Asian Journal of Chemistry; Vol. 25, No. 13 (2013), 7571-7574

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15261

Formation of NH_3 During Temperature-Programmed and Isotherm Pyrolysis of Different Rank Coals

J.L. ZHANG, W.S. CHEN, H.M. YANG, M.J. WANG, X.R. REN and L.P. CHANG*

State Key Laboratory Breeding Base of Coal Science and Technology Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, Shanxi Province, P.R. China

*Corresponding author: Tel/Tax: +86 351 6010482; E-mail: lpchang@tyut.edu.cn; gezichunjin@126.com

(*Received*: 4 February 2013; *Accepted*: 1 July 2013) AJC-13754

Coals from Yanzhou, Yima, Zunyi and Ximeng mines were used to study the formation of NH_3 during pyrolysis in a fixed-bed reactor under argon atmosphere. Results show that the release of NH_3 is mainly affected by coal properties and its heating course. Total and accumulated yields of NH_3 basically takes the order of volatile content in coal, but the relative stability of heterocyclic nitrogen is very important. Low rank coal with high volatile content is favorable for NH_3 formation. NH_3 mainly yields from the rapid cracking of heterocyclic structure containing pyrrolic nitrogen at low temperature, initially releases at 400 ºC and presents the maximum at 700 ºC. The yield of NH_3 in holding stage increases with increasing pyrolysis final temperature and reaches maximum at 600 ºC. When the temperature is below 600 ºC, the yield of NH_3 in holding stage (Yc) is higher than that in heating stage (Yp). From 600 ºC to 800 ºC, Yc is lower than Yp because of the release of volatile is easy and rapid at high temperature.

Key Words: Coal, Pyrolysis, Fixed-bed reactor, NH_3.

INTRODUCTION

Coal is one of the most important primary energy in China and it will still last for a long time in future. But the inappropriate transformation and utilization way of coal has caused the serious environmental pollution. The low energy consumption and low pollution emission during coal utilization are the essence of low-carbon utilization of high-carbon energy sources[1-3], which will promote the development of efficient and clean use of coal. Nitrogen oxide, the contributor of acid rain and photochemical smog, is one of main pollutants in the process of coal utilization. Pyrolysis is the basis of all coal utilization processes. It is essential to study the release characteristics of compounds containing nitrogen during coal pyrolysis in order to provide a reliable foundation for the clean utilization of coal. It has been proved that NH_3 and HCN are the precursors of nitrogen oxide and some results are also reported based on the pyrolysis researches of the coal samples[4-9] and model compounds containing nitrogen[10-12]. The direct or indirect hydrogenation of the nitrogen in relative stable heteroaromatic structures is the main cause of NH_3 formation in coal pyrolysis[6]. And the active H radicals required for the hydrogenation of nitrogen in heteroaromatic ring systems is generated during the thermal cracking reactions in solid coal particles[6,7]. The secondary reaction of tar during volatiles escaping initially from coal pyrolysis is also suggested as the main source of NOx precursor formation[5-9]. But it is not clear how the volatiles and H radicals take effects in the formation of NH_3 and what factors influence them. To investigate the effects of volatiles and H radicals on the formation of NH_3, the coal pyrolysis experiments in different stages of heating and holding period at final temperature were carried out in this work.

EXPERIMENTAL

Preparation of coal sample: Ximeng (XM), Yima (YM), Yanzhou (YZ) and Zunyi (ZY) coals from China main mines were collected in this study. They were crushed and grinded to the particle sizes ranging from 0.154-0.250 mm and preserved in containers away from light. The proximate analysis and ultimate analysis of coal samples were shown in Table-1.

Experimental procedure: A fixed-bed quartz tube reactor with an external heated electrical furnace was used in the experiments at normal pressure. The pyrolysis atmosphere is argon with the gas flow rate of 600 mL/min. About 0.5 g coal sample weighed accurately was preset to the quartz frit in tube reactor and purged for 5 min by argon from the top of reactor to discharge air in quartz tube. When the preset final temperatures of 300, 400, 500, 600, 700, 800, 900 and 1000 ºC were reached by programmed temperature of 10 ºC/min (regarded

TABLE-1
PROXIMATE AND ULTIMATE ANALYSES OF COAL SAMPLES

Sample	Proximate analysis (w/%)			Ultimate analysis w/% (daf)				
	Mad	Ad	Vdaf	C	H	N	S	O*
XM	28.1	10.5	45.5	66.1	2.2	1.3	2.9	27.5
YM	6.6	19.6	45.7	75.3	4.8	1.1	1.9	16.9
YZ	2.3	13.6	43.4	81.5	5.1	1.3	5.0	7.1
ZY	0.9	22.0	10.8	84.3	3.2	0.9	7.3	4.3

Note: ad, air-dried basis; d, dry basis; daf, dry and ash-free basis; *, determined by difference.

as heating stage), then holding for 40 min at these final temperatures (regarded as holding stage). NH_3 in gaseous product from a separate experiment was absorbed in 0.02 mol/L CH_3SO_3H solution and then was measured with a Dionex 500 ion chromatograph equipped with a ED40 Electrochemical detector.

