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THERMODYNAMIC ASSESSMENT OF CARBAMIDE USE FOR REDUCING BOILER NO_X, CO FLUE GAS EMISSIONS

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Abstract. Some aspects of boiler toxic pollutant emission reduction in the presence of carbamide are discussed in the paper. Theoretical pollution reduction investigation was conducted by using thermodynamic function calculation methods and evaluating the Gibbs' energy value changes at various temperatures. The equations of these changes were derived. It was determined that the most reliable compounds, formed during the reaction between carbamide and nitrogen oxides, are CO_2, nitrogen and water. Other products are formed when carbamide is oxidized. Also, it was found that carbamide could reduce sulphur oxides to sulphur, and in some cases – to H_2S. The pyrolysis of carbamide is possible at temperatures above 450 K.

Keywords: carbamide, Gibbs' energy, oxidation, reduction, pyrolysis, gas decontamination.

1. Introduction

After Lithuania joined the European Union, pollution from industrial enterprises became even more relevant. One of the main sources of air pollution comes from power stations and boiler-houses. They emit nitrogen oxides, CO and SO_2 into the atmosphere. In order to lower SO_2 emissions, magnesium oxide can be interblended into the fuel (Kaminskas *et al.* 1997; Valužienė *et al.* 1998). To reduce nitrogen oxides emissions magnesium oxide, containing traces of ammonia, could be added to the fuel (Zhang *et al.* 2002; Jeong *et al.* 2007; Kröcher *et al.* 2006; Kozub *et al.* 2001; Amblard *et al.* 1999, 2000; Gang *et al.* 1999; Lietti *et al.* 1999). The use of SO_2 converts the magnesium oxide under the influence of air oxygen into magnesium sulphate. The most desirable reaction product in the process of nitrogen oxide decontamination using ammonia is nitrogen (Birmantas and Kaminskas 2001). Recently it was proposed to use carbamide for the decontamination of nitrogen oxides (Kiely 1998). Carbamide as well as ammonia reduce nitrogen oxides to elementary nitrogen. A reducing agent, typically ammonia or nitrogen, is injected into the combustion process gases. At suitably high temperatures (871–1149 °C), the desired chemical reactions occur (Institute of… 2007; Tayyeb *et al.* 2007). Besides the mentioned oxides, there are carbon oxides, and also surplus oxygen present in the flue gases. What reactions occur in the flue gases during the flue gas decontamination process using carbamide has not been investigated fully up till now. The objective of this investigation was to determine the reactions, which occur between carbamide and the compounds present in the boiler-house flue gases, also to estimate and compare the reliability of those reactions. The evaluation of reliability was accomplished by using thermodynamic calculations.

2. Methods

The reliability of the reactions was estimated according to their Gibbs' energy change values at different temperatures. The enthalpy and entropy variation values were calculated while the sum of enthalpies and entropies of reaction products minus the sum of enthalpies and entropies of reactive materials. The Gibbs' energy variation values ($\Delta G_T{}^\circ$) were calculated according to the following formula (Kazragis 1998; Simanavičius 2005):

$$\Delta G_T{}^\circ = \Delta H_T{}^\circ - T\Delta S_T{}^\circ ,$$

where: $\Delta G_T{}^\circ$ – Gibb's energy change value, kJ/mol; $\Delta H_T{}^\circ$ – enthalpy change value, kJ/mol; T – standard temperature, K (T = 298 K); $\Delta S_T{}^\circ$ – entropy change value, J/(mol·K).

The carbamide enthalpy and entropy formation values were determined at different temperatures, using their standard temperature values and calculated according to the Gibbs' energy formula (Table 1).

The enthalpies and entropies formation values of other compounds are listed in the references (Sthal *et al.* 1971). The values of enthalpy changes, used in this investigation, are expressed in kJ/mol, the entropy values, are expressed in J/(mol·K). According to Gibbs' energy variation values, the reliability of the reactions were evaluated.

Table 1. Values of carbamide enthalpy and entropy formation values at different temperatures

Thermodynamical function	T, K								
	298	300	400	500	600	700	800	900	1000
S°, J/(mol·K)	104.60	105.22	131.99	152.76	169.73	184.05	196.52	207.43	217.24
ΔH_T°, kJ/mol	–333.10	–332.91	–323.60	–314.29	–304.97	–295.66	–286.34	–277.03	–267.72

