Mechanochemical Synthesis of Carbamide Forage Additives with an Adjustable Solution Rate

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Abstract

Dissolving nitrogen-containing forage additives based on carbamide, grain, and mechanochemically obtained filling material has been studied. Samples were made by mechanical mixing, processing in an extruder, planetary and centrifugal activator mills. Variation of the grain and filler (straw, fats, bentonite) contents in the additive can serve as an efficient method for controlling the rate of carbamide isolation from forage additives. Conditions of mechanochemical production of forage additives are chosen according to the selection criteria, which are based on the requirement for the maximal admissible disturbance of the internal medium (acidity) of the organism during assimilation of the additive by an animal. The viability of application of mechanochemically obtained carbamide-containing additives has been shown by tests on animals.

INTRODUCTION

Traditional forages used in animal husbandry in Russia, such as hay, silo, haylage, non-enriched grain mixtures do not contain enough protein to satisfy the physiological needs of highly productive animals. The lack of vegetative forages of high quality does not allow the rations to be balanced out over the major elements, first of all over the nitrogen necessary for the synthesis of protein. For these reasons, the efficiency is 50–60 % of the potential, and the country receives ~4 million tons of meat and 22–23 million tons of milk products less than required annually. Thus, high-protein forages is an urgent problem for animal husbandry. Domestic and foreign experience shows that application of synthetic nitrogen-containing substances in ruminant animals feeding opens up prospects for solving the forage protein problem.

Of non-protein nitrogen compounds, carbamide (urea) is of greatest interest. High solubility and fast hydrolysis in the alimentary canal of ruminant animals inhibit the application of carbamide. The released ammonia has not enough time to be assimilated by the microflora of the proventriculus, and a significant part of it gets into blood channels. The latter results in chronic or acute poisonings of animals and, as a consequence, in their death. Therefore, this way of increasing the protein nutritive value of rations has not yet found widespread application in domestic animal husbandry.

For effective utilization of urea in ruminant animals feeding it is essential to create conditions of retarded dissolution and hydrolysis of urea [1, 2]. Various variants of carbamide addition to forage rations are known. One of the effective methods is encapsulation of carbamide particles by creating protective lipidic-dextrin coatings. Sluggish dissolving of the coatings in cicatricial liquid provides slow isolation of ammonia and its effective utilization by animals [3, 4]. Encapsulation through precipitation of coatings from solutions is a rather expensive technology, but an alternative has not yet been offered. The mechanochemical technology of additives production through processing of dry mixtures of components in activator mills may appear to be a real alternative to encapsulation.

The purpose of this work is investigation of the dissolving process of nitrogen-containing forage additives based on carbamide and produced by mechanical treatment of a mixture of carbamide, grain matrix, and additional components from local raw materials. Another aim is to determine the optimum composition of the additives and processing conditions providing lower solution rate of carbamide compared to granular mixtures now in use.

EXPERIMENTAL

The solution rate of carbamide was investigated on a high-precision pH-metric installation [5]. A sample was placed in a temperature-controlled reactor filled with distilled water. The temperature stability of the reactor at the level of 0.1 at 25 °C was maintained by connecting it to a U15 ultrathermostat. The results were recorded in the form of pH dependences of the solution (sensitive to the concentration of the hydrolyzed carbamide in the solution) versus the solution time. pH measurement was conducted on a modified serial device pH-121. The gauging system was calibrated with the standard buffer solutions. The accuracy and reproducibility of the measurements were at a level of 0.005 pH units. Five concurrent measurements were carried out for each experiment; the results were processed statistically at confidence probability of 0.95.

Mechanochemical processing of initial bulk mixtures was carried out on APF and AGO-2 activator mills (design of IKhTTM, SB RAS, Novosibirsk): acceleration of milling bodies 200 and 400 m/s^2, 50 and 15 g batches of the samples under study, 250 and 150 g batches of spheres, respectively, processing time 60–120 s.

