ХИМИЯЛЫҚ ТЕХНОЛОГИЯ ЖӘНЕ МҰНАЙ ХИМИЯСЫ
ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ И НЕФТЕХИМИЯ

UDC 66.095:541.128

Zhou Qixiong[1], Niu Ben[2], Li Zhijuan[3], Ma Fengyun[4], Z.B.Absat[5], E.V.Kochegina[5], A.B.Karimova[5], N.Zh.Rakhimzhanova[5], G.K.Mukusheva[5], J.Bulax[5]

[1]Key Laboratory of Oil and Gas Fine Chemicals;
[2]Ministry of Education and Xinjiang Uyghur Autonomous Region;
[3]College of Chemistry and Chemical Engineering;
[4]Xinjiang University, Urumqi, Xinjiang, China
[5]Ye.A.Buketov Karaganda State University
(E-mail: zaure.absat.76@mail.ru)

Effect of iron-based catalysts on hydropyrolysis behavior of coal

This work determines the effect of hydropyrolysis of coal through a stabilizing reaction by impregnation method using catalysts such as $Fe(NO_3)_3$, $FeCl_3$, $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$. If you add three kinds of catalyst the hydropyrolysis change degree are increases. Adding semi-iron ammonium sulfate of 5 % the tar yield increased from 14.3 % without catalysts to 17.9 %. The preservation of ammonium radical gives the possibility to increase the formation of coal tar and degree of coal pyrolysis.

Key words: coal hydropyrolysis iron-based catalysts, impregnation method.

Typically, the formation of coal tar is the main objective in hydropyrolysis of coal method. Why getting a coal tar using the hydropyrolysis of coal method is the main objective, rather, in the pyrolysis of coal the rate formation and the rate of return of a free radical hydrogen is similar. Assuming that the rate of formation of coal pyrolysis free radicals is a function of the heat, the rapid formation and the stage management depends on the return speed of free hydrogen radical. Previously, scientists pay more attention to the problem of increasing the rate of return of a free radical hydrogen. In the hydropyrolysis as catalysts are used in series metals Fe, Co, Ni, Mo. The last layer and a second layer of metal is not filled with electrons, only one d electron with d orbit, in the chemical absorbed this d electron is connected to the s electron of hydrogen and forms a free hydrogen radical, in which it is possible advantageously to increase the return speed of a free hydrogen radical. In the use of a MoS_2catalyst, which degree of coke tar formation reaches 60 %, it can compete with direct liquefaction of coal, but this large volume and also difficult catalyst return, which prevents future production. These research works was used the impregnation method for the iron catalyst by stabilization reaction, it determines the impact on the hydropyrolysis properties, along with semi-iron ammonium sulfate which exactly affect to the formation of coal tar during the pyrolysis of coal which makes the first analysis on the influence to pyrolysis [1].

The main raw material in the experiment is — coal, the value of the dimension of coal are 20–60 mu, industrial analysis and elemental analysis are shown in Table 1. All reagents were used in this experiment have been analyzing check. The catalyst is added by impregnation: coal, a catalyst (iron), distilled water at the ratio of 100×200 (quality ratio) mixed in a heated bowl, here X — volume of the mixture, it kept in a water bath at 40 ºC , at the same time device was stirring, the speed agitation is 200 r/min; at the end of the method of impregnation place the file into a flash dishes, then dried in an oven at 105 ºC .