3. Investigation results and discussions

3.1. Carbamide reaction with nitrogen oxides and nitric acid

Carbamide reduces nitrogen oxides first to nitric acid and then to nitrogen. In the presence of oxygen in the flue gas, it can participate or not in the reaction. The reaction proceeds according to the following possible derived equations:

$$CO(NH_2)_2 + N_2O = C + 2N_2 + 2H_2O, \quad (1)$$

$$CO(NH_2)_2 + NO = C + 3/2N_2 + 2H_2O, \quad (2)$$

$$CO(NH_2)_2 + NO = CO + 3/2N_2 + H_2O + N_2, \quad (3)$$

$$CO(NH_2)_2 + 2NO = CO + 2H_2O + 2N_2, \quad (4)$$

$$CO(NH_2)_2 + NO_2 = CO + 3/2N_2 + 2H_2O, \quad (5)$$

$$CO(NH_2)_2 + 2NO_2 = CO_2 + 2H_2O + 2N_2 + 1/2O_2, \quad (6)$$

$$CO(NH_2)_2 + 2HNO_3 = 2N_2 + CO_2 + 3H_2O + 2N_2 + O_2, \quad (7)$$

$$CO(NH_2)_2 + N_2O + O_2 = CO_2 + 2N_2 + H_2O, \quad (8)$$

$$CO(NH_2)_2 + NO + O_2 = CO_2 + 3/2N_2 + 2H_2O, \quad (9)$$

$$CO(NH_2)_2 + 2NO + 1/2O_2 = CO_2 + 2H_2O + 2N_2, \quad (10)$$

$$CO(NH_2)_2 + NO_2 + 1/2O_2 = CO_2 + 3/2N_2 + 2H_2O. \quad (11)$$

The enthalpy changes also stimulate reactions, since the values of enthalpy changes of all the reactions are negative. Besides that, the absolute values of enthalpy changes increase with an increase in temperature. The more complete the carbamide oxidation process, the higher the absolute values of enthalpy changes. The maximum values of enthalpy changes correspond to equation 10 when nitrogen oxides, being reduced up to nitrogen, oxidize carbon and hydrogen, in the carbamide compound up to CO_2 and water. The minimum values of enthalpy changes are obtained in the case of reaction 3, where non-oxidized hydrogen is evolved into the atmosphere.

The entropy changes stimulate the nitrogen oxide and nitric acid decontamination process, since the values of entropy changes of all the reactions are positive. The entropy change values increase only slightly with increases in temperature. The maximum entropy change values are for the reaction, in which nitric acid is present (reaction 7). They are slightly less when nitrogen dioxide participates (reactions 5 and 6). The minimum entropy change values occur during the nitrogen oxide and carbamide interaction, in the absence of oxygen, when carbon is formed (reaction 2). When the reaction takes place between carbamide and N_2O in the presence of oxygen (reaction 8), entropy changes are greater than those in a non-oxygen atmosphere (reaction 1). This means that oxygen initiates this interaction. Conversely, when the reaction occurs between carbamide and nitrogen dioxide in the absence of oxygen (equations 5 and 6), entropy change values are larger than those in the presence of oxygen (equation 11). This means that, according to the entropy change values, nitrogen dioxide is a much more active carbamide oxidator than oxygen. Oxygen is unnecessary for this reaction.

The reaction‘s reliability can be judged according to the Gibbs' energy change values, which are presented in Fig. 1.

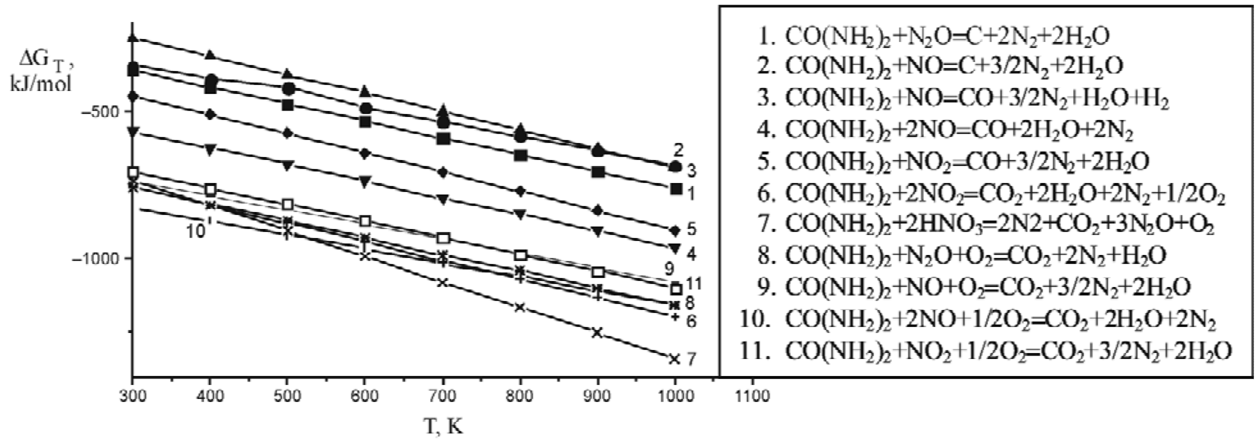

Fig. 1. The Gibbs' energy value changes dependency on temperature while carbamide reduces nitrogen oxides

