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The Results of Experiments on Pilot 2-staged Selective Non-catalytic Reduction unit Along with Maximal Efficiency and Minimal Secondary Pollutants Formation

Olga Kulish[1], Konstantin Zaporozhskii[2]
[1]National University of Oil and Gas «Gubkin University»
65, Leninsky Avenue, Moscow, Russia
olgakulish@yandex.ru
[2]National University of Oil and Gas «Gubkin University»
65, Leninsky Avenue, Moscow, Russia
konstantin.zaporozhskiy@mail.ru

Abstract-In this paper the results of experiments on pilot 2-staged selective non-catalytic reduction unit are described. Efficiency of this variety of selective non-catalytic reduction, outlet concentrations of ammonia and carbon monoxide in comparison with 1-staged process are showed.

Keywords**:** Nitrogen oxides control, Selective non-catalytic reduction, Secondary pollutants

1. Introduction

Selective non-catalytic reduction (SNCR) technology is widely applying as nitrogen oxides control method. [1, Kutlovsky, Von der Heide, 4, Schuttenhelm, Teuber, 2, Von der Heide 3, 5, Kulish]. This technology is applying on utility and industrial boilers, waste incinerator plants and other combustion units to reduce nitrogen oxides concentration in flue gases. SNCR is the best available technique along with selective catalytic reduction (SCR) and techniques for the prevention of nitrogen oxides emissions. Advantage of SNCR technology is lower capital cost due to catalyst absence.

Fig.1 shows "cost-efficiency" ratio of SNCR, SCR and techniques for the prevention of nitrogen oxides emissions.

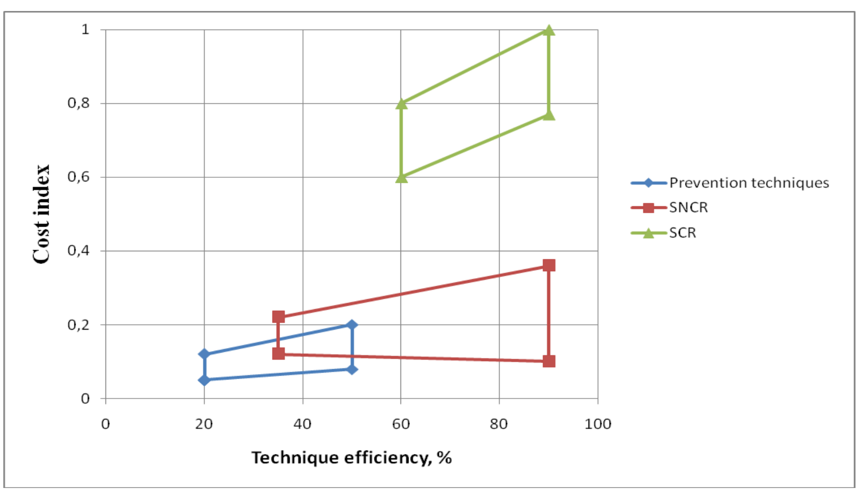

Fig. 1: Relative cost index and reduction of nitrogen oxides efficiency when using of different techniques of prevention and control of nitrogen oxides on combustion units.*

* - prevention techniques include: low excess air firing, exhaust gas recirculation, usage of low-NOx burners.

Fig.1 shows that efficiency of SNCR technology is comparable with efficiency of SCR technology, but SNCR efficiency spread is more broad-ranged. SNCR process can provide from 30 to 90 percent efficiency of nitrogen oxides reduction. For example, we use information about efficiency of SNCR technology applied on various boilers. It described in the US EPA paper by [7, Sorrels, Randall, Fry, Schaffner, 10, ICAC] (see table 1).

Table 1: Summary of nitrogen oxides reduction efficiencies obtained using SNCR on different types of boilers in the U.S.

Type of source category	Fuel	NOx reduction reagent	Average boiler size, MW	Median nitrogen oxides reduction, %
Electric utility	Coal	Urea	320	25
Co-generation	Primarily wood, coal, biomass and tires	Urea	105	50
Pulp and paper	Primarily bark and wood waste, supplemented with a variety of other fuels	Urea	120	50
Municipal waste combustion	Municipal solid waste	Urea	80	37
Refinery CO boilers	Refinery fuel gas	Urea	95	60
Miscellaneous combustion units	Wood, municipal solid waste, coal	Ammonia	120	65

SNCR technology is applying at 80-320 MW boilers with using urea and ammonia as reactants. Efficiency of SNCR is at range from 25 to 65%. At the same time in the papers [3, 5, Kulish] results of practical using in Russia of SNCR-technology with 80-90% efficiency are described.

