)

Semi-coke yield $Y_{\text{char}}$

$$Y_{\text{char}} = \frac{W_{\text{char}} - W_o \times M}{W_o \times (1 - A - M)} \times 100\%$$ (3)

Among them: $W_{\text{water}}$: water quality during pyrolysis; $W_{\text{char}}$: semi-coke quality; $W_0$: coal sample quality; $W_{\text{tar}}$: tar quality; $A$: ash content in raw coal (wt.%, as received); $M$: moisture content in raw coal (wt.%, as received).

3. Research Experiment on Coupling Oil Increase by Coal Liquefaction Residue Pyrolysis and Coal Pyrolysis Depolymerization Based on Big Data

3.1 Coal Sample Preparation

The coal sample is selected from Shenmu raw coal, crushed to -100 mesh, and stored in a jar for later use.

3.2 Thermogravimetric Analysis

In this experiment, the Swiss Mettler-Toledo TGA/SDTA851 thermogravimetric analyzer was used. During the experiment, the sample weight was about 20mg and placed in the aluminum oxide crucible
of the thermogravimetric analyzer. The carrier gas was high-purity nitrogen and the flow was set to 60ML/min. After nitrogen is introduced to replace the air in the system, the temperature is programmed, the heating rate is set to 10°C/min, and the pyrolysis temperature is set to 25–900°C.

3.3 Preparation and Characterisation of Catalysts

3.3.1. Preparation of catalysts. The catalysts were prepared mainly by the isovolume impregnation method. A loaded catalyst with molybdenum trioxide as the active component and HZSM-5 (silicon-to-aluminium ratio of 38), as the carrier, was prepared as follows.

1) Roasting the HZSM-5 in a muffle furnace at 400 °C for 1h.
2) Dissolve ammonium molybdate in warm water and stir.
3) Adding a quantity of HZSM-5 to the above solution and stirring.
4) Impregnation at room temperature for 16h
5) The impregnated catalyst is dried in an oven at 120°C for 4h and then roasted in a muffle furnace at 500°C for 6h
6) Pressed into pellets with a particle size of 20-40 mesh and set aside.

3.3.2. Characterisation of the catalyst

1) Specific surface area and pore structure (BET)
   The specific surface area was determined using an ASAP2020HD88 fully automatic specific surface and microporous physisorption instrument (Mack Instruments, USA), using liquid nitrogen as the adsorption medium and an adsorption temperature of 77 K. The BET equation was used to calculate the specific surface area. The samples need to be dried at 200°C for 2h prior to the determination.

2) Cold field emission scanning electron microscopy (SEM)
   SEM experiments were carried out using a JSM 6700F cold field emission scanning electron microscope (JSM, Japan) to determine the surface microstructure of the samples, which were prepared and scanned after gold spraying.

3.4 Analysis of Coal Tar

In this paper, the analysis of coal tar mainly uses the simulated distillation method and the GC method.

3.4.1. Simulated distillation analysis of coal tar. Due to the complexity of coal tar composition and the characteristics of many high-boiling substances, it needs to be pre-treated before its simulated distillation. The processing procedure is as follows: first dissolve the mixture of coal tar and water obtained from the pyrolysis experiment with carbon disulfide, then add anhydrous sodium sulfate to absorb the water, filter to remove the sodium sulfate, distill the solution in a flask at 300°C, and take the distillate Produced for analysis.

3.4.2. Chromatographic analysis of coal tar. Before the color-mass spectrometry analysis of coal tar, pretreatment is also required to meet the chromatographic requirements. The treatment procedure is as follows: first dissolve the mixture of coal tar and water obtained from the pyrolysis experiment with dichloromethane, then add anhydrous sodium sulfate to absorb the water, filter to remove the sodium sulfate, and distill the solution in a flask at 300°C. Take the distillate for analysis.

The chromatograph used was Agilent GC6890N gas chromatograph.

4. Experimental Analysis of Coal Liquefaction Residue Pyrolysis and Coal Pyrolysis Depolymerization Coupling Oil Increase Research Based on Big Data

4.1 Effect of Mo Loading on the Pyrolysis Products of the Coupled Process of Methane Aromatization Pyrolysis (MAP)
Figure 1 shows the change curve of tar yield and water yield in the MAP process under different molybdenum supported catalyst conditions under the process conditions of methane flow rate of 25mL/min, pyrolysis temperature of 700°C, and reaction time of 30min.

### Table 1. The effect of molybdenum loading on tar yield and aquatic yield

| Mo loading (wt.%) | 2%  | 4%  | 6%  | 8%  |
|-------------------|-----|-----|-----|-----|
| Tar yield         | 15.8| 21.5| 17.8| 18.1|
| Water yield       | 3.8 | 3.5 | 3.6 | 4.3 |

It can be seen from the figure that the tar yield increases first and then decreases with the increase of Mo loading. When the loading is 4%, the catalyst has the best catalytic reaction performance, and its tar yield is 21.5wt. %. The catalyst with 2% Mo has less active Mo species, so only a small amount of methane is activated. Therefore, the tar yield is relatively low compared to the catalyst with 4% Mo. When supporting 6% and 8% Mo catalysts, on the one hand, excessive molybdenum oxide particles agglomerate and block the pores of the molecular sieve; on the other hand, as the amount of Mo loading increases, the number of acid sites in the molecular sieve is covered and gradually decreases, thereby affecting the reaction performance of the catalyst is improved. Different Mo loadings have little effect on the aquatic yield in the MAP process, and basically remain unchanged.