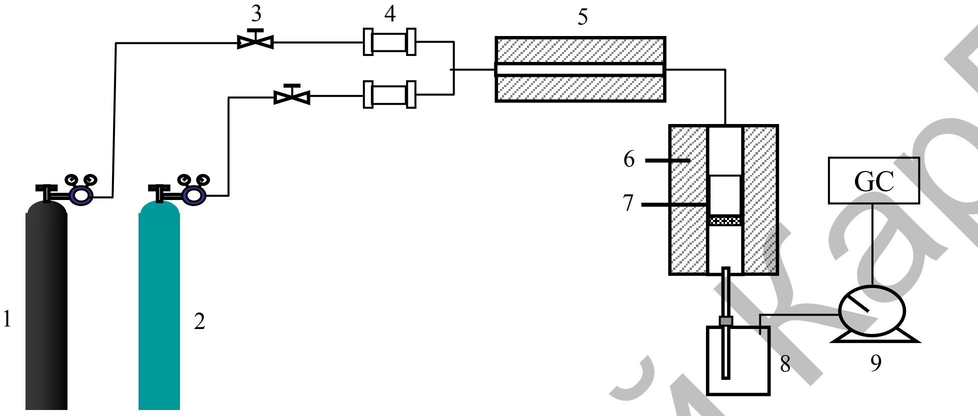
As indicated on Figure 1, the pyrolysis reaction is carried out in an apparatus for the pyrolysis, experimental conditions: coal 10 g, temperature 600 ºC, pressure is constant, the flow of hydrogen 0.4 l/min, the final temperature should be kept for 30 min. The liquid product was stored at a temperature of 15 ºC in a cool ware, quality determines the difference of initial and final reaction, liquid product is a mixture coal tar and hydrogen, which used ionization method ASTM D95–05[el] (2005). The volume of the liquid product is determined by the gas flow by soaking. Weigh the residue solid.

Table 1

Proximate and ultimate Analysis of coal

Proximate analysis (wt. %)				Ultimate analysis (wt. % daf)						
M_{ad}	A_d	V_{daf}	FC_d^a	C	H	N	O^a	S	H/C	O/C
5.20	7.91	43.73	51.81	77.02	4.82	1.01	15.75	1.4	0.75	0.15

Note. a — by difference.



1 — N_2 gas cylinder; *2* — H_2 gas cylinder; *3* — Valve; *4* — Mass flow controller; *5* — Preheater; *6* — Furnace; *7* — Reactor; *8* — Cool trap; *9* — Gas flow meter

Figure 1. Schematic diagram of apparatus

Gravimetric analysis of primary coal is conducted on Swiss analysis apparatus Mettler-Toledo TGA / SDTA851. Test conditions: about 15 mg raw materials, the temperature should be 25–900 ºC. Diagram of the primary coke is carried out by nitrogen adsorption at 77 K on a machine Beijing BK-122. Including the surface area is calculated by equation Brunauer-Emmett-Teller (BET). Total volume is the nitrogen liquid absorbed amount in 0.98 hours in a comparative pressure. The volume of the aperture is calculated on the model of Barrett, Joyner and Halenda (BJH). Distillation analysis of coal tar uses the Varian 450-GC of Brooker, test conditions: should be carried out according to standard ASTM D2887.

Figure 2 shows the change in the formation of coal tar and primary coal tar which was formed during the catalysis of $Fe(NO_3)_3$, $FeCl_3$ and semi-iron ammonium sulfate of hydropyrolysis of coal.

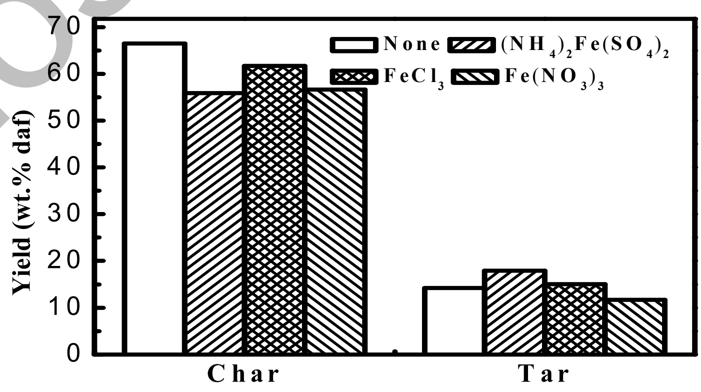


Figure 2. Char and tar yield of coal hyropyrolysis with various iron-based catalysts

From this figure we see the order of the primary coal tar product in the coal pyrolysis: without catalyst > $FeCl_3$ > $Fe(NO_3)_3$ > semi-iron ammonium sulfate. In this series the $FeCl_3$ during the formation of coal tar doesn't give some influence, formation coal tar: semi-iron ammonium sulfate > $FeCl_3$ > without catalyst > $Fe(NO_3)_3$. In this series of $FeCl_3$ during the formation of coal tar gives a certain influence, and $Fe(NO_3)_3$ generally useless. When adding: semi-iron ammonium sulfate is the most attractive, and without the catalyst the forming increases from 14.3 % to 17.9 %. This shows that semi-iron ammonium sulfate in the pyrolysis of coal depends on the formation of grooves, increases the spread of free hydrogen radical, in addition to using the absorption of iron to hydrogen is possible the decomposition of hydrogen. These two processes accelerate the return speed of free radical hydrogen, the greatest amount of coal formation tar [2].