SNCR-technology is based on reduction of nitrogen oxides by ammonia-based reactants at 850-1050^{0}C temperature. The most popular reactants are ammonia or urea but urea is more convenient due to ecological safety. Reduction of nitrogen oxides results in nitrogen, water and carbon dioxide (Eqs. 1-2):

$$2CO(NH_2)_2 + 4NO + O_2 = 4N_2 + 2CO_2 + 4H_2O \quad (1)$$
$$2CO(NH_2)_2 + 2NO_2 + O_2 = 3N_2 + 2CO_2 + 4H_2O \quad (2)$$

SNCR-process starts with thermal destruction of urea with forming ammonia and isocyanic acid (Eq.3):

$$CO(NH_2)_2 = NH_3 + HNCO \quad (3)$$

These reducing agents react with nitrogen oxides. Mechanism of this process is described in [8, Lyon, Benn, 9, Lyon, Cole]. Their kinetic model of SNCR-process has high rate of correlation between calculated and experimental results.

In that time SNCR-process gives secondary pollutants as ammonia and carbon monoxide. Presence of secondary pollutants in treated flue gases decreases ecological safety of SNCR-process and disables applying of SNCR-technology in certain cases.

In our researches we estimated minimal formation of secondary pollutants in SNCR-process with urea using.

2. Results and discussion

The pilot unit scheme is showed on Fig.2. Experiments were conducted at quartz cylindrical reactor. Mixed gas consisting of nitrogen oxides, nitrogen and oxygen met with reductive mixture formed from thermal destruction of urea solution. SNCR-process went in reactor.

SNCR-process options varied in next ranges and was equaled to:

- reactor temperature 700 – 1100 ºC;
- ratio of injected reagent (β) 0,5 – 3,0;
- residence time in every reactor (τр) 1,0 sec;
- average inlet nitrogen oxides concentration is 280 mg/m^3;
- oxygen concentration is 6 vol.%;
- using of reactor #1 only (results of reactor#1 and reactor #2 using are described below in Tables 2-3).

Component concentrations (oxygen, nitrogen oxides and carbon monoxide) of gas mixture before and after reduction was measured by "MRU Optima 7" gas analyzer, Germany.

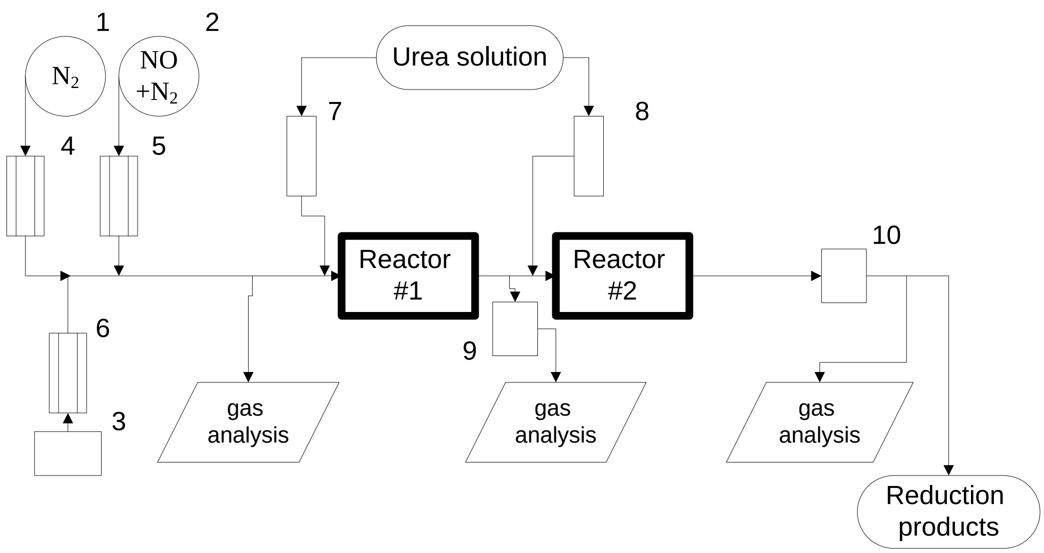

Fig. 2: Pilot unit scheme 1,2 - gas cylinders; 3 - air compressor; 4,5,6 - flow meters; 7,8 - urea solution evaporators; 9,10 – condensate storages.