To prepare a combined additive in granular form, we employed a granulating accessory of an oil-separating press PShM-250 designed at the SibNIPTIZh design office, SB RAS (Novosibirsk). The temperature of heat treatment was 95–110 °C.

The experimental study of mixture composition was divided into three stages. Grain-and-straw (carbohydrate) mixtures – carbamide additives to the food ration of animals – were investigated at the first stage. The content of carbamide in the composition under study was maintained at a level of 20 mass %, but the grain to straw ratio and additive preparation methods (simple mixing, processing in an extruder, mechanochemical treatment) were varied. At the second stage, we tested the compositions of the carbohydrate-fat carbamide additives with 10 mass % urea, 40 mass % of rye as a carbohydrate component, and fat component for the rest of the additive. At the third stage we investigated the compositions where the solution rate was decreased by introducing an inert inorganic compound of

TABLE 1

Composition of forage additive samples and methods for their preparation

Sample*	Content, mass %			Preparation method
	Oats	Carbamide	Bentonite	
1(1)	85	10	5	Initial bulk mixture
2(1)	85	10	5	Extruder + coarse grinding
3(1)	90	10	0	AGO-2 MA
4(1)	63	12	25	The same
7(1)	80	10	10	Bulk mixture + manual grinding
7(3)	50	10	40	APF-2

Note. MA is mechanochemical activation in AGO-2 and APF (acceleration of milling bodies 400 and 200 m/s^2, respectively).

*The number in parenthesis is the sample batch number.

bentonite (clay). The composition and sampling methods for the third stage are listed in Table 1.

RESULTS AND DISCUSSION

As is known, dissolving of pure urea in water with pH ~ 7 at normal temperatures occurs at very high rates. The acidity of the solution does not change unless urea is hydrolyzed. It is also known that hydrolysis is accelerated in acid or alkaline media (acid or alkaline catalysis, respectively) or in the presence of other substances. Therefore, it is assumed that the rate of carbamide hydrolysis in physiological solutions is high enough, and that pH changes in proportion to the variation of the carbamide content.

The acidity of the internal medium (biosystem) in mammals' organisms varies from neutral-alkalescent (oral cavity) via subacidic (blood plasma) to acidic (stomach). In our experiments, initial physiological solutions with pH 5 were used.

The organisms poorly withstand alkaline conditions, so the basic criterion for evaluating the suitability of the samples was that the solution should remain subacidic or alkalescent (pH 7 would be the best value), not exceeding pH 8 (or else the mucosa will be burnt).

It is desirable that the rate of pH variation on dissolving should be comparable to the rates of metabolic processes. Then the internal biosystem of the animal will have enough time to react to an external action (variation of pH). For prolonged treatment (of the order of 3 h) of the additive with a water solution it is desirable that the acidity of the medium should remain constant or decrease, but not increase. The latter circumstance additionally ensures that hydrolysis harmful to the organism (stomach) of ruminant animals would not start.

Data on solution of grain – straw – carbamide mixtures are presented in Fig. 1. The compositions obtained by preliminary mechanochemical treatment of mixed components (curves *1*–*3*) yield better results compared with the control specimen. Note that after the initial increase in the solution rate, pH starts to slowly change in the range 6.3–6.7. Of the three compositions, compositions with moderate (40–40–20 mass %) or high (64–16–20 mass %) contents of grain in the grain – straw – carbamide mixtures (curves *1*, *2*) should be accepted as the best ones according to the above-mentioned criteria. With allowance made

