NUMERICAL MODELING OF BIOMASS GASIFICATION USING COW DUNG AS FEEDSTOCK

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KEYWORDS

Aspen Plus, biomass gasification, manure of livestock and poultry, simulation, syngas

HIGHLIGHTS

- Gasification of cow dung was evaluated using Aspen Plus software.
- Optimum reaction conditions were utilized to maximize hydrogen production.
- Steam gasification can effectively increase hydrogen production.
- Optimum hydrogen production was achieved at 800 °C and steam/biomass of 1.5 and 0.1 MPa.

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GRAPHICAL ABSTRACT



ABSTRACT

In this study, a biomass gasification model was developed and simulated based on Gibbs free energy minimization by using software Aspen Plus. Two reactors, RYIELD and RGIBBS, were moslty used. The biomass feedstock used was cow dung. The model was validated. The composition, H_2 /CO ratio and low heating value (LHV) of the resulting synthetic gas (also known as syngas) was estimated by changing the operating parameters of gasification temperatures, steam and biomass ratios and pressures. Simulation results showed that increased gasification temperature helped to elevate H_2 and CO content and H_2 peaked at 900 °C. When steam increased as the gasification agent, H_2 production increased. However, the steam/biomass (S/B) ratio negatively affected CO and CH₄, resulting in lower LHV. The optimal S/B ratio was 1.5. An increase in pressure lead to a decrease in H_2 and CO content, so the optimal pressure for gasification was 0.1 MPa.

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1 INTRODUCTION

The depletion of fossil energy is one of the factors that stimulate the development of biomass energy over recent years^[1]. The pollution caused by the excessive use of fossil energy has become a global environmental concern^[2]. Therefore, adjusting the energy structure, gradually reducing the use of fossil energy, such as oil and coal, and developing

green, low-carbon and sustainable energy has become a focus research area in recent years^[3]. As a clean renewable energy source, biomass energy is one of the alternative energy sources to fossil energy^[4]. The use of biomass as generate energy sources can effectively reduce the emission of harmful gases, such as CO₂, NO_x, and SO_x^[5]. Biomass refers to the organic material produced by photosynthesis of atmosphere, water, land and the like, which mainly includes crops, trees, animals, organic wastes, and livestock and poultry manure^[6]. In different types of biomass, livestock and poultry manure might pollute the environment to some extent, such as in water, air and soil pollution^[7]. Over recent years, there have been many methods presented for the treatment of livestock and poultry manure, mainly including feed reuse technology, microbial fermentation utilization technology and fertilizer utilization technology^[8]. However, these treatment methods have long treatment cycles, are susceptible to environmental factors and have low a utilization ratio^[9]. With the development of largescale breeding industry in recent years, a large amount of livestock and poultry manure has been produced^[10]. Therefore, the thermochemical treatment of livestock and poultry manure is a suitable choice.

Certain breakthroughs have been made in the thermochemical treatment of livestock and poultry manure^[11]. Gasification is a highly important thermochemical process, which refers to the thermochemical process of converting biomass raw materials into gaseous fuels under the condition of incomplete combustion at high temperatures^[12]. The final product of gasification is syngas, dominated by CO₂, CO, H₂, CH₄ and other gases^[13]. As a chemical raw material, syngas can be directly used for combustion to generate heat and electricity. Syngas can be used in various energy conversion devices, such as internal combustion engines, gas turbines and fuel cells^[14]. According to different gasification agents, gasification can be divided into air, steam and CO₂ gasification^[15].

The gasification process is generally divided into four processes: drying, pyrolysis, gasification (reduction) and combustion. The first step is drying, which generally reduces the moisture content to less than 5%. In the pyrolysis step, biomass is heated to release volatiles and then form coke. The combustion of combustible materials in the gasifier produces CO_2 and H_2O . Some CO_2 and H_2O are reduced to CO and H_2 when they contact with coke. In biomass gasification, the gasification agent supplied to the gasifier reacts with combustible materials to generate synthetic gas^[16].