Ammonia concentration after reactor was measured by linear-color determination method using GH-M, Russia.

The results of researches are described in Figures 3-4.

As described at Figures 3-4, concentrations of secondary pollutants in treated mixture after reactor depend on reactor temperature and ratio of injected reagent. Concentration of "slipped" ammonia was not above 5 mg/m^3 at ratio from 0,5 to 1,0 and was nearby zero at 1000ºC reactor temperature.

Concentration of carbon monoxide was about zero at temperature above 950ºC. Increase of ratio of injected reagent resulted in growth of carbon monoxide concentration, but it was not above 10 mg/m^3 at suitable temperature for process.

Toxic potential of ammonia is not so interesting in our researches. Ammonium salts formation is more important effect. These salts can be deposed at low-temperature boiler zone. It makes run of boiler worse. That's why there is the limit of ammonia concentration in controlled flue gases at 5 mg/m^3. The results of our experiments showed that ammonia concentration in treated gas mixture after reactors is not above this limit.

Obtained carbon monoxide concentration is not above 10 mg/m^3 while legislative limit in Russia is 50 mg/m^3.

Thus, if SNCR-process run at ratio of injected reagent not above 1 and temperature between 900 and 1000ºC it is possible to decrease concentration of secondary pollutants.

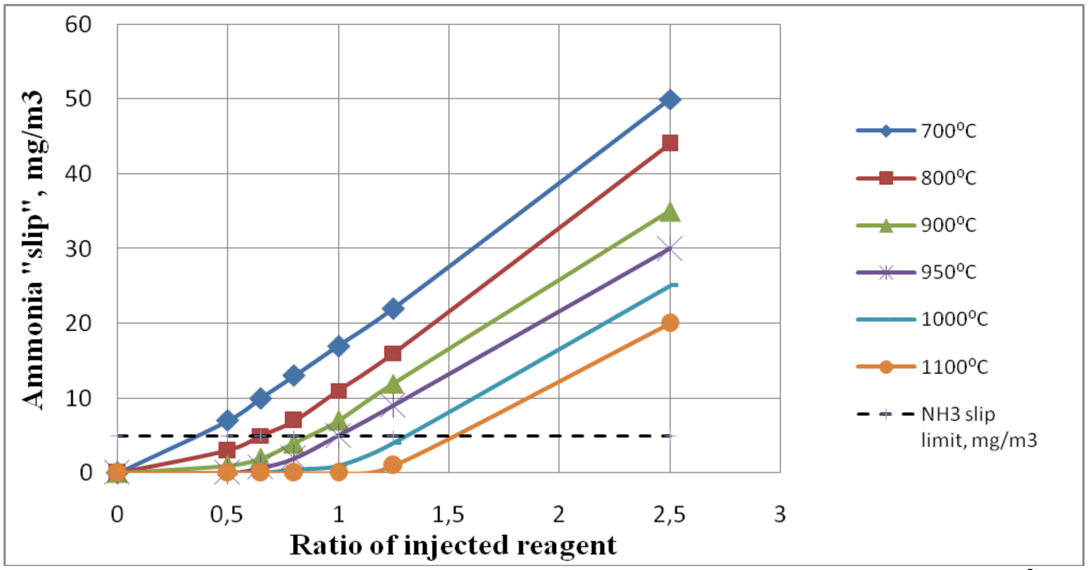

Fig. 3:"Ammonia "slip" - Ratio of injected reagent" dependence at reactor temperature range from 700^{0}C to 1100^{0}C.