### 4.2 Effect of Reaction Temperature on the Pyrolysis Products of the Coupling Process of Methane Aromatization and Coal Pyrolysis

The effect of reaction temperature on coal pyrolysis, hydropyrolysis and MAP process is tested in a fixed-bed pyrolysis reactor, the pressure is 0.1 MPa, the gas flow rate is 25 mL/min, and the catalyst under methane atmosphere is 4% Mo/ HZSM-5, the final temperature residence time is 30min.

### Table 2. The effect of pyrolysis temperature on tar yield

|          | 600°C | 650°C | 700°C | 750°C | 800°C |
|----------|-------|-------|-------|-------|-------|
| MAP      | 16.8  | 19.8  | 21.4  | 20.3  | 18.2  |
| Hydrogen | 15.5  | 15.1  | 15.04 | 14.7  | 13.2  |
| Nitrogen | 15.01 | 14.1  | 13.94 | 12.8  | 12.7  |
Figure 2 shows the effect of the change of reaction temperature on the tar yield when coal is pyrolyzed in nitrogen atmosphere, hydropyrolysis and MAP process. The optimal temperature for pyrolysis of Shenmu coal is about 450°C, and at 600-800°C, it has already deviated from the optimal temperature for pyrolysis. Therefore, it can be seen from Figure 2 that the tar yield of coal pyrolyzed under nitrogen and hydrogen atmospheres decreases slowly as the temperature increases. At different temperatures, the tar yield of hydropyrolysis is always greater than the tar yield of pyrolysis in a nitrogen atmosphere. This is mainly due to the fact that hydrogen generates a large amount of H free radicals at high temperatures, which stabilizes the volatile components from coal pyrolysis, thereby increasing the tar yield. In the MAP process, the tar yield of coal pyrolysis showed a trend of first increasing and then decreasing with the increase of reaction temperature, and the range was obvious. At 700°C, the tar yield reached 21.5 wt.%, which was higher than that of hydrogen under the same conditions. The yield of pyrolysis tar under nitrogen and nitrogen atmosphere increased by 6% and 7%, respectively. At 600°C, the methane aromatization reaction is relatively weak, and it can be seen that the tar yield is only slightly higher than that under hydrogen and nitrogen atmospheres. As the temperature of the methane anaerobic aromatization reaction increases, the equilibrium conversion rate increases accordingly. Therefore, the tar yield begins to increase with the increase of the reaction temperature. When it reaches 700°C, the cracking reaction of methane begins to dominate. As the catalyst deposits more seriously, it affects the activity of the catalyst and causes the yield of tar to begin to decline.

Figure 3 shows the effect of changes in reaction temperature on water yield during coal pyrolysis, hydropyrolysis and MAP process pyrolysis in nitrogen atmosphere. It can be seen that in the three processes, the water yield decreases steadily with the increase of pyrolysis temperature. Among them, the water yield of hydropyrolysis is always the highest at different temperatures. This is mainly due to the combination of a large number of hydrogen radicals and hydroxyl groups cracked from coal during the pyrolysis process to form water, which leads to an increase in water yield: Starting from 700°C, the water yield of the MAP process began to be higher than that of the nitrogen atmosphere pyrolysis. The main reason for this is also due to the cracking of methane after 700°C, and the reaction dominates the anaerobic aromatization reaction, so that methane cracks more hydrogen, so the water yield becomes larger.
Table 3. The effect of pyrolysis temperature on water yield

|          | 600°C | 650°C | 700°C | 750°C | 800°C |
|----------|-------|-------|-------|-------|-------|
| MAP      | 5.2   | 3.8   | 3.2   | 3.3   | 3.5   |
| Hydrogen | 5.3   | 5.2   | 4.3   | 3.8   | 3.5   |
| Nitrogen | 5.3   | 5.1   | 3.4   | 2.8   | 3.3   |

Figure 3. The effect of pyrolysis temperature on water yield

Figure 4 shows the effect of changes in reaction temperature on the yield of semi-coke during coal pyrolysis, hydropyrolysis and MAP process pyrolysis in nitrogen atmosphere. Pyrolysis in the high temperature zone (greater than 700°C), the polycondensation reaction is the most obvious and intense, and part of the semi-coke will further decompose and emit a small amount of gas. A similar conclusion can be drawn from Figure 4, the semi-coke yields of the three processes all decrease with the increase of pyrolysis temperature. When there are no additional small molecule free radicals, the volatile components in the coal cannot be stabilized during pyrolysis. They are either further cracked into small molecule gases, or mutually condensed into semi-coke. Therefore, the semi-coke yield of pyrolysis in nitrogen atmosphere is always the highest at different temperatures, which also proves the free radical mechanism of coal pyrolysis process from the side.