The gasification of livestock and poultry manure can convert organic waste into renewable energy, effectively saving the consumption of fossil energy and reducing the pollution

caused by standard treatment methods. Gasification of livestock and poultry manure is a novel treatment method that converts waste into renewable energy, while also producing a variety of products, such as methane and hydrogen. These products can be used in multiple fields such as power generation, heating and chemical engineering. The gasification process has developed rapidly over recent years, and the integrated process of gasification system has also been developed. The process integration of livestock manure gasification can be simply summarized as pretreatment, gasification reaction, clean treatment, energy recovery and solid waste treatment. The pretreated livestock and poultry manure is sent to a gasification reactor, which converts it into combustible gas at high temperatures. The generated gas is then cleaned, energy is recovered and the residue of the gasified livestock and poultry manure is treated. This method can efficiently and environmentally treat livestock manure and convert it to renewable energy.

Livestock manure is a waste product of animal husbandry and, compared with other biomass types, it has a stable yield that is not affected by weather and seasonal changes^[17,18]. Also, livestock and poultry manure have the characteristics of strong renewability and abundant supply^[19]. Most of livestock and poultry excrement has high moisture content. The water vapor after drying and evaporation can effectively promote steam gasification, thus achieving higher hydrogen production^[20,21]. Therefore, the use of livestock and poultry manure as a gasification feedstock has high prospects and can effectively alleviate environmental pollution problems caused by fossil energy.

The optimization of various parameters in the gasification process is the key to the gasification process^[6]. However, the complexity and variability of the gasification process have led to complexity of the structure of gasification devices in experimentation^[22-24]. Also, the process is limited by field test conditions and gasification devices and it is difficult to fully grasp gasification characteristics^[25]. However, the analyses and predictions from simulation methods can effectively compensate for the inherent disadvantages of the experimental system^[26]. Therefore, the development of gasification models helps optimize the gasification process. As a process simulation software, the business software Aspen Plus has been widely used in various thermochemical simulations, such as gasification and combustion^[27], with some progress made in recent years. Beheshti et al.^[28] have simulated a biomass gasification model using Aspen Plus and a dedicated FORTRAN subroutine. Simulation results show that high temperature is more conducive to the production of useful syngas and H₂ yield. Niu et al.^[29] have used Aspen Plus to

simulate gasification of municipal solid waste in a bubbling fluidized bed and analyzed the effects of gasification temperatures, equivalent ratios, oxygen content, municipal solid waste moisture and other parameters on syngas components and gasifier efficiency. Therefore, Aspen Plus software can be applied to simulation of livestock manure gasification. The purpose of this study was to evaluate the gasification process of livestock manure using Aspen Plus software. Simulations were conducted under different operating conditions, including temperature, steam/biomass (S/B) ratio, and pressure, to optimize various operating conditions in the gasification process and produce the best gasification products. The model data were then compared with experimental data to examine model reliability.

2 GASIFICATION MODEL

This section primarily presents the establishment of the livestock and poultry manure gasification model, including model assumptions, reactor selection and characterization of gasification feedstock parameters.

2.1 Establishment of gasification model

A gasification model was established using the simulation software Aspen Plus (Fig. 1). In this study, two reactors, pyrolysis (RYIELD) and gasification (RGIBBS), were used to simulate the manure gasification process. The RYIELD reactor module was a simple yield rate calculation reactor, whose role

was to break down manure into single-element molecules. The RGIBBS reactor module was a gasification reactor based on the Gibbs free energy minimization principle, which was used to process the combustion and reduction of manure gaseous products. The RGIBBS reactor module was a thermodynamic equilibrium gasification reactor based on Gibbs free energy minimization principle. It calculated the system composition and phase distribution that can reach chemical equilibrium and phase equilibrium at the same time, and did not need to know the reaction equation and chemical kinetics. This reactor was used to estimate the possible chemical equilibrium and phase equilibrium results of the system. The RGIBBS reactor was used to address the combustion and reduction of fecal gas products. Thermodynamic equilibrium method was used to simulate without reactor shape, but it also had limitations. It did not calculate tar. The simplification of the model also led to high hydrogen content.

The basic idea of the gasification process was that livestock and poultry manure feedstock were deemed to be non-standard components in the system, which first entered the RYIELD module for pyrolysis and the pyrolysis products standard single-element molecules (C, H₂, O₂, N₂, S and ash). It was then gasified in the RGIBBS reactor with steam. Gasification products were separated from the ash by a cyclone separator. Flash evaporation was performed to obtain dry syngas and water vapor.