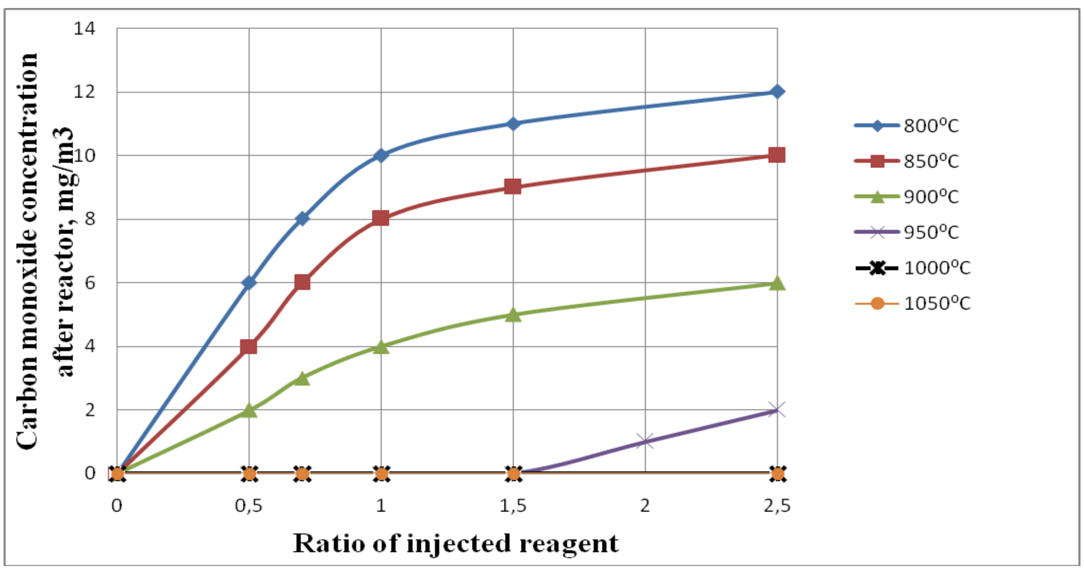

Fig. 4:"Carbon monoxide concentration after reactor - Ratio of injected reagent" dependence at reactor temperature range from 800^{0}C to 1050^{0}C.

It is known that SNCR-process efficiency depends on process temperature and ratio of injected reagent.

We have to strike the right balance between maximal efficiency of SNCR-process and minimal concentration of secondary pollutants in reduction products. This can be achieved by in-parallel 2-staged reactant injection.

We conducted experiments on pilot 2-staged unit (Fig.2) with reactors #1 and #2. Options of experiments was similar described above:

- reactor #1 temperature 850 – 1000 ºC;

- reactor #2 temperature 850 – 950 ^{o}C;
- ratio of injected reagent (1-staged reduction process) (β) 1,5;
- ratio of injected reagent (2-staged reduction process) (β) 0,90 (1st stage) + 0,45 (2nd stage) (referred to inlet nitrogen oxides concentration);
- residence time in every reactor (τp) 1,0 sec;
- average inlet nitrogen oxides concentration is 280 mg/m3;
- oxygen concentration is 6 vol.%;

Results of experiments are showed in Tables 2-3.

Table 2: SNCR efficiency and secondary pollutants concentration after reactor at 800-1000^{0}C in 1-staged reduction process.

№	Reactor temperature, ^{o}C	Inlet nitrogen oxides concentration, mg/m^3	Ratio of injected reagent	Outlet concentrations of nitrogen oxides and secondary pollutants, mg/m^3			SNCR efficiency, %
				NOx	NH_3	CO	
1	1000	287	1,50	101	8	2	65
2	950	273	1,50	74	12	4	73
3	900	275	1,50	83	16	6	70
4	850	281	1,50	143	18	8	49
5	800	283	1,50	164	22	11	42

Table 3: SNCR efficiency and secondary pollutants concentration after reactor at 850-1000^{0}C in 2-staged reduction process.

№	Reactor temperature, ^{o}C		Inlet nitrogen oxides concentration, mg/m^3	Ratio of injected reagent	Outlet concentrations of nitrogen oxides and secondary pollutants, mg/m^3			SNCR efficiency, %
	#1	#2			NOx	NH_3	CO	
1	1000	950	285	0,90+0,45	86	1	1	70
2	950	900	270	0,90+0,45	38	1	1	86
3	900	900	280	0,90+0,45	50	2	3	82
4	900	850	277	0,90+0,45	64	4	4	77
5	850	850	283	0,90+0,45	91	5	4	68

In-parallel 2-staged injection of reactant at reactor #1 temperature in range 850-1000^{0}C and reactor #2 temperature in range 850-950^{0}C and at ratios of injected reagent in every reactor below 1 provides for SNCR efficiency at range from 68% to 86%; at the same time efficiency of 1-staged injection is 42-73%. Concentrations of ammonia is below 5mg/m^3 and concentration of carbon monoxide is below 4mg/m^3 in 2-staged process and 22 and 11 respectively in 1-staged reduction.