As it can be seen from Fig. 1, all the nitrogen oxides can be reduced to nitrogen in the presence of carbamide. The reaction reliability increases with an increase in temperature. The least reliable reactions are reactions 1–3 during which elementary carbon with hydrogen is evolved. The most reliable reactions may be represented by equations 6, 7, 8, and 10. The decontamination process of N_2O and nitrogen oxide is more reliable, when oxygen participates in the reaction and when, during the decontamination process of nitrogen dioxide and nitric acid, oxygen is emited to the atmosphere (equations 6 and 7). The reliability of these reactions increases with an increase of nitrogen valency in the compound. Carbamide reduces nitric acid most easily by equation 7, and the least reliable reactions are those, in which N_2O and nitrogen oxide takes part (equations 1–3). However, the reliability increases when oxygen is introduced into the reaction (equations 8–10). The reaction reliability increases with an increase of nitrogen oxide concentration because possibility for one carbamide molecule to react with a larger number of nitrogen oxides molecules increases. It is known that the more negative $\Delta G_T°$ value, the more reliable the reaction. As we can see from Fig. 1, carbamide reacts more reliably with NO_2 than with NO in this case.

As it can be seen from the data in Fig. 1, the efficiency of nitrogen oxide decontamination process is relatively high enough and is determined by the reaction products. Here, the maximum $\Delta G_T°$ values are reached, when during the reaction carbon and hydrogen are oxidized up to CO_2 and water, and nitrogen oxides are reduced to nitrogen. Therefore, there should be enough of nitrogen oxides present in the flue gas, and in their absence or in the presence of their insufficient quantities additional oxygen is required.

3.2. Pyrolysis of carbamide

Carbamide belongs to the class of toxic substances, therefore, its concentration in the indoor air environment cannot be higher than 0.2 mg/m^3. In the absence of oxygen, carbamide decomposes as follows:

$$CO(NH_2)_2 = CO + N_2 + 2H_2, \tag{12}$$

$$CO(NH_2)_2 = CO + NH_3 + 1/2H_2 + 1/2H_2, \tag{13}$$

$$CO(NH_2)_2 = HCN + NH_3 + 1/2O_2. \tag{14}$$

As follows from equations 12–14, during carbamide pyrolysis new noxious substances can be evolved into the atmosphere: CO – its MAC is 3 mg/m^3, ammonia – 0,04 mg/m^3 and hydrogen cyanide – 0,01 mg/m^3. This means that during the carbamide pyrolysis process more noxious substances are evolved, which present a greater danger than the carbamide itself. The carbamide pyrolysis reactions $\Delta G_T°$ value dependencies on temperature are given in Fig. 2. As it follows, the carbamide pyrolysis process according to equation 13 is possible only above 70 K, while according to equation 12 – only above 85 K, and according to equation 14 – above 880 K. The most reliable pyrolysis of carbamide reaction up to 400 K proceeds according to equation 13, while above 400 K – according to equation 12. The least reliable is the carbamide pyrolysis equation during which hydrogen cyanide is produced (equation 14). All the carbamide pyrolysis reaction $\Delta G_T°$ values are substantially lower than those for the case of carbamide reactions with nitrogen oxides. This means that carbamide can be used for decontamination of nitrogen oxides if nitrogen oxides and oxygen are present in the atmosphere, without concern that its pyrolysis will proceed further.

3.3. Carbamide reaction with oxygen and carbon

The flue gases of boiler-house smokestacks contain CO_2 and oxygen playing a dominant role which is only next to that of nitrogen. The quantity of these substances depends on the air surplus coefficient. When carbamide is introduced into the atmosphere with small quantities of nitrogen oxides, it can react with oxygen and CO_2, according to our derived equations, as follows:

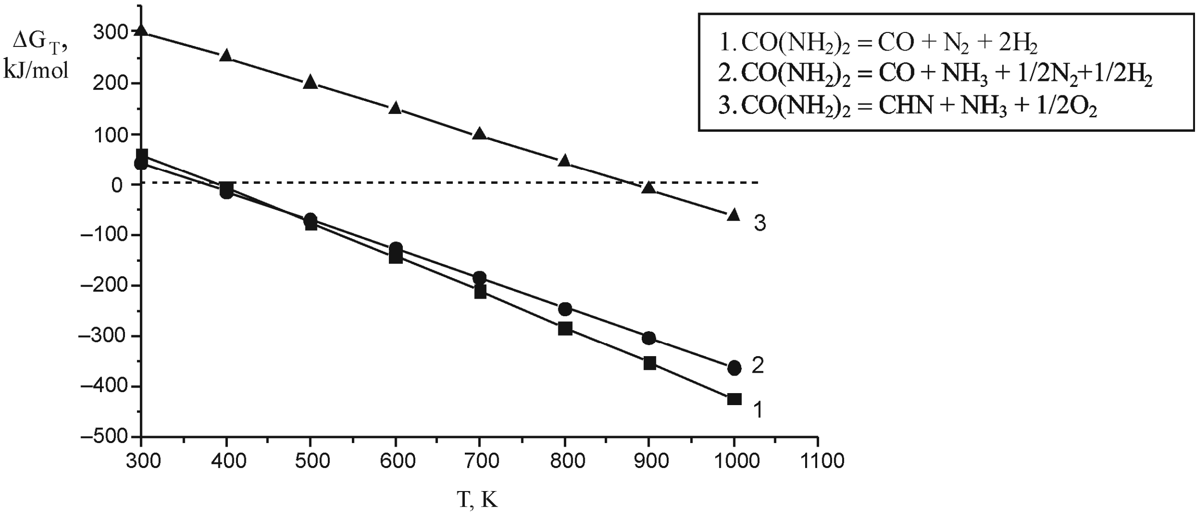

Fig. 2. The Gibbs' energy value change dependency on temperature during carbamide pyrolysis according to the equations presented in the diagram

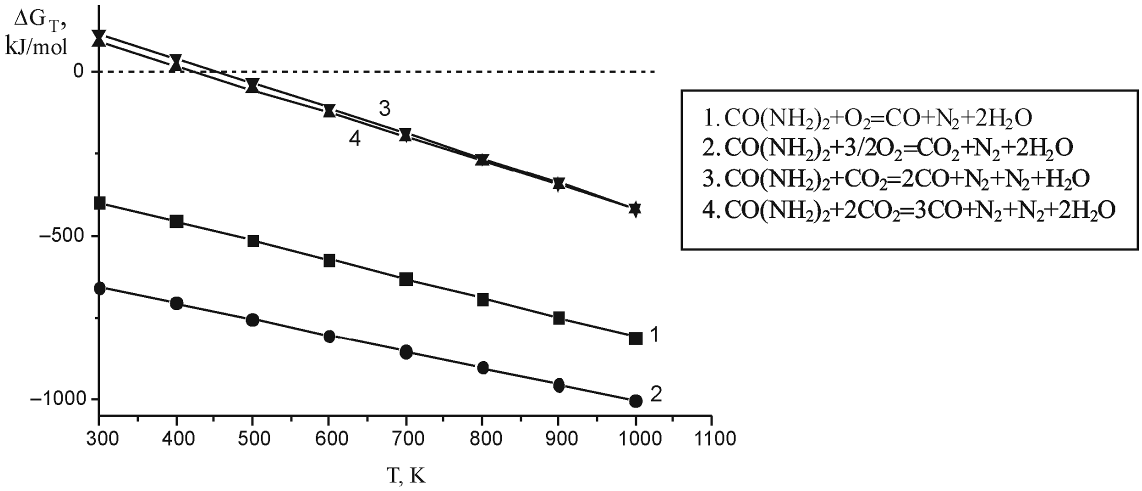

Fig. 3. The Gibbs' energy value change dependency on temperature during reactions between carbamide and CO_2 and air oxygen according to the equations presented in the diagram

$$CO(NH_2)_2 + O_2 = CO + N_2 + 2H_2O, \tag{15}$$

$$CO(NH_2)_2 + 3/2O_2 = CO_2 + N_2 + 2H_2O, \tag{16}$$

$$CO(NH_2)_2 + CO_2 = 2CO + N_2 + H_2 + 2H_2O, \tag{17}$$

$$CO(NH_2)_2 + 2CO_2 = 3CO + N_2 + 2H_2O. \tag{18}$$

The Gibbs' energy change values of these reactions are dependent on the temperature and are presented in Fig. 3. As follows, the carbamide oxidation process by air oxygen is possible at a room temperature (equations 15, 16). The higher the temperature, the larger the absolute $\Delta G_T°$ values. However, they are relatively smaller than the values which are obtained for carbamide reactions with nitrogen oxides. Carbamide reacts with oxygen much more effectively when there is a sufficient amount of it (equation 16) and when the reaction product is CO_2. As follows from Fig. 3 data, carbamide can reduce CO_2 to CO above 400 K according to equation 18, and above 450 K – according to equation 17. Such a process is possible when the air surplus coefficient is low enough and is introduced into the flue gases with an insufficient oxygen concentration.

Comparison of $\Delta G_T°$ values in its oxidation process with air oxygen (Fig. 3, curves 1, 2) and with reaction equations, in which carbamide reacts with nitrogen oxides (Fig. 1), shows that when nitrogen oxides do not participate in the oxidation reaction, $\Delta G_T°$ values are equal to 1000 kJ/mol under 1000 K, and when nitrogen oxides take part – under 700 K. So it follows that nitrogen oxides can lower the carbamide oxidation reaction process temperature by not less than 300 °C.