Discussing role of the iron ammonium sulfate in pyrolysis of coal. Due to the above studies, have identified that the use of ammonium sulfate iron as a catalyst profitable for change of coal. If the iron content is 5 % formation of the coke resin is the most accurate, without the addition of the catalyst reaches from 14.3 % to 17.9 %. There is made an initial analysis of the role of iron ammonium sulfate during the coal pyrolysis process by comparison of difference of properties of the primary coke under the influence of four different catalysts and difference of propagation of catalysts such as $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, $NH_4Fe(SO_4)_2{\cdot}12H_2O$ and $Fe_2(SO_4)_3{\cdot}xH_2O$.

The propagation of different Fe-based catalysts in the hydropyrolysis of coal products. In Figure 3 it is shown the quantity of primary coke res and coke oil which formed during the pyrolysis of coal with different iron sulfates. There are a order of formation of primary coal tar: semi-iron sulfate > without catalyst> iron ammonium sulfate > iron sulfate > semi-iron ammonium sulfate; and order of formation of coal tar: semi-iron ammonium sulfate> iron ammonium sulfate > semi-iron sulfate > without catalyst> iron sulfate. From these conditions we can understand, that from a variety of forms of iron its catalytic effect on the pyrolysis of coal differ, the presence of ammonium radical increases the formation of coal tar and change coal pyrolysis [3].

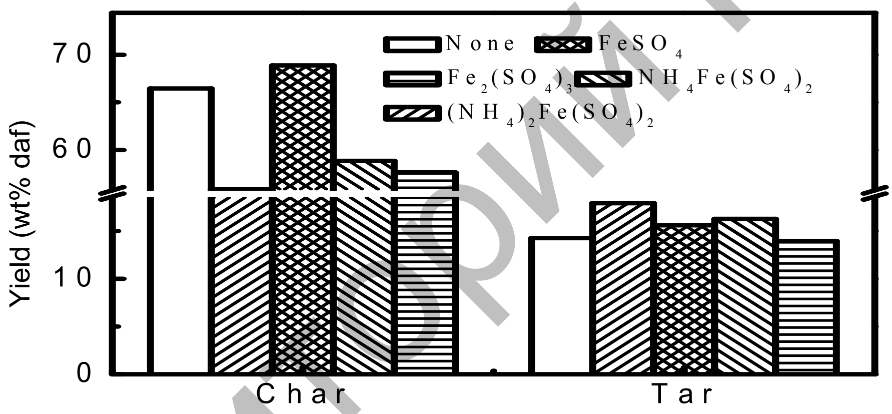


Figure 3. Char and tar yield of coal hyropyrolysis with different Fe-based catalysts

Signs of coal tar recess as different Fe-based catalysts and analysis. Surface area, volume of recess and diameter of the smooth recess of the char formed with as different Fe-based catalysts are shown in Table 2.

Table 2

Pore structure properties of chars from different Fe-based catalysts treating N_2 as balance

Catalyst	Surface area/ $m^2{\cdot}g^{-1}$	Pore volume/$cm^3{\cdot}g^{-}$	Average pore size/nm
None	96.58	0.094	3.88
$(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$	104.07	0.105	4.02
$FeSO_4{\cdot}7H_2O$	106.63	0.108	4.04
$NH_4Fe(SO_4)_2{\cdot}12H_2O$	119.92	0.120	4.01

After adding a few catalysts to surface area volume of recess and diameter of the smooth recess of the char increases, also percent of change. There is no direct connection between increasing of volume and increasing percent of change of pyrolysis.

But if the talk volume surface, offer large or small extent can be associated with crystal water of metal salt, when water rises then coal char surface increases too. Yield crystal water gives char gasification properties, and leads to increasing of the recess. Also carbon structure leads to lack of char recess due to a difference obtained for the output of water through the various catalysts.