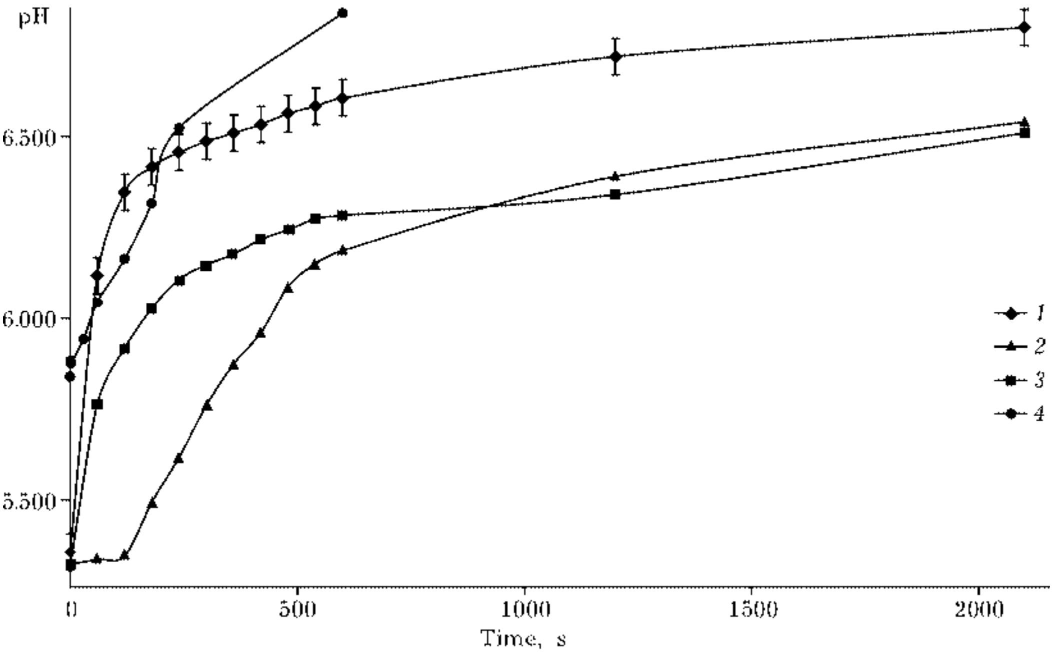

Fig. 1. Curves of solution rates for forage additives obtained by mechanochemical treatment. Mass ratio of the grain, straw, and carbamide components, %: 40/40/20 (*1*), 16/64/20 (*2*), 64/16/20 (*3*); *4* – the sample was obtained by processing in an extruder.