3.4. Carbamide reactions with sulphur (VI) oxide

The use of sulphureous fuel in boiler-houses leads to large amounts of sulphur dioxide emitted into the atmosphere (Nimmo *et al.* 2004). It is well known that SO_2 easily oxidizes up to SO_3 in the presence of oxygen, and a catalyst for this reaction is nitrogen oxide. Nitrogen oxides are used as a catalyst during the production of sulphuric acid by the nitrosation way. Therefore, when carbamide is introduced into the boiler-house flue gases, it can react not only with nitrogen oxides, but also with SO_2. The reactions can be illustrated by the following equations:

$$CO(NH_2)_2 + SO_3 = CO_2 + N_2 + 2H_2O + S, \tag{19}$$

$$CO(NH_2)_2 + SO_3 + 1/2O_2 = CO_2 + N_2 + 2H_2O + SO_2, \tag{20}$$

$$CO(NH_2)_2 + 2SO_3 + 1/2O_2 = CO_2 + 2SO_2 + 2H_2O + N_2, \tag{21}$$

$$CO(NH_2)_2 + 2SO_3 = CO_2 + 2S + NO_2 + NO + 2H_2O, \tag{22}$$

$$CO(NH_2)_2 + SO_3 = CO_2 + H_2O + N_2O, \tag{23}$$

$$CO(NH_2)_2 + 3SO_3 = CO_2 + N_2 + 2H_2O + SO_2. \tag{24}$$

The $\Delta G_T°$ values of these reactions under different temperatures are given in Fig. 4. As it can be seen from Fig. 4, the most reliable is reaction 20, during which SO_3 is reduced to SO_2, and carbon and hydrogen, present in the carbamide composition, is oxidized up to CO_2 and H_2O. Oxygen also participates in this reaction. The absolute $\Delta G_T°$ values are slightly lower in equations 21, 24 when larger quantities of SO_3 take part in the reaction and more molecules of SO_2 are formed. Substantially less reliable is reaction 19 in which oxygen does not take part, and even less reliable is reaction 23 during which N_2O is generated. The formation possibility of nitrogen oxides NO_2 and NO according to equation 22 is possible only above 700 K. The lower reliability of nitrogen oxide formation is determined by the fact that their formation enthalpies are positive. As it follows from Fig. 4, carbamide introduction into the flue gases disturbs the SO_2 oxidation process.

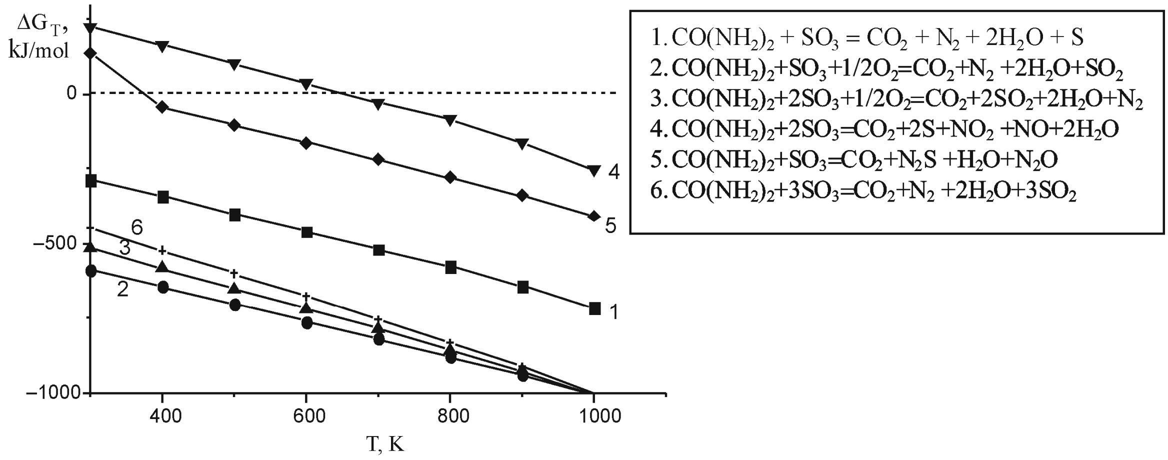

Fig. 4. The Gibbs' energy value change dependency on temperature during carbamide reaction with sulphur (VI) oxide according to the equations presented in the diagram