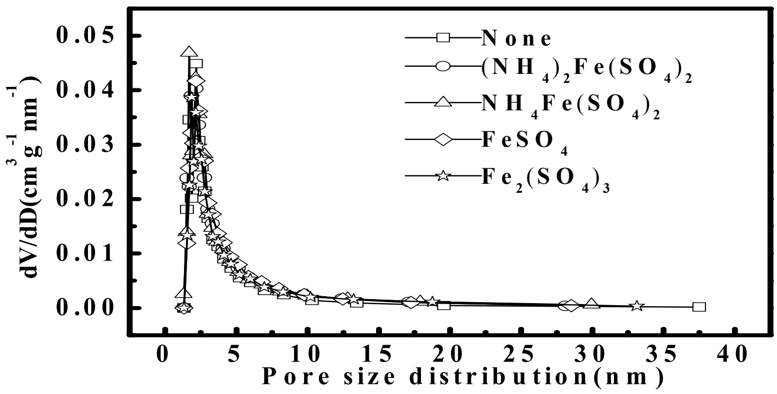


Figure 4. Pore size distribution of chars from different Fe-based catalysts

From the figure 4 we can see the accumulation of char on various catalysts in diameter recess 2.16 nm, the amount of absorption around 2.16 nm is identical to the order of magnitude of the volume of the surface. It shows that these catalysts are influenced by several char forming structure similar manner. In conclusion, the catalyst affects the formation of the structure of recess char, also increases distribution in coal [4].

Analyzing of the weight of the char as different Fe-based catalysts. At the Figure 5 it's noticeable difference of reactivity of coal pyrolysis product with the addition of iron in different states char, but difference isn't too large, char reactivity obtained in presence of ammonium radical higher than the one obtained without ammonium radical. It shows that iron at the separation of hydrogen gives the role of accelerator. For this reason, an increase in density causes free radicals of hydrogen and reduction reaction effectively lowering the body reaction, and increases the amount of distribution in the pyrolysis of coal.