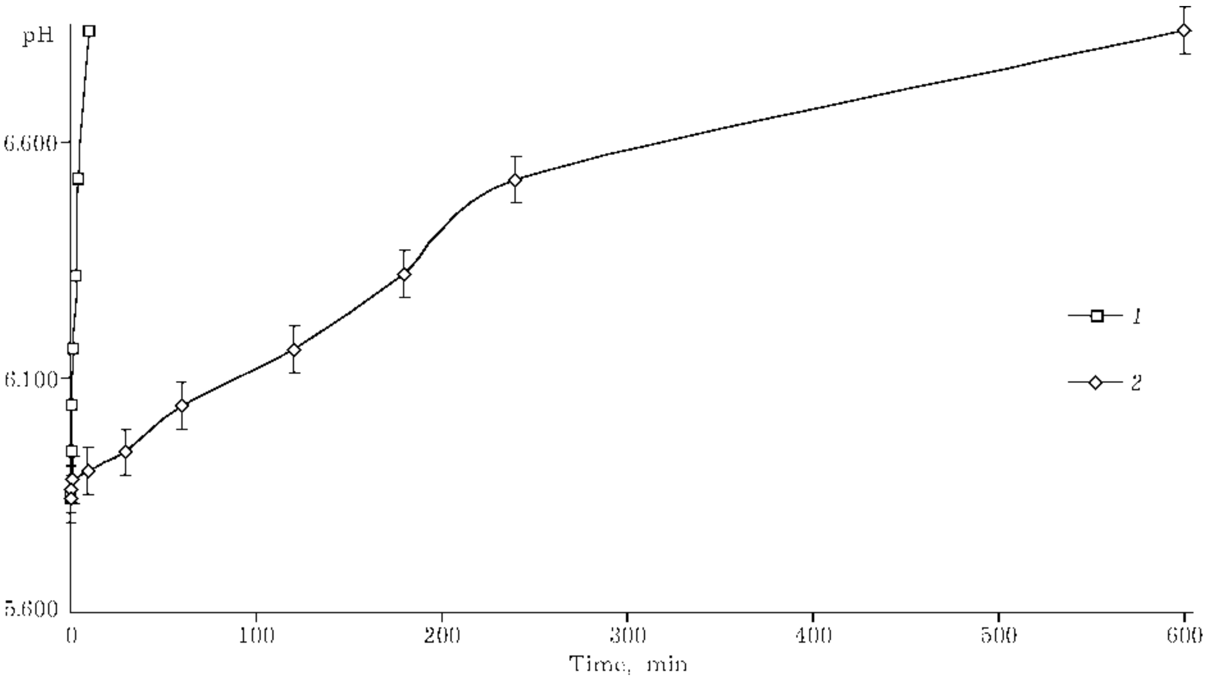

Fig. 2. Curves of solution rates for the carbohydrate-fat carbamide additive (*2*): *1* – treatment in an extruder (control sample).

for the cost of the produced additive, the composition of 40–40–20 % should be accepted as the optimum one. Curve *4* presented for comparison (for the sample obtained by thermal treatment on an extruder) exhibits both increased pH and increased rate of acidity variation. For samples obtained by mechanochemical treatment of the components, the rate of pH variation decreases, which is in better agreement with the above requirements.

The grain – fat – carbamide mixtures were investigated at the second stage. In the course of processing, the fat melts and envelopes the urea particles. Under the effect of pressure and temperature, the colloidal state of the main components changes; the rye starch partially transforms into dextrins. Variation of the carbohydrate composition increases the nutritive value of the forage [6].

The time dependence of pH during dissolving the control and trial mixtures in water is shown in Fig. 2. The sample obtained in an extruder was used as the control sample. As is the case of mechanochemical treatment of the grain-straw mixture, an appreciable decrease can be noted in the rate of pH variation: thus, pH 6.8 is reached in 600 min for the sample under investigation and in 10 min for the control sample.

The effective solution rate of urea for the control mixture was evaluated in the following way. An increased value of pH corresponds to the increased content of OH^- ions; therefore it is more convenient to investigate the concentration of this component. The initial value of pH 5.5 corresponds to the concentration $[OH^-] = 3\ 10^{-9}$. After 600 s the changed value (pH 6.3) corresponds to $[OH^-] = 15\ 10^{-9}$. In this case, the effective solution rate determined from the change in the content of hydroxyl ions $\Delta C/\Delta\tau$ will be $2 \cdot 10^{-11}$ mol/l. A similar analysis performed for solution of a granulous additive in water shows that at the initial moment of time pH was 5.8; after 4 h, it was 6.5. Hence, the effective solution rate is $1.6\ 10^{-12}$ mol/l. It should be noted that mechanochemical treatment and subsequent granulation of the additive decreased the solution rate by ~2–3 orders of magnitude; the total time of nitrogen passing into solution increased to several hours, which is comparable to the time of nitrogen assimilation by an animal from natural forages.

Thus, the data obtained give us grounds to believe that the nitrogen of urea subjected to mechanochemical and subsequent thermal treatment in the presence of other components of the forage mixture is better assimilated by the