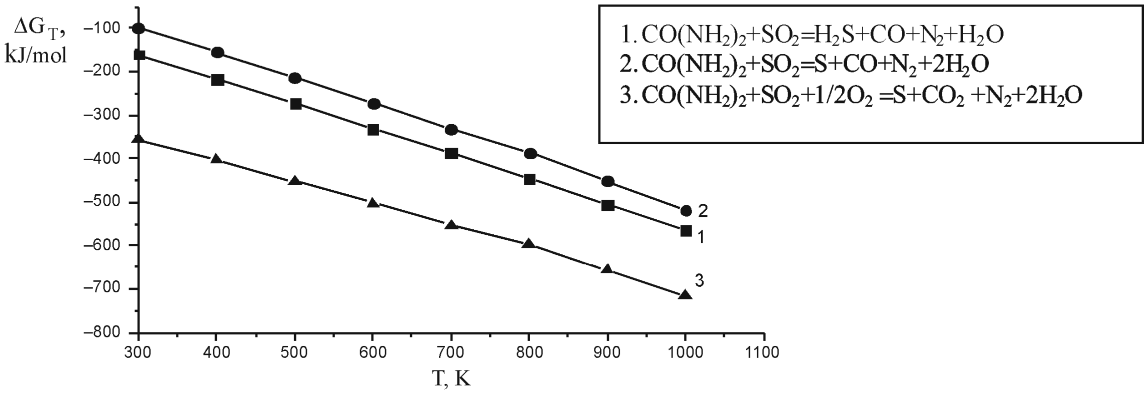

Fig. 5. The Gibbs' energy value change dependency on temperature during reaction between carbamide and SO_2 according to the equations presented in the diagram

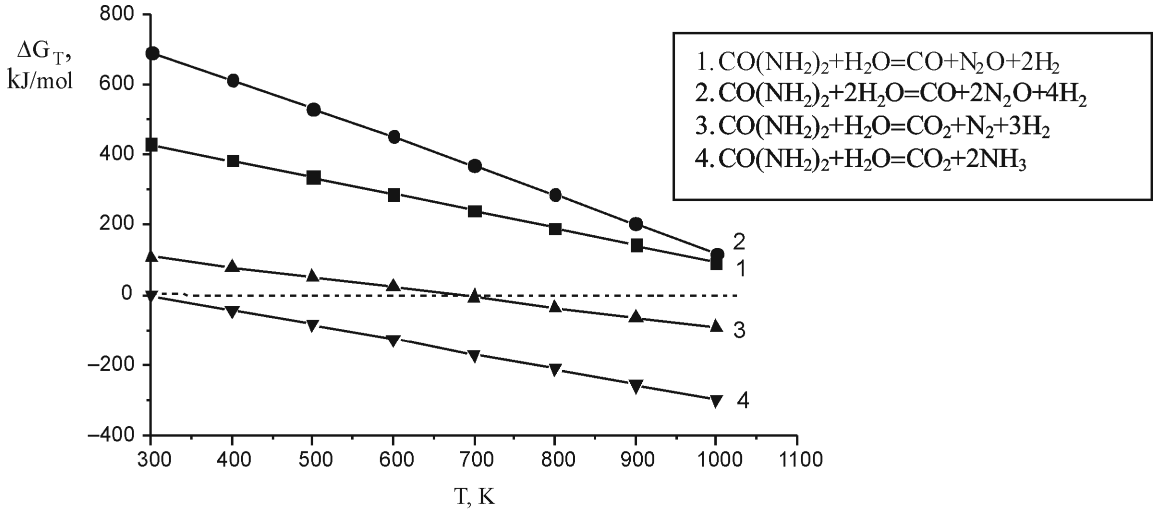

Fig. 6. The Gibbs' energy value change dependency on temperature during reaction between carbamide and water vapour according to the equations presented in the diagram

3.5. Carbamide reactions with sulphur (IV) oxide

Sulphur in the boiler-house flue gases is present mainly in the form of SO_2. Carbamide, introduced into the flue gases, can react with SO_2, while reducing it to hydrogen sulphide and sulphur according to the following equations:

$$CO(NH_2)_2 + SO_2 = H_2S + CO + N_2 + H_2O, \tag{25}$$

$$CO(NH_2)_2 + SO_2 = S + CO + N_2 + 2H_2O, \tag{26}$$

$$CO(NH_2)_2 + SO_2 + 1/2O_2 = S + CO_2 + N_2 + 2H_2O. \tag{27}$$

The $\Delta G_T°$ values of these reactions dependent on temperature are given in Fig. 5. As it follows from Fig. 5, carbamide is a potential SO_2 reduction agent. It can reduce SO_2 to sulphur or even up to hydrogen sulphide at any temperature. The most reliable SO_2 reaction (equation 27) is when oxygen participates in the reaction and the reaction product is sulphur. Since carbamide reduces SO_2, this factor must be taken into account, while evaluating the amount of carbamide introduced into the boiler-house flue gases, to prevent formation of hydrogen sulphide, the MAC of which is equal to 0,008 mg/m^3. The formation of H_2S should be avoided if oxygen is present in the boiler-house flue gases because hydrogen sulphide is easilly oxidized with air oxygen.