Data processing: The ratio of the nitrogen in NH_3 from different stages and the total nitrogen in raw coal were expressed as the yield of NH_3 in raw coal pyrolysis. The yields of NH_3 in different periods are obtained according to following formulas.

$$\Delta Y = Y(T) - Y(T-100);\ Yy = \Sigma Yp;\ Yc = Y - Yy$$

where, T is the temperature of coal pyrolysis, Y is the total yield of NH_3 in the entire experimental stage including heating and holding stages, ΔY is the yield of NH_3 from (T-100) to T temperature including heating and holding stages, Yy is the accumulated yield of NH_3 in the heating stage with 10 ºC/min, Yp is the yield of NH_3 from (T-100) to T temperature in the heating stage, Yc is the yield of NH_3 in the holding stage at final temperature.

RESULTS AND DISCUSSION

When coal samples are pyrolyzed, the small molecules and free radicals are formed through the breakage of the bridge linkage of molecules. The structure of three dimensional macromolecules formed by the N-containing heterocyclic ring and other cyclic structure or the branch were cracked. And at this time, nitrogen rings were exposed outside. Different forms of N-containing compounds are released with the cracking of ring structures and the working of the free radicals. One part of N is released in the form of volatile nitrogen, such as tar nitrogen, NH_3, HCN and N_2. Other nitrogen is remained in solid semicoke as coke nitrogen[12]. The fracturing degree of nitrogen-containing structures in coal and the form of N-containing gas is varying from different temperatures and coal ranks[12-14].

The yields of NH_3 during coals pyrolysis at different final temperature are shown in Fig. 1. The results show the release trend of NH_3 are basically the same for four coals pyrolysis. Total yield (Y) of NH_3 increases with rising final temperature of coal pyrolysis and then approaches to moderation at above 700 ºC. The accumulated yield (Yy) of NH_3 in the heating stage also presents the increase trend with final temperature, but its change rate is obviously lower than Y at below 700 ºC. The results of NH_3 yield in heating stages show that NH_3 occurs initially at 400 ºC and reaches the maximum at 700 ºC. And in the holding stage, NH_3 can be obviously released at 300 ºC and the maximum temperature occurs at 600 ºC. The formation

