

The Catalytic Cracking Mechanism of Lignite Pyrolysis Char on Tar

¹Zhang Lei, ¹He Huibin, ²Zhang Lei, ¹Sha Xiangling, ¹Ma Zhenhua, ¹Shu Hao and ³Tian Ye

¹*Xi'an University of Science and Technology, Xi'an, 710054, China.*

²*China National Heavy Machinery Research Institute, Xi'an, 710054, China.*

³*Xi'an west mine environmental protection technology co., LTD, 710054, China.*

leizh1981@sohu.com*

(Received on 2nd December 2015, accepted in revised form 21st September 2016)

Summary: The influence of different pyrolysis conditions for tar catalytic cracking will be analyzed according to the lignite pyrolysis char as catalyst on pyrolytic tar in this paper. The pyrolysis char what is the by-product of the cracking of coal has an abundant of pore structure and it has good catalytic activity. On this basis, making the modified catalyst when the pyrolysis char is activation and loads Fe by impregnation method. The cracking mechanism of lignite pyrolytic tar is explored by applying gas chromatograph to analyze splitting products of tar. The experimental results showed that: (1) The effect of tar cracking as the pyrolysis temperature, the heating rate, the volatilization of pyrolysis char and particle size increasing is better and better. The effect of the catalytic and cracking of lignite pyrolysis char in tar is best when the heating rate, the pyrolysis temperature, the volatiles of pyrolysis char, particle size is in specific conditions.(2) The activation of pyrolysis char can improve the catalytic effect of pyrolysis char on the tar cracking. But it reduces the effect of the tar cracking when the pyrolysis char is activation loading Fe.

Key word: Coal cracking; Tar cracking; Lignite Pyrolysis Char; Catalyst; Activation; Pyrolysis.

Introduction

Tar is an inevitable by-product in the process of thermal chemical conversion of low rank coal. The mass fraction of the heavy components in the tar is about 50% ~ 72%, that their boiling point is higher than 360 °C; The value of the tar reduces because the heavy components of tar is hard to use; and due to the condensation point of heavy tar is high and easy condensation, so it is easy to cause the clogging in subsequent line; The heavy components of tar affects the system stable operation and hinders the industrial application of pyrolysis technology. So it is necessary to improve the quality of the oil and gas from coal pyrolysis for developing advanced pyrolysis technology. And there are many carcinogens in the tar. If it is discharged into the air, it will cause the environmental pollution and be harm to people's health. In a word, it has important significance that reduces the coal tar in the process of production [1, 2].

As the representative of non-metal and metal catalyst now, the calcined dolomite and nickel-based catalysts are most used in the tar catalytic cracking. They have a higher rate of tar cracking, but the hardness of dolomite after calcining reduce leading to abrasion easily and nickel-based catalysts is easy poisoning at high temperatures[3-5]. And selecting metal oxidants or molecular sieve as the catalyst, the operating conditions are harsh and

the cost is high. So we should focus on the optimization of catalyst composition and preparation technology and develop the catalyst of economy, high efficiency and long life [6-8]. So in this paper, it adopts the new research direction of lignite pyrolysis char in the pyrolytic tar catalytic cracking. The tar what is the by-product of lignite, and it often can not make full use and is abandoned by industrial, but the pyrolysis char has a lot of pore structure and it can be used to catalyst. Both the economical is great and energy utilization can be improved by using the pyrolysis char in the process of tar catalytic pyrolysis. This is the way that makes good use of waste materials. It focus on researching the effect of pyrolysis char in tar cracking and analyzing the mechanism in the cases of different pyrolysis temperature, heating rate, the volatilization of pyrolysis char, particle size and the modified pyrolysis char.

Experiment

The experiment used 70 mesh screen to screen the coal sample of lignite as the cracking coal sample of the Initial cracking furnace. The lignite was dried by nature. Using 20, 30, 40, 70 mesh sieve to screen out 20~30 mesh, 30~40 mesh, 40~70 mesh coal sample; Coal sample is roasted for the preparation of pyrolysis char in the case of anaerobic.

*To whom all correspondence should be addressed.