Livestock manure was defined as a non-standard component in the simulation and its chemical composition evaluated by



ultimate analysis and approximate analyses. For livestock manure and ash of non-standard components, the selected enthalpy and density models were HCOALGEN and DCOALIGT, respectively. In this model, the thermodynamic properties of standard components were calculated using the Peng-Robinson equation of state and physical property method of Boston-Mathias (BM). The PR-BM property method was recommended for non-polar or weakly polar mixtures and was applied to all temperature and pressure ranges.

The RYIELD reactor gave the product composition and yield according to the total mass balance and used the FORTRAN statement to define the yield distribution of biomass decomposition products in the calculator module. The FORTRAN statement is given in Table 1. The gasification reaction was simulated in the RGIBBS reactor, the calculation option "Limit chemical equilibrium—specify temperature difference or reaction" was selected and zero temperature difference used in a single reaction for normalization. The functions of the modules used in this simulation study are described in Table 2.

The composition of syngas and low heating value (LHV) were

Note: FACT, the factor to convert the ultimate analysis to a wet basis; CARB, decomposition yield of carbon; SULF, decomposition yield of sulfur. evaluated. The LHV of the resulting gas was calculated as:

$$LHV = 126.36CO + 107.98H_2 + 358.18CH_4$$
(1)

where, LHV is the low heating value of biomass gasification gas component (kJ·m⁻³), CO is the volume percentage content of CO, CH₄ is the volume percentage content of CH₄, and H₂ is the volume percentage of H₂.

2.2 Simulation process assumptions

To accurately simulate the manure gasification process and simplify the simulation process, some assumptions were considered when simulating the livestock and poultry manure gasification process:

(1) Reactor operated stably, temperature distribution was uniform and there was no pressure loss^[30];

(2) Tar formation was ignored, only H₂, CO, CO₂, CH₄, N₂, NH₃, and H₂S were considered for gasification products^[31];

(3) Ash in biomass was an inert component and did not participate in gasification reactions^[32];

(4) Manure particles were homogeneous without a temperature gradient^[33].

The gasification module comprises oxidation and reduction stages and the main chemical reactions considered for the gasification process are given in Table 3. Reactions R1 and R2 denote carbon combustion reactions, R3 denotes the Boudouard reaction, R4 and R5 denote water-gas reactions, R6 denotes water-gas shift reaction, R7 denotes a methane reforming reaction, and R8 denotes a methanation reaction.

2.3 Simulation computation parameters

In this study, manure was subject to simulation computation under different gasification temperatures, steam/manure mass ratio and pressure conditions. The proximate analysis and ultimate analysis of feces under dry conditions are given in Table 4. The various parameters in simulated gasification of livestock and poultry manure are given in Table 5.

Table 2 Functions of Aspen Plus modules						
Block ID	Function introduction					
RYIELD	Conversion of non-standard substances to single component substances					
RGIBBS	Estimates the phase equilibrium and chemical equilibrium of the system by minimizing the Gibbs free energy					
CYCLONE	Separation of gaseous and solid states					
SEP	Divides incoming material into multiple discharge streams according to specified flow rates or splitting ratios					

Table 3 Gasification reactions							
Heat of reaction (kJ·mol ⁻¹)	Reaction number						
-394	R1						
-111	R2						
+172	R3						
+131	R4						
+77	R5						
-41	R6						
+206	R7						
-75	R8						
	Heat of reaction (kJ·mol ⁻¹) -394 -111 +172 +131 +77 -41 +206 -75						

Table 4 Biomass composition analys	is		
Proximate analys	sis (wt%, ad)	Ultimate analy	sis (wt%, ad)
ASH	18.16	C	41.13
Volatile matter	65.98	Н	5.89
Fixed carbon	7.6	0	49.92
Moisture	9.21	Ν	2.69
1	1	S	0.37
1	1	ASH	18.16

Note: Except for the Moisture value (this study), data sourced from Liu et al.^[34]. ad, air-dried.

Table 5 Manure gasification simulation parameters					
Parameter	Value				
mbient temperature 25 °C					
Ambient pressure	1 atm				
Gasifier operating temperature	600, 700, 800, 900, and 1000 °C				
Gasifier operating pressure	0.1 MPa				
Steam/livestock manure	0.5, 1, 1.5, 2, 2.5, 3				
Steam parameters	0.1 MPa, 105 °C				

3 SIMULATION RESULTS AND DISCUSSION OF BIOMASS GASIFICATION

3.1 Simulation verification

To verify the accuracy of the simulation process, experimental data from the literature^[34] were used to verify the biomass gasification model, and compare experimental and simulated values under the same conditions (Table 6). In this experiment,

manure gasification was performed with steam at 900 °C.