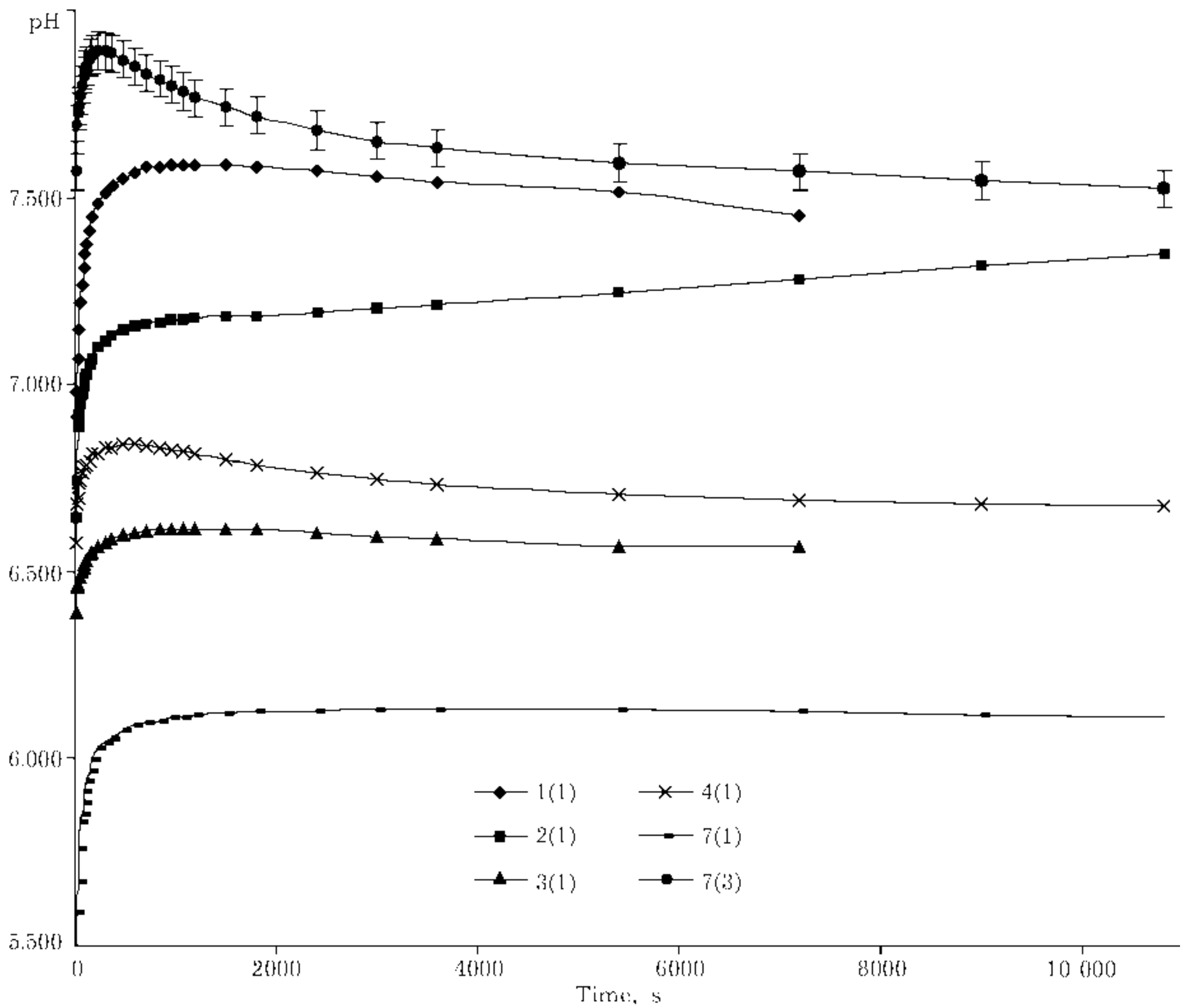

Fig. 3. Curves of solution rates of bentonite-containing forage additives produced by mechanochemical treatment.

organism of animals. During granulation, urea interacts with dextrins and fats. It is well known that dextrins form inclusion compounds as a result of mechanical treatment of mixtures [7]. Slow release of ammonia from urea complexes in the gastrointestinal tract ensures the best digestibility. It seems that heat treatment in an extruder alone is not enough for urea to interact with the components of the mixture.