Pyrolysis char is generated in the initial cracking furnace and the pyrolysis char is screened out. Pyrolysis char catalyzes the tar in the different temperature, heating rate, particle size and the volatilization, and the pyrolysis char is modified by activating and loading Fe. The pyrolysis char is activated and loaded Fe by impregnation method for making modified catalysts. Thus using pyrolysis char and modified pyrolysis char catalyze tar in the experiment. Using a bag collects the gas at the end of the device and analyzes the products of tar cracking with gas chromatograph.

The experimental device is shown in Fig. 1.

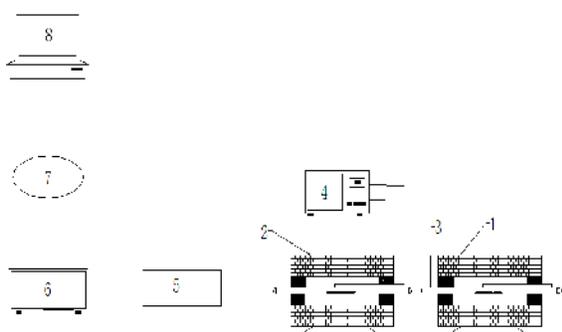


Fig. 1: Connected devices.

(1.initial cracking furnace 2.the secondary cracking furnace 3.dry distillation tube 4.mass flow meter 5.condensing unit 6.drying device 7.gas collecting bag 8.gas chromatograph)

Results and Discussion

The Influence of Different Pyrolysis Temperature on the Tar Cracking

The heating rate is 5°C/min. The selected cracking temperature here is respectively 500°C, 600°C, 700°C and 800°C. The terminal water, tar and gas are collected when they are cool. Then we should weigh the quality of mixed tar water and we analyze the composition of gas, the last we determine the temperature when the tar is least. (Table-01)

Table-1: The influence of different pyrolysis temperature on the tar water and gas production.

Pyrolysis temperature(°C)	Collecting gas(L)	Tar water(g)
500	2.7	3.012
600	2.8	2.907
700	2.9	2.929
800	3.3	3.083

The Fig. 2 shows that the quantity of

generated pyrolysis gas is more and more and generated mixed tar water changes a little when the temperature rises. The quantity of gas from tar cracking is most under 800°C. The Fig. 3 shows that the combustible gas in the gas content from pyrolysis is on the rise when the temperature of tar cracking rises. Compared to the other temperatures, the production of H₂, CH₄ and CO is most under 800°C. The reason is that the temperature is higher, the impact of coal structure is more and the achieved energy is greater. Aromatic hydrocarbon and other organic carbon are easier to crack into lightweight small molecule organic matter in the tar; so the generated gas and lightweight combustible gas are higher. It reflects that the production of tar increases as the rise of temperature [9-11]. The basic of this experiment is under the condition of hypoxia or anaerobic, the moisture in the coal sample is very little in the same quality, there is no oxygen in the reaction and little generated water; so the difference of mixed tar water is a little in the each temperature. (Table-02)

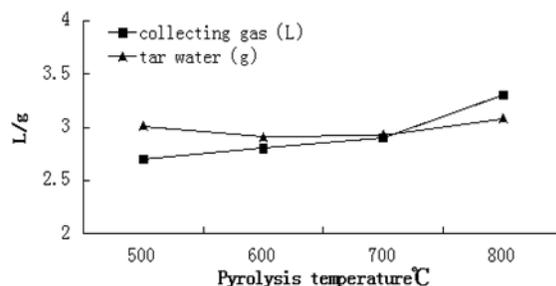


Fig.2: The influence of different pyrolysis temperature on the tar water and gas production.

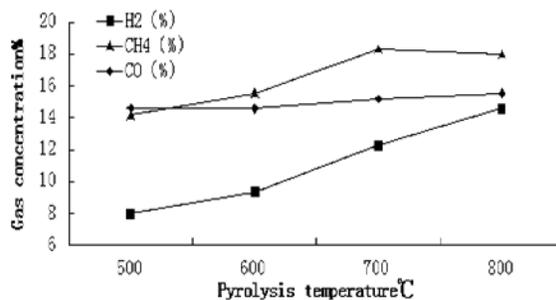


Fig. 3: The cracking gas component concentration of different pyrolytic temperature.

Table-2: The cracking gas component concentration of different pyrolytic temperature.