As seen from the data, simulation values were close to experimental values (Table 6). The H_2 content in simulation results was higher than the content in experimental results. Given that the generation of hydrocarbons, such as tar and C_NH_M , were not included in the model, and the H_2 content in simulation results would be higher than the content in experimental results following the law of elemental equilibrium. Also, the direct decomposition of biomass in the RYIELD reactor had H_2 as a product, which also increases the

Table 6 Comparison of simulated and experimental values										
Volume fraction of each component in the syngas				\mathbf{U}_{1}						
H ₂	СО	CO ₂	CH ₄	Heating value (M)·m ⁹)	Syngas yield (L·g ⁻¹)	Gas efficiency (%)				
55.8	28.8	15.1	0.03	9.67	1.29	70.4				
49.1	24.00	18.8	7.89	11.2	1.34	84.4				
	n of simulate Volume fract H ₂ 55.8 49.1	In of simulated and experim Volume fraction of each con H2 CO 55.8 28.8 49.1 24.00	Hold of simulated and experimental values Volume fraction of each component in the H ₂ CO CO ₂ 55.8 28.8 15.1 49.1 24.00 18.8	N of simulated and experimental values Volume fraction of each component in the syngas H2 CO CO2 CH4 55.8 28.8 15.1 0.03 49.1 24.00 18.8 7.89	N of simulated and experimental values Volume fraction of each component in the syngas Heating value (MJ·m ⁻³) H ₂ CO CO ₂ CH ₄ 55.8 28.8 15.1 0.03 9.67 49.1 24.00 18.8 7.89 11.2	In of simulated and experimental valuesVolume fraction of each component in the syngasHeating value (MJ·m ⁻³)Syngas yield (L·g ⁻¹) H_2 COCO2CH41.2955.828.815.10.039.671.2949.124.0018.87.8911.21.34				

 H_2 content in the syngas. The CO content in simulation results was higher than the content in experimental results and CO_2 was smaller than that in experiments. This was because the essence of the simulation was that C underwent incomplete combustion under hypoxic conditions and reacted with other elementary substances. Therefore, under hypoxic conditions, CO was high and CO_2 low. The CH_4 in the simulation was negligible because only single-element molecules were formed by decomposition in the RYIELD reactor and no CH_4 generated, with CH_4 only obtained in the C methanation reaction. In the experiments, CH_4 was generated in the pyrolysis process of biomass as well as in the CH_4 reforming stage. Thus, the experimental value was higher than the simulated value. Therefore, the simulation model might be deemed effective for describing the gasification process.

3.2 Effects of temperature on gasification

Temperature controls the equilibrium of chemical reactions, such that the gasification temperature is an important factor affecting biomass gasification. The results of gasification temperatures of 700–1100 °C affecting the process when the manure feed quantity was 5 g·min⁻¹, steam 1.66 g·min⁻¹ and pressure 0.1 MPa (Fig. 2).



Fig. 2 Effects of temperature on gasification results.

Simulation results showed that from 700-1100 °C, the H₂ content increased from 44.9% to 54.4% and CO content increased from 9.7% to 34.1%, which was consistent with previous reports. The CO₂ content decreased from 32.5% to 11.6% and CH₄ from 12.9% to 0.001%, with similar trends reported in the literature^[7]. The reason for this was that, when gasification temperature increased, the Boudouard reaction (R3), reforming reaction (R7) of CH₄ and the water vapor shift reaction (R4), being endothermic reactions, shifted to the right. This was in clear agreement with Le Chatelier's principle^[35]. In a RGIBBS reactor that reaches thermodynamic equilibrium, an increase in temperature would shift the reaction equilibrium in the direction of endothermic heat and a decrease in temperature shift the reaction in the exothermic direction. Therefore, temperature increase was conducive to the formation of H₂ and CO. The water-gas shift (R6) and methanation (R8) reactions were exothermic and increased temperature shifted the reaction equilibrium to the left to inhibit the formation of CO2 and CH4. Concurrently, the water vapor shift reaction also consumed part of the H₂, which was also the reason H₂ reached a maximum content at 800 °C and then slightly decreased. The water-gas reaction (R5) led to more CO₂ production, but the Boudouard reaction (R3) was highly endothermic and increased temperature increased CO₂ consumption^[36]. When the gasification temperature was increased from 700 to 1100 °C, the Boudouard reaction mainly controlled this process, which led to increased CO production and decreased CO₂. In short, temperature increase facilitated the formation of gases.