3.6. Carbamide reaction with water vapour

Water vapour, which is formed during combustion of organic fuel, is always present in the boiler-house flue gases. The thermodynamic investigation of the following equations can answer the question whether or not carbamide can reduce water and evolve hydrogen into the atmosphere:

$$CO(NH_2)_2 + H_2O = CO + N_2O + 2H_2, \tag{28}$$

$$CO(NH_2)_2 + 2H_2O = CO + 2NO + 4H_2, \tag{29}$$

$$CO(NH_2)_2 + H_2O = CO_2 + N_2 + 3H_2, \tag{30}$$

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3. \tag{31}$$

The dependency of the Gibbs' energy change values on the temperature of these equations is presented in Fig. 6. Here it follows that, during the carbamide and water interaction up to 1000 K, nitrogen oxides cannot be formed, but ammonia can be evolved according to equation 31, while carbon oxide, arising from the carbamide composition, is oxidized to CO_2. Equation 30 is less reliable when hydrogen is released during the reaction. This reaction is possible only above 700 K.

4. Dependency of the Gibbs' energy value changes on temperature

The $\Delta G_T°$ values of all our analysed reactions decrease with an increase in temperature. The $\Delta G_T°$ value dependency on temperature can be described by the reaction curves of equations which are presented in Table 2.

As follows from the data in Table 2, the $\Delta G_T°$ dependency on temperature is expressed by linear equations with negative angular coefficients. This means, that with an increase of temperature, the probability of all the reactions increases. The higher the angular coefficient, the greater the Gibbs' energy value decrease. The highest values of equation coefficients were obtained by reaction 1 (–0.860) when carbamide reacts with nitric acid, by reaction 7 (–0.7614) when carbamide reacts with CO_2, by reaction 2 (–0.623) when carbamide reacts with nitrogen oxide. The lowest angular coefficient values were obtained for reaction 6 (–0.4271) when carbamide reacts with water vapour and by reaction 3 (–0.4914) when carbamide reacts with air oxygen. The free members of the curves characterize $\Delta G_T°$ values at low temperatures. Their positive values indicate that carbamide doesn't react at room temperatures (equation 8) and cannot react with CO_2 (equation 7). The $\Delta G_T°$ values are equal to zero during the pyrolysis reaction of carbamide at 384 K and in the reaction with CO_2 at 451 K.

5. Conclusions

1. Carbamide can be used for the decontamination of boiler-house pollutants, present in flue gases. Carbamide reduces nitrogen oxides up to nitrogen. It was determined that $\Delta G_T°$ values, during carbamide reaction with nitrogen, sulphur or carbon oxides, water vapour, and also during its oxidation process with air oxygen and

Table 2. The Gibbs' energy change value dependency on temperature of main reactions between carbamide and other substances, present in the boiler-house flue gases

No.	Reaction equation	Linear equation
1.	$CO(NH_2)_2 + 2\ HNO_3 = 2\ N_2 + CO_2 + 3\ H_2O + O_2$	$\Delta G_T = –0.860T–480.0$
2.	$CO(NH_2)_2 + 2\ NO_2 = CO_2 + 2\ H_2O + 2\ N_2 + 1/2\ O_2$	$\Delta G_T = –0.623T–573.14$
3.	$CO(NH_2)_2 + 3/2\ O_2 = CO_2 + N_2 + 2\ H_2O$	$\Delta G_T = –0.4914T–808.57$
4.	$CO(NH_2)_2 + SO_3 + 1/2\ O_2 = CO_2 + N_2 + 2\ H_2O + SO_2$	$\Delta G_T = –0.5986T – 406.43$
5.	$CO(NH_2)_2 + SO_2 + 1/2\ O_2 = S + CO_2 + N_2 + 2\ H_2O$	$\Delta G_T = –0.5129T – 202.14$
6.	$CO(NH_2)_2 + H_2O = CO_2 + 2\ NH_3$	$\Delta G_T = –0.4271T – 126.14$
7.	$CO(NH_2)_2 + 2\ CO_2 = 3\ CO_2 + N_2 + 2\ H_2O$	$\Delta G_T = –0.7614T + 343.43$
8.	$CO(NH_2)_2 = CO + N_2 + 2\ H_2$	$\Delta G_T = –0.6871T + 264.14$

pyrolysis, also during the increase of temperature it decreased according to a linear dependency. The linear equation formulae of this dependency were derived.

2. It was also determined that, during the decontamination process of nitrogen oxides with carbamide, the most reliable reaction products were CO_2, water and nitrogen, independent of what nitrogen oxides participated in the decontamination process.

3. The carbamide pyrolysis process can proceed above 450 K, in the absence of oxygen, nitrogen and sulphur oxides in the flue gases. CO, nitrogen, hydrogen and ammonia are evolved during the reaction. The ammonia reaction is activated by water vapour.

4. The carbamide oxidation process with air oxygen is possible under any temperature. The most reliable reaction products are CO_2, water and nitrogen.

5. Carbamide reduces the sulphur (VI) oxide up to sulphur (IV) oxide, and the latter – up to the elementary sulphur or even hydrogen sulphide, if there are no nitrogen oxides present in the smokestack flue gases, since nitrogen oxides up to 1000 K temperatures participates in the reaction with carbamide more actively than with sulphur oxides.