Pyrolysis temperature(°C)	H ₂ (%)	CH ₄ (%)	CO(%)
500	7.971	14.15	14.59
600	9.335	15.53	14.57
700	12.27	18.32	15.17
800	14.58	17.99	15.54

The influence of different heating rate on the tar cracking

The experiment selects 800°C temperature that the generated gas is most and the composition of combustible gas is most. The experiment makes sure the heating rate what's the production of tar is least in order, so the heating rate respectively selected 7°C/min, 10°C/min, 15°C/min (Table-03 and 04).

Table-3: The influence of different heating rate on the tar water and gas production.

Heating rate(°C/min)	Collecting gas(L)	Tar water(g)
5	3.3	3.083
7	3.1	3.155
10	3.4	2.861
15	2.9	2.991

Table-4: The cracking gas component concentration of different heating rate.

Heating rate(°C/min)	H ₂ (%)	CH ₄ (%)	CO(%)
7	9.635	13.2	13.75
10	14.93	19.25	17.97
15	15.81	18.45	17.79

The Fig. 4 shows that the gas reduces firstly, then increases to the peak, finally reduces slowly, and the mixed tar water changes little as the increase of the heating rate. It has led to the error result because the heating rate of laboratory equipment is less than 15°C/min. The Fig. 5 shows that the generated composition of combustible gas in tar cracking is augment as the increase of heating rate. The reason is that the faster heating rate leads to the residence time of volatile increasing under the high temperature; the secondary cracking is prompted; the rate of tar cracking speeds up; the rate of transformation from macromolecular organic matter to the small molecule organic matter is increase; so both the generated gas and combustible gas are increase [12].

The influence of different volatilization of pyrolysis chars on the tar cracking

The experiment selects the temperature (800°C) and the heating rate (10°C/min) leading to the generated gas is most and the composition of combustible gas is most. The experiment researches the influence of different volatilization of pyrolysis

char on the tar cracking with the volatilization of pyrolysis char respectively selects 5%,8%,11%.

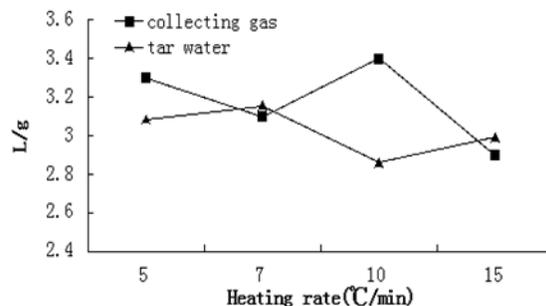


Fig. 4: The influence of different heating rate on the tar water and gas production.

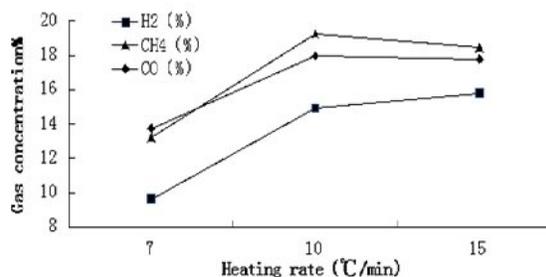


Fig. 5: The cracking gas component concentration of different heating rate.

The Fig. 6 shows that the quantity of generated gas is more and more and mixed tar water changes a little as the volatile of pyrolysis char rising. The Fig. 7 shows that the generated H₂ in the combustible gas composition has the trend of growth; CH₄ and CO change a little as the increase of pyrolysis char volatilization. Compared the former two groups experiment, the gas and combustible gas have obvious increase and the tar water has obvious reduction after putting in the pyrolysis char. The reason is that pyrolysis char starts its cracking of volatilization in the secondary cracking furnace firstly and produces a part of combustible gas when the pyrolysis char is putted in; then it splits the tar what generated in the initial cracking furnace. Compared the former two groups of experiments, the mixed tar water obviously decreases, the reason is that some water what is generated by cracking coal in the initial cracking furnace is stopped by pyrolysis char and it can't go through the secondary cracking furnace and gather in the front end of the secondary cracking furnace quartz tube [13]. (Table 5-8)

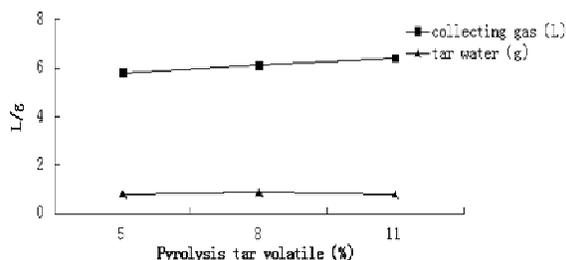


Fig. 6: The influence of different volatile of pyrolysis tar on the tar water and gas production.