3.3 Effects of steam addition on gasification

The gasification agent is a highly important factor in biomass gasification and steam was chosen here as the gasification agent in this experiment. The flow rate of gasification agent into the gasification reactor is one parameter affecting the balance and gas distribution of biomass gasification. The gasification results change with the S/B ratio increasing from 0.5 to 3 at 900 °C and 0.1 MPa as shown in Fig. 3.

With increased S/B ratio, the H_2 content increased from 57.6% to 63.7%, CO content decreased from 24.1% to 6.72%, CO₂



Fig. 3 Effects of steam/biomass (S/B) ratio on resulting gasification results.

content increased from 18.2% to 29.6% (Fig. 3). When steam as a gasification agent, the gas composition varied quite substantially, especially in CO and CO2 content. Increased steam facilitated H₂ formation and water vapor, as a gasification agent, not only activated the biomass feedstock to provide part of the O₂, but also provided H₂ for the production of syngas and contributed to reforming of the pyrolytic gas produced^[32]. Decreased CO and increased CO₂ were due to the fact that, with steam introduction, H₂O increased, which promoted the water-gas reaction (R6), resulting in increased CO consumption, which was then converted to more CO2 and H₂. The results indicated that increased H₂O led to decreased temperature of the gasification reaction and the Boudouard (R3) and water-gas (R4 and R5) reactions inhibited and shifted to the left, resulting in decreased CO and H₂. The water-gas (R5) reaction could occur at a lower temperature than the Boudouard (R3) reaction, such that, when CO decreased, CO₂ and H₂ increased. However, H₂ did not increase significantly, such that excess H₂O might inhibit H₂ production. CH₄ decreased significantly after water vapor addition, possibly due to the fact that, when the S/B ratio increased, the reforming reaction of CH₄ (R7) intensified, resulting in a gradual decrease in the CH₄ volume fraction. With the increase of S/B ratio, the maximum increase of H_2 is 5.1% when S/B ratio is less than 1. When S/B ratio is greater than 1, the range of H₂ yield decreases and reaches an inflection point. Therefore, it is considered that when S/B ratio is 1, it is a suitable choice.

3.4 Effects of pressure on gasification results

Gasifier pressure is another important factor that affects gasification results. Increasing the pressure accelerates the reaction rate of gasification reactions. However, the standard gasification process generally occurs under atmospheric pressure conditions due to the complexity of the pressurization process^[37]. Therefore, it would be a more feasible method to conduct a simulation study on the distribution and calorific value of biomass gasification gas through Aspen Plus software.

Examination of the effects of reaction pressure on biomass gasification, over 1-9 atm (Fig. 4). As the pressure increased, the H₂ content decreased from 55.8% to 47.2%, the CO content decreased from 28.8% to 24.1%, the CO2 content increased from 15.2% to 21.0%, and the CH₄ content increased from 0.003% to 7.79%. According to Le Chatelier's Principle, increased pressure would cause the reaction to shift in the direction of decreased moles of gas and decreased pressure causes the equilibrium to move toward more moles of gas. Thus, increased pressure would lead to an increase in CH4 production by shifting the methane reforming (R7) and methanation (R8) reactions to the left. In addition, the Boudouard reaction (R3) equilibrium would shift to the left, resulting in increased CO₂ and decreased CO. As pressure increased, the water-gas reaction (R4) shifted to the left, such that the H_2 content kept decreasing. Overall, the content of H_2 and CO reached the maximum at 1 atm. More CH₄ and CO₂ were produced under increased pressure, which were not the most desired products for the syngas. Due to the complexity of the pressurization process, running a gasifier simulation under 1 atm was a suitable choice.