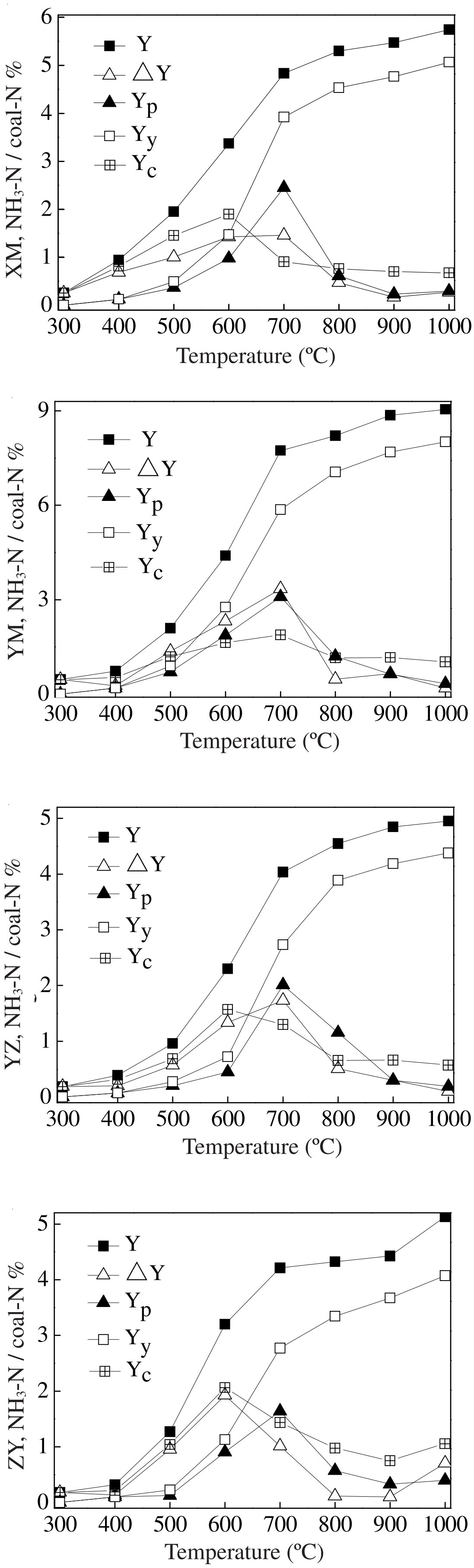

Fig. 1. Yields of NH_3 during coal pyrolysis in heating and/or holding stages at different final temperature

of NH_3 is mainly dominated by the interaction of H-radicals and N-radicals in volatiles or N-containing heteroaromatic ring in the char during coal pyrolysis. At lower temperature, the yield of NH_3 from heating stage is low because the amounts of H radicals and N radicals in volatile is small resulting to the little probability of their interaction. In the holding stage, the higher yield of NH_3 should be dominated by N-containing heteroaromatic ring in char. With the temperature increasing, the abundant H radicals are formed with the rapid release of volatiles, which is favorable to react with the N radicals in volatile and the functional groups of nitrogen in char. The higher yield of NH_3 in the holding stage (Yc) than in heating stage (Yp) below at 600 ºC show that the decomposition of char-N and then reacts with H radicals is the main source of N-containing gas. At the high temperature of 700 ºC, the volatiles are almost entirely released at heating stage and the formation of NH_3 is dominated by N radicals in volatile leading to Yc < Yp. The release yield of NH_3 obviously reduce at above 800 ºC because the relative unstable N-heterocyclic rings in coal have been cracked and entrained by volatile in the heating process at lower temperature. But the release yield of NH_3 in the holding stage at above 800 ºC is also obvious. The stable N-heterocyclic rings in char and the H radicals from the condensation reaction between aromatic rings are the main sources of NH_3 formation at holding stage when the high final temperature is reached. The results of ΔY > Yp below at 700 ºC and ΔY< Yp above at 700 ºC also show that the formation of NH_3 during coal pyrolysis is related with the releasing process of volatile and it is significantly affected by the final temperature.

Figs. 2 and 3 respectively show the total yield (Y) of NH_3 in the entire experimental stage and the accumulated yield (Yy) of NH_3 in the heating stage with 10 ºC/min of four coal samples. It can be seen that the change trends Y and Yy with temperature are identical, namely, Y and Yy of four coals gradually increase with the increasing of the pyrolysis temperature and become steady after 700 ºC. The change degree of Y and Yy with temperature are impacted by coal ranks and it takes the order of YM > XM > ZY ~ YZ, which is similar to the order of volatile content in Table-1. The results reveal that the low rank coal with high volatile content is favorable for the formation of NH_3. But ZY coal with the lowest volatile presents nearly the same release amount of NH_3, which shows that there is other factors influencing the transformation of nitrogen forms in coal and formation of NH_3 during pyrolysis.

It has been proved that four types of nitrogen, *i.e.*, pyrrolic nitrogen, pyridinic nitrogen, quarternary nitrogen and oxidized nitrogen, present in coal[4,12]. Pyrolysis temperature affects the types of nitrogen in char[12,14]. Quarternary nitrogen has completely degraded at the temperature of 945 ºC and the degradation rate of pyridinic nitrogen increases with the increasing of temperature. The degradation of pyrrolic nitrogen is affected by coal rank and its rate is high for the low rank coal. The stability of pyrrolic nitrogen in the polycyclic aromatic or nearby the multi-ring aromatic system is higher than that of pyridinic nitrogen, but NH_3 can be formed from the conversion of the stable heterocyclic compounds if there is enough H radicals[8,15,16]. If not, it will be converted to HCN and N_2 in gases or macromolecular nitrogen-containing structure in char. The formation of NH_3 should be dominated by the relative stable nitrogen heterocycle in the char and H radicals generated from the nascent char cracking.