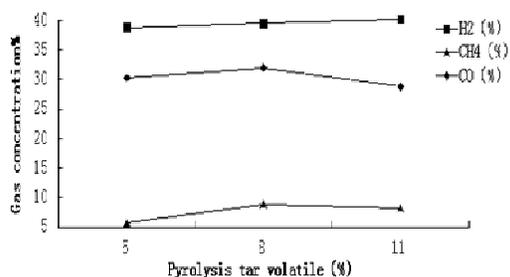


Fig. 7: The cracking gas component concentration of different volatile of pyrolysis tar

Table-5: The influence of different volatile of pyrolysis tar on the tar water and gas production.

Pyrolysis tar volatile(%)	Collecting gas(L)	Tar water(g)
5	5.8	0.806
8	6.1	0.869
11	6.4	0.795

Table-6: The cracking gas component concentration of different volatile of pyrolysis tar.

Pyrolysis tar volatile(%)	H2(%)	CH4(%)	CO(%)
5	38.81	5.671	30.33
8	39.55	8.929	32.05
11	40.29	8.211	28.76

Table-7: The influence of different particle size of pyrolysis tar on the tar water and gasproduction.

Pyrolysis tar particle size(mesh)	Collecting gas(L)	Tar water(g)
20~30	6.6	0.593
30~40	6.4	0.560
40~70	6.4	0.709

Table-8: The cracking gas component concentration of different particle size of pyrolysis tar.

Pyrolysis tar particle size(mesh)	H2(%)	CH4(%)	CO(%)
20~30	51.99	10.82	38.85
30~40	49.49	10.09	28.92
40~70	41.87	9.13	32.01

The influence of different particle size of pyrolysis

char on the tar cracking

The experiment selects the temperature (800°C), the heating rate(10°C/min) and the volatilization of pyrolysis char(11%) that the generated gas and the composition of combustible gas are most. The experiment in order to research the influence of different particle size of pyrolysis char on the tar cracking, so the particle size of pyrolysis char respectively selects 20~30,30~40,40~70mesh.

The Fig. 8 shows that the generated gas is more than the other two experiments when the particle size of pyrolysis char is 20~30mesh and the mixed tar water changes a little in three groups of experiment. The Fig. 9 shows that the content of combustible gas increases and the content of H₂ is most as the increase of particle size of pyrolysis char. The reason is that the particle size of pyrolysis char is bigger, the aperture of pyrolysis char is more on the surface; the effect of catalytic is better; and the content of combustible gas composition is bigger [14-16].

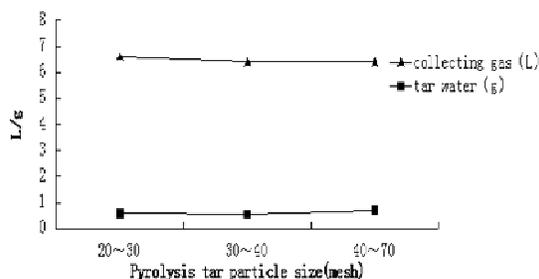


Fig. 8: The influence of different particle size of pyrolysis tar on the tar water and gas production.

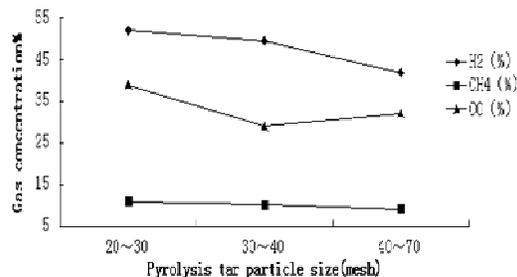


Fig.9: The cracking gas component concentration of different particle size of pyrolysis tar.

The influence of pyrolysis char activation and activate the load Fe on tar cracking

In order to research the effect of the tar pyrolysis, the experiment selects the conditions that the temperature (800°C), the heating rate(10°C / min), the volatilization of pyrolysis char(11%) and the particle size of pyrolysis char(20~30/mesh) in what the gas is most and the composition of combustible gas is most, and activate the pyrolysis char.