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TERMODINAMINIS KATILINIŲ IŠMETAMŲJŲ DUJŲ NO_x IR CO TARŠOS KENKSMINGUMO ŠALINIMO NAUDOJANT KARBAMIDĄ ĮVERTINIMAS

D. Stepanonytė, J. J. Blynas

Santrauka

Vienos iš didžiausių oro teršėjų yra elektrinės ir katilinės. Jos išmeta į atmosferą azoto oksidus, anglies monoksidą, sieros dioksidą. Pastaruoju metu azoto oksidams nukenksminti pradėtas naudoti karbamidas, kuris redukuoja azoto oksidus iki elementaraus azoto. Nagrinėjami katilinės teršalų nukenksminimo aspektai naudojant karbamidą. Šio darbo tikslas yra ištirti reakcijas, vykstančias tarp karbamido ir katilinės kamino dūmuose esančių junginių, nustatyti ir palyginti šių reakcijų patikimumą. Teoriniai nukenksminimo proceso tyrimai atlikti termodinaminiais metodais, įvertinant reakcijų Gibso energijų pokyčio vertes, esant įvairioms temperatūroms (298–1000) K. Išvestos šių pokyčių lygtys. Reakcijų patikimumas įvertintas remiantis termodinaminiais skaičiavimais ir gautomis Gibso energijos pokyčio vertėmis. Aptikta, kad, kylant temperatūrai, visų nagrinėtų reakcijų tikimybė didėja.

Nustatyta, kad, vykstant azoto oksidų nukenksminimo procesui, esant karbamidui, patikimiausi reakcijos produktai yra anglies dioksidas, vanduo ir azotas; karbamidas gali redukuoti SO_2 iki sieros ir tam tikrais atvejais – iki vandenilio sulfido. Nesant kamino dūmuose deguonies ir azoto bei sieros oksidų, karbamido terminis skilimas vyksta esant daugiau kaip 450 K. Reakcijos metu išsiskiria anglies monoksidas, azotas, vandenilis ir amoniakas. Nustatyta, kad katilinės teršalams nukenksminti galima naudoti karbamidą, kuris azoto oksidus redukuoja iki azoto; Gibso energijų pokyčio vertės, karbamidui reaguojant su azoto, sieros, anglies oksidais, vandens garais, taip pat ir vykstant jo oksidacijos procesui oro deguonimi ir pirolizei, kylant temperatūrai mažėja pagal tiesinę priklausomybę. Išvestos šios priklausomybės tiesinių lygčių formulės.

Reikšminiai žodžiai: karbamidas, Gibso energija, oksidacija, redukcija, pirolizė, dujų nukenksminimas.

ТЕРМОДИНАМИЧЕСКАЯ ОЦЕНКА ПРИ ДЕКОНТАМИНАЦИИ ЭМИССИИ NO_x И CO ВЫХЛОПНЫХ ГАЗОВ КОТЕЛЬНЫХ ПУТЕМ ИСПОЛЬЗОВАНИЯ КАРБАМИДА

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Резюме

Одними из главных источников загрязнения воздуха являются электростанции и котельные. Они выделяют в атмосферу оксиды азота, CO и SO_2. Недавно для дезактивации оксидов азота было предложено использовать карбамид. Карбамид редуцирует оксиды азота до элементарного азота. В настоящей статье обсуждаются некоторые аспекты деконтаминации эмиссии загрязнителей из котельной с использованием карбамида. Целью исследования было определить реакции, происходящие между карбамидом и соединениями, находящимися в газах выпускной трубы котельной, а также оценить и сравнить надежность этих реакций. Теоретическое исследование деконтаминации загрязнения проводилось с применением термодинамических методов и оценки величины изменений энергии Гиббса в реакциях при различных температурах – (298 – 1000) K. В результате исследований были получены уравнения этих изменений. Оценка надежности реакций была достигнута на основании термодинамических расчетов и полученных величин изменения энергии Гиббса. Надежность реакции увеличивается с увеличением температуры.

Определено, что наиболее надежными составами, полученными в ходе реакции между карбамидом и оксидом азота, являются CO_2, азот и вода. Кроме того, установлено, что карбамид может редуцировать оксид серы до элементарной серы и в некоторых случаях – до H_2S. Пиролиз карбамида возможен при температурах выше 450 K при отсутствии кислорода, азота и оксидов серы в газах выпускной трубы. В течение реакции выделяются CO, азот, водород и аммиак. Определено, что карбамид можно использовать для деконтаминации загрязнения из котельной. Карбамид редуцирует оксиды азота до азота. Определено, что значение ΔG_T° в течение реакции карбамида с азотом, серой или углеродистыми оксидами, водным паром, а также в течение процесса его оксидации с воздушным кислородом и пиролиза с увеличением температуры уменьшается согласно линейной зависимости. В ходе исследований получены формулы уравнений этой линейной зависимости.

Ключевые слова: карбамид, энергия Гиббса, оксидация, редукция, пиролиз, деконтаминация газа.

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