It is known that insignificant raise of ratio of injected reagent results in increase of ammonia "slip". In addition SNCR efficiency decreases along with boiler loading because of lowering SNCR temperature [6, T. Lecomte, J.F. Ferreria De La Fuente, F. Neuwahl, M. Canova, A. Pinasseau, I. Jankov, T. Brinkmann, S. Roudier, L. Delgado Sancho]. In this paper variation of SNCR-technology with acceptable ammonia "slip" and stable process efficiency is described.

Thus, 2-staged SNCR-process with in-parallel reactant injection makes process efficiency high and stable at different temperatures of SNCR-process and at different boiler loadings. In addition, this variation of SNCR-process gives ecological safety of flue gases control due to reduction of secondary pollutants concentrations at different boiler loadings.

3. Conclusion

Selective non-catalytic reduction technology is widely applying as nitrogen oxides control method. This technology is applying on utility and industrial boilers, waste incinerator plants and other combustion units to reduce nitrogen oxides concentration in flue gases.

Efficiency of SNCR is at range from 25 to 65%. For improving process efficiency ratio of injected reagent have to be raised. This results in high ammonia "slip" (above legislative limit) and formation of ammonium salts.

In this paper variation of SNCR-technology with acceptable ammonia "slip" and stable process efficiency is described.

In-parallel 2-staged injection of reactant at ratios in every reactor below 1 provides for SNCR efficiency at range from 68% to 86%; at the same time efficiency of 1-staged injection is 42-73%. Concentrations of ammonia is below 5mg/m^3 and concentration of carbon monoxide is below 4mg/m^3 in 2-staged process and 22 and 11 respectively in 1-staged reduction.

2-staged SNCR-process described in this paper gives high and stable process efficiency and low secondary pollutants concentrations.

Acknowledgements

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References

[1] Kutlovsky J., von der Heide B. Experience in Controlling NOx from Utility Boilers with SNCR using Urea and Ammonia as Reagent, *Proceedings of POWER GEN International Conference*, Frankfurt, 1999.

[2] Von der Heide B. Advanced SNCR Technology for Power Plants. POWER GEN, Las Vegas, 2011.

[3] Kulish O., Kuzhevatov S., Gleizer I., Orlova M., Ivanova E. Removal of Nitrogen Oxides from Combustion Gases of Industrial Heat Aggregates by Noncatalytic Reduction. *Ecology and Industry of Russia*. 2015;19(9):12-16. (In Russ.)

[4] Schuttenhelm W., Teuber Z. Most Recent Operational Experience with SNCR Applications for Coal-Fired Boilers. *Proceedings of POWER GEN International Conference*, Cologne, 2014.

[5] Kulish O.N., Kuzhevatov S.A., Sister V.G. Non-catalytic reduction of nitrogen oxides in flue gases: results of the practical implementation. *Ecology and Industry of Russia*. 2004; 4 :14-18. (In Russ.)

[6] T. Lecomte, J.F. Ferreria De La Fuente, F. Neuwahl, M. Canova, A. Pinasseau, I. Jankov, T. Brinkmann, S. Roudier, L. Delgado Sancho. *Best Available Techniques (BAT) Reference Document for Large Combustion Plants*. Publications Office of the European Union, 2017.

[7] Sorrels J.L., Randall D.D., Fry C.R., Schaffner K.S. *SNCR Cost Manual Chapter 7th Edition. Chapter 1. Selective Noncatalytic Reduction.* EPA Form 2220-1 (Rev. 4-77). 2016. 70 p.

[8] Lyon R.K., Benn D. Kinetics of the NO-NH_3-O_2 reaction. *Proceedings of the 17-th Symposium (Int.) on Combustion Institute.* Pittsburg. 1978. P. 601-610.

[9] Lyon R.K., Cole J.A. A Reexamination of the RapreNOx Process. *Combustion and Flame.* 1990. 82. P.435-443. L.

[10] Institute of Clean Air Companies (ICAC). *Selective Non-Catalytic Reduction (SNCR) for controlling NOx Emissions; White Paper*. Prepared by the SNCR Committee of ICAC. February 2008.