The Fig. 10 shows that the production of gas is more and the tar water is less after pyrolysis char activation without loading Fe than pyrolysis char activation loading Fe. The Fig. 11 shows that the content of H₂ and CO is more and the content of CH₄ is less after pyrolysis char activation without loading Fe than pyrolysis char activation loading Fe. Compared to the previous group experiment, the gas increases slightly when the pyrolysis char is activation without loading Fe than no activation, but the gas and the combustible gas composition obviously reduce after loading Fe. The reason is that the process of activation and the roasting of catalyst after loading Fe(NO₃)₃ may be lost some volatile of the catalyst; it results in that it lack of some active ingredient and gas from tar cracking. The tar can clog the interspace of pyrolysis char and cover some active ingredients of pyrolysis char in the process of tar cracking because of the viscous properties of tar; so it result in that the activity decreases. The activation of pyrolysis char improves this situation because the interspace of pyrolysis char becomes more and bigger. The Fe₂O₃ will cover the interspace of pyrolysis char and reduce a part of original active ingredients of the pyrolytic tar; the Fe₂O₃ makes the catalyst poison easily. Thus it results in that the effect of loading Fe is not very good [17-19] (Table 09 and 10).

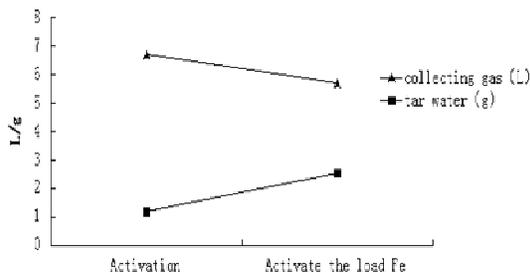


Fig.10: The influence of activated pyrolysis tar and activate the load Fe on the tar water and gas production.

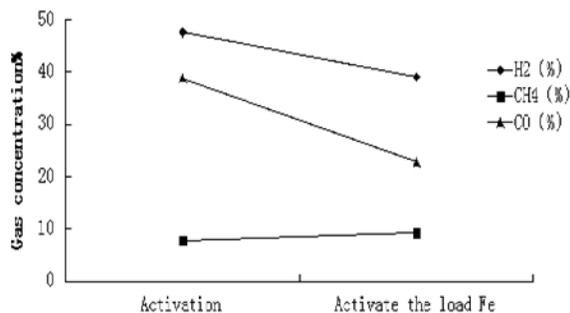


Fig. 11: The cracking gas component concentration of activated pyrolysis tar and activate the load Fe.

Table-9: The influence of activated pyrolysis tar and activate the load Fe on the tar water and gas production.

	Collecting gas(L)	Tar water(g)
Activation	6.7	1.180
Activate the load Fe	5.7	2.539

Table-10: The cracking gas component concentration of activated pyrolysis tar and activate the load Fe.

	H2(%)	CH4(%)	CO(%)
Activation	47.63	7.714	38.85
Activate the load Fe	39.08	9.168	22.78

Conclusion

Pyrolytic tar what is the by-product of lignite can be used to catalyst and decompose the tar by experiment research. As follow are the specific experimental results.

- (1) The effect of the pyrolytic tar cracking is higher as the increase of pyrolysis temperature, heating rate, volatilization of pyrolysis char and particle size of pyrolysis char.
- (2) The effect of tar cracking is best when the pyrolysis temperature is 800°C; the heating rate is 10°C/min; the volatilization of pyrolysis char is 11%; and the particle size is 20~30 mesh.
- (3) The activation of pyrolysis char can improve the catalytic effect of pyrolysis char on the tar cracking. But it reduces the effect of the tar cracking when the pyrolysis char is activation loading Fe.

Acknowledgements

Financial support of this research was

provided by Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Land and Resources (Program No.KF2015-1) in P.R. China, the Shaanxi Provincial Scientific and Technical Innovation Project (ProgramNo.2012 KTZB03 -01-02).