It was shown [8] that for feeding with carbamide-rich additives the animals should previously be accustomed to small dozes and further uninterrupted carbamide supply to the organism. Once delayed, the entire procedure of adaptation should be started all over again. To establish whether it is possible to feed with additives without preliminary adaptation, a check experiment has been carried out in the experimental farms of SibNIPTIZh, SB RAAS. The animals in the experiment received at once an additive containing 100 % of the daily urea rate. Neither chronic poisonings nor lethal outcomes have been observed. The incorporation of the additive containing 12 % urea in the forage has enabled the amount of assimilated nitrogen-containing substances to be brought to the recommended rates, which had a favorable effect on the intensity of animals' growth. Animals weight data show that the application of the additive causes the live weight to increase by 21 %.

At the third stage, we investigated additive samples with bentonite (a mineral inorganic substance with a well-developed surface) used for binding nitrogen.

The time dependences of pH of the solution are presented in Fig. 3. The values of the initial and final rates of variation of H^+ ion concentration expressed in mol/s are given below:

Sample	Initial rate	Final rate
1(1)	$1.7 \cdot 10^{-9}$	$1.1 \cdot 10^{-12}$
2(1)	$4.5 \cdot 10^{-9}$	$-1.9 \cdot 10^{-12}$
3(1)	$5.9 \cdot 10^{-9}$	$1.2 \cdot 10^{-12}$
4(1)	$5.4 \cdot 10^{-9}$	$1.1 \cdot 10^{-12}$
7(1)	$1.0 \cdot 10^{-7}$	$7.6 \cdot 10^{-12}$
7(3)	$6.8 \cdot 10^{-10}$	$7.8 \cdot 10^{-13}$

Analyzing these data, one should pay attention to the absolute values of the initial rate and to the sign of the final rate (positive values mean decreased pH or increased acidity).

In this context, samples 3(1), 4(1), and 7(3), in our opinion, meet all criteria. The best results are achieved with a less intensive treatment, leading to a bentonite-containing forage additive, in an APF activator mill (the best sample is 7(3)). More vigorous treatment in an AGO-2 mill yields additives characterized by increased solution rates both at the initial and final stages (samples 3(1) and 4(1)). In comparison with the samples prepared through manual abrasion of a bulk mixture (sample 7 (1)), samples 1–4 of the first batch exhibit 40 times smaller initial rate of solution; for the third batch, this parameter is even higher, 150 times as high as the initial value. It is generally agreed that treatment in the energy-intensive AGO-2 mill considerably increases the reaction rates by creating increased concentrations of defective structures. The energy reserved in the latter accelerates both the physical (adsorption) processes and the chemical reactions between the components. An APF type mill, which is less energy-intensive, possibly provides the interaction of urea with the components of the mixture, but does not cause destruction of the vegetative raw material.

Testing bentonite-containing mixtures in the ration of dairy cattle has revealed that the new high-protein forage additive for ruminant animals will be highly efficient and promising. Using this additive for feeding cows without prior adaptation did not cause poisoning and ensured 3.9 % growth of lactic efficiency for the daily milk yield of 21.5 kg. The new additive can replace cake in the cows ration and balance the ration in proteins. Similar results were obtained when testing the forage protein additive in sheep. Growth of meat efficiency for young sheep animals comprised 10.4 % with 7.3 % economy of forages.

CONCLUSIONS

1. Using mechanochemical technology for the production of nitrogen-containing forage additives based on carbamide decreased the initial rate of ammonia solution and isolation by 2–3 orders of magnitude compared to the values for products obtained by processing in an extruder.
2. The optimum mass fraction of carbamide in the structure of forage additives is 10–20 % depending on the type of additive. Grain – straw – carbamide, grain – fats – carbamide, and grain – bentonite – carbamide compositions of additives have been worked out.
3. Conditions of mechanochemical treatment of the compositions have been determined, which allow the necessary acidity of the medium to be maintained during dissolving.
4. The additives may be used in animal husbandry without the preliminary stage of adaptation for ruminants.
5. Introduction of the additive in the food ration of ruminants increases the live weight increment by 15–20 % and decreases forage cost per unit produce.

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