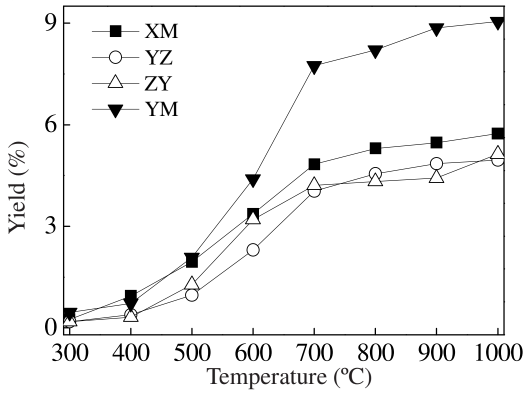

Fig. 2. Total yield of NH_3 from four coals pyrolysis in the entire experimental stage

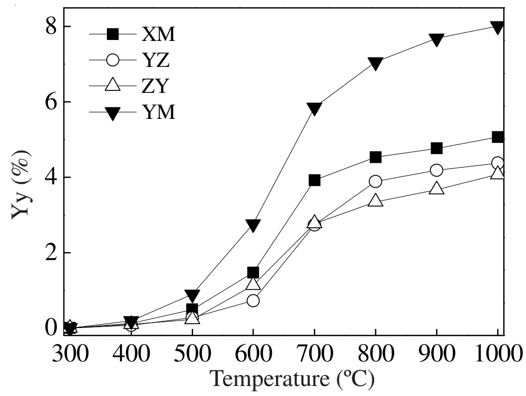

Fig. 3. Accumulated yield of NH_3 from four coals pyrolysis in the heating stage with 10 ºC/min

Conclusion

The results of NH_3 yields during pyrolysis of four different ranks coal show that the release of N-containing gaseous compounds are affected by coal properties and its heating course. The yield of NH_3 is mainly dominated by the decomposition of N-containing hereroaromatic ring in char at low temperature. When the pyrolysis temperature is increased, the volatile matters are effectively released and enough H radicals react with N-containing functional groups in the volatiles, so the yield of NH_3 in heating stage increases quickly and the amount of NH_3 is higher than that from holding stage in the temperature ranges of 600-800 ºC. The relative stable N-containing heteroaromatic ring in the char is the main source of the formation of NH_3 at high pyrolysis temperature and the maximum temperature range of the formation of NH_3 is 600-700 ºC despite of heating stage or holding stage. The low rank coal with high volatile content is favorable for the formation of NH_3. In the heating stage, NH_3 mainly yields from the rapid degradation of the pyrrolic nitrogen and the conversion of the relative stable nitrogen heterocycle in the coal/char in the condition of sufficient H radicals during holding temperature.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial supports of National Natural Science Foundation of China (21176165, U1261110), Research Fund for Doctoral Program of High

Education (20111402110009) and Shanxi Province Basic Conditions Platform for Science and Technology Project (2012091018).

REFERENCES

1. N.J. Gawande, A.R. Chaudhari and R.U. Khope, *Asian J. Chem.*, **24**, 5753 (2012).
2. B.H. Shen and L.Z. Zhao, *J. Energy China*, **32**, 9 (2010).
3. M. Zerta, P.R. Schmidt, C. Stiller and H. Landinger, *Int. J. Hydrogen Energy*, **33**, 3021 (2008).
4. Z.H. Feng, L.P. Chang, J. Ren and K.C. Xie, *Coal Conversion*, **23**, 6 (2000).
5. W. Zhao, L.P. Chang, Z.H. Feng and K.C. Xie, *Fuel Chem. Technol.*, **30**, 408 (2002).
6. L.L. Tan and C.Z. Li, *Fuel*, **79**, 1883 (2000).
7. J.R. Pels, F. Kapteijn and J.A. Moulijn, *Carbon*, **33**, 1641 (1995).
8. C.Z. Li and L.L. Tan, *Fuel*, **79**, 1899 (2000).
9. S. Kambara, T. Takarada and Y. Yamamoto, *Energy Fuels*, **7**, 1013 (1993).
10. J.C. Mackie and M.B. Colker, *J. Phys. Chem*., **94**, 4099 (1990).
11. A. Lifshitz, C. Tamburu and A. Suslensky, *J. Phys. Chem.*, **93**, 5820 (1989).
12. J. Friebel and R.F.W. Köpsel, *Fuel*, **78**, 923 (1999).
13. J.E. Johnsson, *Fuel*, **73**, 1398 (1994).
14. W.C. Xu and M. Kumagai, *Fuel,* **81**, 2325 (2002).
15. P.F. Nelson, C.Z. Li and E.B. Ledesma, *Energy Fuel*, **10**, 264 (1996).
16. F.J. Tian, S. Zhang, J.I. Hayashi and C.Z. Li, *Fuel*, **89**, 1035 (2002).