References

1. M. X. Han and H. M. Li, Chinese Coal Consumption and the Emissions of Atmospheric Pollutants, *Coal Eng.*, **76**, 3 (2006).
2. X. M. Chen, H. Peng and K. H. Lin, The Status Quo and Trend of Development of the Coal Tar Processing Technology and Industrialization, *Coal Chem. Ind.* **26**, 6 (2005).
3. L. Zhang and X. Q. Shu, The Impact of Silver Load on Hydrogen Production from Coal Pyrolysis with Hf-Solvated $\text{Ag}_2\text{-Co}_4\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ Catalyst Activity, *J. Sol. Energ.*, **910**, 33 (2012).
4. X. P. Feng, Z. W. Zhang and J. L. Xie, Light Burned Dolomite Calcining Technology's Influence on the Activity, *Comp. Util. miner. Res.*, **13**, 1 (2007).
5. L. Q. Gong, J. X. Chen, Z. Li, J. Y. Zhang, J. Liu, The Influence of Reduction Method and Reduction Temperature on the Partial Oxidation of Methane Nickel Catalyst Structure and Reaction, *J. Chem. Fuel.*, **192**, 2 (2008).
6. X. C. Yang, Y. N. Wei and W. J. Li, Tar Cracking with the Research Progress of Catalysts, *Chem. Prog.*, **326**, 3 (2006).
7. J. R. Jiang, Domestic Coal Tar Processing Industry Present Situation and Development, *Guangdong Chem.*, **52**, 4 (2009).
8. F. T. Hu, X. J. Zhang and P. L. Li, Coal Tar Processing Technology Progress and Present Situation of Industrialization, *Clean coal Technol.*, **31**, 5 (2011).
9. S. W. Zhang, D. S. Xu, X. P. Zhou, S. C. Yin, P. X. Zhang, Research of Coal Tar Hydrogenation Cracking Reaction and Catalyst, *Mod. Chem. Ind.*, **73**, 11 (2011).
10. B. L. Dou, J. S. Gao, X. Z. Sha, S. W. Baeka, Catalytic Cracking of Tar Component from High Temperature Fuel Gas, *Appl. Therm. Eng.*, **2229**, 17 (2003).
11. Q. Miao, H. A. Zheng, S. J. Zhang, X. Q. Li, J. S. Chen, Low Temperature Coal Pyrolysis Tar Yield and the Factors Influencing the Quality of the Research, *Clean Coal Technol.*, **77**, 4 (2014).
12. Z. J. Shi, M. S. Thesis, *Deep Processing of Coal Pyrolysis Tar Precipitation Characteristics and Experimental Research*, Zhejiang University (2014).
13. J. M. Shi, M. S. Thesis, *A Typical Coal Pyrolysis Gasification Characteristics Research*, Huazhong University of Science and Technology, (2010).
14. P. Lu, F. Lu, T. Shu, Q. C. Wang, The Experimental Study of the Biomass Pyrolysis Tar Adsorption SO_2 and NO can be Simulated in a Flue Gas, *Proc. Csee.*, **37**, 35 (2012).
15. L. Wang, C. Z. Wu and Z. L. Zhao, The Effect of Focal Biomass Pyrolysis Tar Catalytic Cracking, *J. Sol. Energ.*, **514**, 5 (2006).
16. Z. G. Wei, Y. Q. Huang, X. L. Yin, C. Z. Wu, Corn Cob Hydrolysis Residue Pyrolysis Coke Gasification Reactivity Studies, *J. Chem. Fuel.*, **685**, 6 (2012).
17. N. Laosiripojana, W. Sutthisripok, S. Charojrochkul, S. Assabumrungrat, Development of Ni-Fe Bimetallic Based Catalysts for Biomass Tar Cracking/Reforming: Effects of Catalyst Support and Co-Fed Reactants on Tar Conversion Characteristics, *Fuel Process. Technol.*, **26**, 127 (2014).
18. Z. Li, X. C. Zhao, B. B. Miao, Y. R. Jiang, Y. J. Zhao, Load type $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ Catalyst Preparation and Catalytic Activity of Microwave Pyrolysis of Coal, *J. mater. Sci-Eng.*, **826**, 6 (2014).
19. H. B. Liu, T. H. Chen, X. L. Zhang, J. H. Li, D. Y. Chang, L. Song, Additives for Nickel-Based Catalysts Biomass Gasification Tar Catalytic Cracking Performance Influence, *J. Catal.*, **409**, 4 (2010).