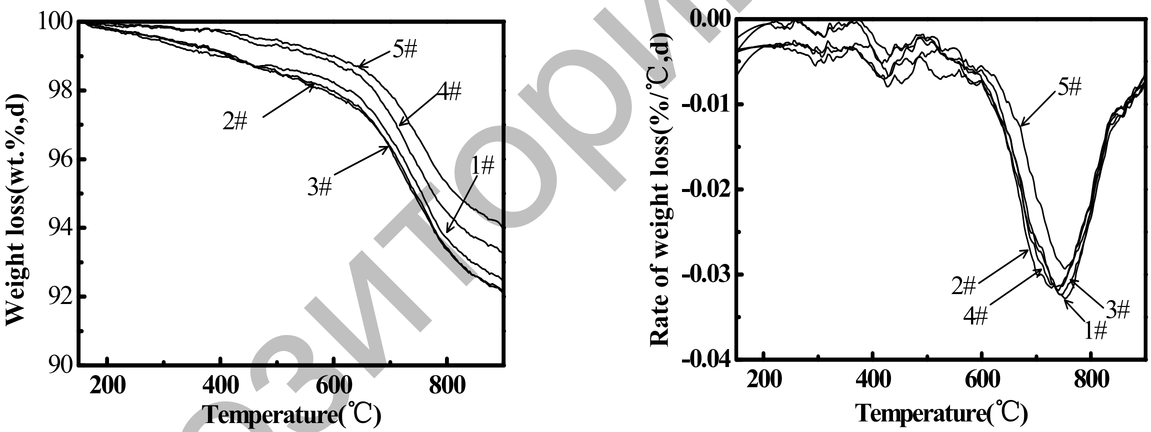


Figure 5. TG-DTG curves of chars with different Fe-based catalysts

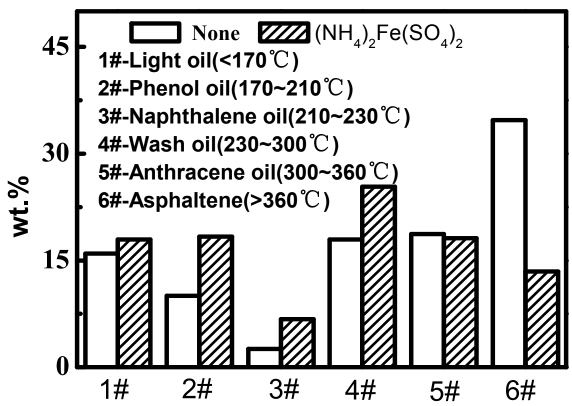


Figure 6. Simulating distillate fractions of tar with $(NH_4)_2Fe(SO_4)_2$

The Comparing and analyzing of coal tar of pyrolysis in the influence of different Fe-based catalysts. Figure 6 shows the analysis of evaporation of coal tar in the catalytic influence of Fe-based catalyst. in the figure, by comparing coal tar formed in the pyrolysis of coal by means of the catalytic properties of iron ammonium sulfate and coal tar formed in the pyrolysis of coal without a catalyst, it is possible to see an increase in oil phenol, naphthalene and oil residues, reducing the amount of asphalt residue, and also that the amount of anthracene amasla remained unchanged.

Conclusion

By the reaction of stabilize the hydropyrolysis of coal Tiechanggou with three iron nitrate, iron chloride and iron ammonium sulfate it can be shown: addition of iron catalyst is beneficial to change the coal, under the influence of iron ammonium sulfate increase coal tar is the most accurate, quantity increased by 3.6 %. It reaches from 14.3 % to 17.9 % without catalyst.

Was finded the reasons of high content of the formed char with different Fe-based catalysts by analyzing the impact of different Fe-based catalysts in the products of pyrolysis of coal and structure of recess and weight of product char: 1) ammonium radical effect on the formation of coaltar; 2) iron has an important role accelerator at hydrogen eduction, but the ызуув of free radical hydrogen is different depending on distinguish the states of iron.

The analysis of evaporating of coal tar: the coal tar formed with the Fe-based catalysts has better quality than the oil produced without catalyst.

References

1 *Snape C.E., Bolton C.* High Liquid Yields from Bituminous Coal via Hydropyrolysis with Dispersed Catalysts // Energy and Fuels. — 1989. — P. 421–425.

2 *Wen Li, Na Wang, Baoqing Li.* Product Analysis of Catalytic Multi-stage Hydropyrolysis of Lignite // Fuel. — 2003. — No. 82(5). — P. 569–573.

3 *Nelson P.F., Tyler R.J.* Catalytic Reactions of Products from the Rapid Hydropyrolysis of Coal at Atmospheric Pressure // Energy and Fuels. — 1989. — No. 3(4). — P. 488–489.

4 *Kouichi Miura.* Review-Mild conversion of coal for producing valuable chemicals // Fuel Processing Technology. — 2000. — No. 62(2–3). — P. 119–136.

Джоу Киксон, Нию Бен, Лю Джихуан, Ма Фэн Юнь, З.Б.Әбсәт, Е.В.Кочегина, А.Б.Кәрімова, Н.Ж.Рахымжанова, Г.К.Мұқышева, Ж.Буляш

Құрамында темір бар катализатордың технологиялық көмірдің гидропиролиздік қасиетіне әсері

Мақалада көмірдің гидропиролиз процесіне $Fe(NO_3)_3$, $FeCl_3$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ секілді катализаторлардың әсері зерттелген. Катализаторлардың үш түрін қолданған жағдайда, процесс өнімдерінің шығымы артатыны анықталған, бірақ 5 %-ды темір мен аммонийдің қос күкіртқышқылды тұзын қолданған жағдайда кокс шайырының шығымы 14,3 %-дан 17,9 % дейін жоғарлайтыны анықталған. Қос тұздағы аммоний радикалының болуы көмірдің конверсиясына және кокс шайырының шығымына оңтайлы әсерін тигізеді.

Джоу Киксон, Нию Бен, Лю Джихуан, Ма Фэн Юнь, З.Б.Абсат, Е.В.Кочегина, А.Б.Каримова, Н.Ж.Рахимжанова, Г.К.Мукышева, Ж.Буляш

Влияние катализатора, содержащего железо, на гидропиролиз технологического угля

Статья посвящена изучению влияния на процесс гидропиролиза угля таких катализаторов, как $Fe(NO_3)_3$, $FeCl_3$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. Установлено, что при добавлении трех видов катализатора выход продуктов процесса повышается, но наибольшее увеличение выхода коксовой смолы с 14,3 % до 17,9 % наблюдается при использовании 5 %-ной двойной сернокислой соли железа и аммония. Наличие иона аммония в двойной соли способствует конверсии угля и увеличению выхода коксовой смолы в процессе гидропиролиза.