Table 4. The effect of pyrolysis temperature on the yield of semi-coke

|          | 600°C | 650°C | 700°C | 750°C | 800°C |
|----------|-------|-------|-------|-------|-------|
| MAP      | 70.6  | 68.4  | 66.3  | 65.1  | 64.8  |
| Hydrogen | 69.7  | 67.4  | 66.2  | 66.5  | 64.5  |
| Nitrogen | 71.2  | 69.1  | 67.2  | 66.8  | 65.1  |
4.3 Effect of Gas Flow Rate on the Pyrolysis Products of the Coupling Process of Methane Aromatization and Coal Pyrolysis

The effect of gas flow rate on coal pyrolysis, hydropyrolysis and MAP process is tested in a fixed-bed pyrolysis reactor, the pressure is 0.1 MPa, the temperature is 700°C, and the catalyst in the MAP process is 4% Mo/HZSM-5. Carry out under the condition that the final temperature residence time is 30 min.

Table 5. The effect of gas flow rate on tar yield

| Gas flow rate (mL/min) | MAP (wt.%) | Hydrogen (wt.%) | Nitrogen (wt.%) |
|------------------------|------------|----------------|----------------|
| 15                     | 20.4       | 15.0           | 14.3           |
| 25                     | 21.6       | 15.4           | 14.4           |
| 50                     | 19.8       | 15.1           | 15.1           |
| 100                    | 15.9       | 15.8           | 15.0           |
| 150                    | 16.1       | 16.1           | 14.8           |
| 200                    | 16.2       | 16.1           | 14.7           |

Table 5 shows the influence of the change in gas flow rate on the tar yield during coal pyrolysis, hydropyrolysis and MAP process pyrolysis in nitrogen atmosphere. It can be seen from Table 5 that with the increase of gas flow rate, the tar yield of coal pyrolysis in a nitrogen atmosphere does not change much; while the tar yield of hydropyrolysis shows an increasing trend, and the tar yield of hydropyrolysis is higher than the tar yield of coal pyrolysis in a nitrogen atmosphere. This is mainly due to the increase of gas flow rate, shortening the residence time of tar in the high-temperature pyrolysis zone, and reducing the possibility of secondary reaction of tar; on the other hand, hydropyrolysis will generate a large amount of hydrogen free radicals, plus The existence of hydrogen free radicals stabilizes the free radicals generated during coal pyrolysis, which increases the tar yield. It can be seen that when the hydrogen flow rate is increased from 15 mL/min to 200 mL/min, the tar yield increases from 15.0 wt.% to 16.1 wt.%. In the MAP process, the pyrolysis tar yield increased first and then decreased with the increase of methane flow rate. When the flow rate is increased from 25 mL/min to 200 mL/min, the contact time between methane and the catalyst gradually becomes shorter, the aromatization reaction becomes weaker, and the methane conversion rate gradually

Figure 4. The effect of pyrolysis temperature on the yield of semi-coke
becomes lower, so there is not enough free radicals to stabilize the coal. The volatile components from pyrolysis make the tar yield of the MAP process drop more obviously; when the flow rate is 15 mL/min, the contact time between methane and the catalyst is increased due to the lower flow rate, which increases the possibility of coking on the catalyst. On the other hand, the lower flow rate will also increase the residence time of pyrolysis tar in the high temperature zone, leading to the secondary decomposition of tar. The experimental results show that when the gas flow rate is 25 mL/min, the tar yield of the MAP process is the highest, which is 21.6 wt.%, which is 1.4 and 1.5 times that of hydrogen and nitrogen atmospheres under the same conditions, respectively.

In summary, the optimal process conditions for the MAP process are: pyrolysis temperature 700 °C, methane flow rate 25 mL/min, 4% Mo/HZSM-5. Within 30 min of the reaction of the MAP process, there was almost no carbon deposit on the catalyst.

5. Conclusions

This article is based on the research of coal liquefaction residue pyrolysis and coal pyrolysis depolymerization coupling oil enhancement based on big data, and tried a new pyrolysis process using the coupling of methane aromatization and coal pyrolysis. The article mainly discusses the optimal process conditions of the process. The tar yield of hydropyrolysis is higher than the tar yield of nitrogen atmosphere pyrolysis under the same conditions. In the presence of a catalyst, the activated methane can replace hydrogen to become one. This kind of pyrolysis atmosphere can increase the yield of tar. The coupled process of methane aromatization and coal pyrolysis is a coal pyrolysis process that can increase the yield of tar. Under the optimal process conditions, that is, the reaction temperature is 700°C, the methane flow rate is 25 mL/min, and the catalyst is 4% Mo/HZSM-5, the tar yield of the MAP process reaches 21.5 wt.%, respectively, under the same conditions. The yield of tar pyrolysis in hydrogen and nitrogen atmosphere is 1.4 and 1.5 times.

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