3.5 Effects of temperature and steam/biomass ratio on LHV and H₂/CO ratio

LHV is one of the important factors in judging syngas quality. Changes in the LHV of syngas with S/B ratio were revealed at five temperatures examined (Fig. 5(a)). The LHV of syngas as a



Fig. 4 Effects of pressure on gasification results.

whole, had an upward trend with increasing temperature, which was consistent with trends reported in a previous study^[38]. The Boudouard (R3) and water-gas shift (R6) reactions will increase the production of CO with the increase of temperature. H₂ remained basically stable after 900 °C. Meanwhile, the CH₄ content continued to decrease due to the leftward shift of the reactions (R7 and R8). CH₄ is the largest contributor to syngas LHV, CO the second, and H₂ the third. Although the CH₄ content decreased with increased temperature, the degree of influence of CH₄ on the calorific value became smaller because the CH₄ content was already relatively low. Meanwhile, the CO content increased while H₂ content remained relatively stable, so the LHV had an increasing trend. With increased S/B ratio, the LHV of syngas had an overall downward trend. As CH4 and CO decreased with increased S/B ratio, H₂ increased, but the amplitude was small, and the impact H₂ on LHV was lower than for CO and CH₄, such that the LHV had an overall downward trend.

The H₂/CO ratio is an important parameter for evaluating syngas quality and the downstream process of syngas. The effects of the S/B ratio on the H₂/CO ratio of syngas at five temperatures showed that H₂/CO always decreased as temperature increased (Fig. 5(b)). This was related to the Boudouard (R3) and water-gas shift (R6) reactions, which both increased CO production and H₂ consumption with temperature rise. CO continued to increase with temperature rise and H₂ remained basically stable above 800 °C, such that the H₂/CO ratio was decreased. According to Fig. 5, the H₂/CO ratio continued to increase decreased H₂ and decreased CO content would necessarily lead to a continuous increase in the H₂/CO ratio.

3.6 Effects of pressure on syngas LHV and H₂/CO ratio

Figure 6 shows the variation of H_2/CO ratio and LHV with pressure during syngas generation. It is clear that the LHV of the syngas showed a slow rising trend when the pressure increased from 1 to 9 atm. This was because the CH₄ content was favored to rise under high pressure. Although the H₂ and CO contents decreased, the effect of CH₄ on LHV was greater than that of H₂ and CO, and the increase of CH₄ content was relatively large, so the overall LHV had an increasing trend. However, it was also clear that the rising trend of LHV gradually tends to level off as the pressure continues to grow, which indicates that the effect of pressure gradually decreased. The H₂/CO content basically remained stable, because although both the H₂ content and the CO content decreased, the decrease was the same, so the H₂/CO was only a slight changed or remained unchanged.

4 CONCLUSIONS

In this study, the gasification process of livestock and poultry manure was simulated using the Aspen Plus software according to Gibbs free energy minimization. The simulation values of gasification were verified by comparison with experimental values and the model was found to have acceptable accuracy. After a sensitivity analysis, the effects of gasification temperatures, steam/biomass ratios and pressures on syngas composition were used to derive the optimal operating conditions and probes into syngas quality examined the syngas calorific value and H_2/CO ratio. This study provide four main outcomes: (1) When the gasification temperature was 1 atm,







Fig. 6 Effect of pressure on syngas low heating value (LHV) and H_2/CO ratio.

which were the most suitable process condition for biomass gasification. (2) According to the model, increasing temperature reduced the H₂/CO ratio, while increasing the S/B ratio would increase the H₂/CO ratio. Overall, increasing the S/B ratio would have greater effects due to the fact that H₂O can increase H₂ to syngas. The increase in pressure had a negative impact on the gasification, with both H₂ and CO content decreasing with increasing pressure. (3) The syngas LHV had an increasing trend with temperature rise, which was associated with the endothermic Boudouard and water vapor shift reactions. (4) The model developed here could potentially be used to predict syngas composition from other biomass feedstocks and to stimulate further research on improvement of biomass gasification processes, such as the evaluation of biomass gasification results under other gasification agent conditions.

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Compliance with ethics guidelines

Yajun Zhang, Sen Yao, Jianjun Hu, Jiaxi Xia, Tao Xie, Zhibin Zhang, and Hai Li declare that they have no conflicts of interest or financial conflicts to disclose. All applicable institutional and national guidelines for the care and use of animals were followed.

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