doi:10.6041/j.issn.1000-1298.2016.03.028

Adiabatic Compression Heating Characteristics of Selected Food Materials during High Pressure Processing

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Abstract: During high pressure processing (HPP), the work of compression always causes the food materials to undergo a reversible adiabatic temperature increase. This phenomenon results in non-uniform temperature distribution during processing. The compression heating can also influence the inactivation of bacteria, spore and enzyme. But knowledge in this filed is still very limited. In this study, adiabatic compression heating characteristics of food materials during HPP was investigated using a specially designed experimental setup. Selected liquid and solid food materials were studied at different pressure levels (100 ~ 400 MPa) and different initial temperatures (15 ~ 45℃). At 25℃ initial temperature, ethanol had the highest δ (adiabatic temperature increase up to 12.8℃/(100 MPa)) of the samples examined, and δ value was decreased with increasing pressure. Compared to high water content foods(2.6 ~ 4.0℃/(100 MPa)), fats and oils showed higher δ values (7.3 ~ 10.7℃/(100 MPa)), which were also decreased with increasing pressure. For high water content foods, δ values was increased with increasing initial temperature, but fats and oils had little or no effect of initial temperature. An empirical equation was established to predict the adiabatic temperature increase value during HPP at different pressure levels and different initial temperatures for food materials. The third-order polynomial was used to fit the δ values of orange juice, honey, whole milk, semi-skimmed milk, soybean oil, beef and ethanol. The regression coefficients of these equations were all above 0.97. This study provides useful information for the optimization of high pressure processing.

Key words: food material; thermal effect; high pressure processing; thermodynamics

0 Introduction

High pressure processing (HPP) refers to a new technology that is the use of more than 100 MPa pressure (use water or other liquid as the pressure medium) under normal temperature or low temperature to the food materials (agricultural products or biological materials) sealed in the elastic container to achieve sterilization, enzymes inactivation and improve the physical and chemical properties[1-4]. During HPP, the work of compression causes the materials to undergo a temperature increase, called Compression heating. If the materials have no heat exchange with the environment, it becomes Adiabatic compression heating. Different materials have different adiabatic compression heating characteristics. Bacterial spores in low-acid foods are highly resistant to high pressure (up to 1 000 MPa) at normal temperature during HPP. But increasing processing temperature appropriately can play a good role in killing these microorganisms[5-8]. In addition, the temperature gradient will appear among the materials, the pressure medium and the inner wall of high pressure vessel because of their different compression heating characteristics. It will cause temperature uneven distribution and affect the high pressure process[9]. It can effectively improve the HPP results by reasonable utilizing the adiabatic compression heating characteristics of materials.

In recent years, scholars at home and abroad have made some studies on the compression heating characteristics of different materials and pressure transmission medium under high pressure. RASANAYAGAM et al.[10] studied the adiabatic compression heating values of fats, vegetable oils, etc., and found that the compression heating values of fatty materials were higher than that of water and the

Received date: 2015-12-26 Accepted date: 2016-01-04
Supported by National Natural Science Foundation of China (Grant No. 31171779)
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initial temperature also affects the compression heating values. PATAZCA et al.[11] studied the adiabatic compression heating values of some food materials such as cream cheese, avocado under different pressures and initial temperatures. They also established prediction model of the adiabatic compression heating values of the materials based on pressure and initial temperature. BUZRUL et al.[12] and KNOERZER et al.[13-14] considered that the heat insulation devices and pressure transmission mediums could make the temperature uneven distribution during HPP, and they tested the adiabatic compression heating values of different thermal insulation materials and pressure transmission mediums. Domestic scholars WANG et al.[15-16] studied the temperature increase under high pressure at the condition of simulated small heat loss and established prediction model.

At present, the function of domestic high pressure equipment is not perfect. The lack of effectively working temperature detection and control devices under high pressure restrict the study of materials thermal characteristics during HPP. The objectives of this work were to add temperature detection and control devices to the existing HP equipment through self-made polyformaldehyde adiabatic pressure devices, to detect the temperature and pressure in high pressure chamber real-time, and to study the adiabatic compression heating characteristics of variety of materials under different pressure and temperature.

1 Materials and methods

1.1 Materials

Absolute ethanol (analytical grade, Sinopharm Chemical Reagent Co., Ltd), orange juice, honey, milk(whole milk, semi-skimmed milk and skim milk), yogurt, soybean oil, colza oil, pork fats, beef, chicken and potato were purchased from local Wal-Mart supermarket, polytetrafluoroethylene packing bags. The liquid materials didn't have to pretreat. The meats were minced in a mincing machine. The potatoes were cooked in an induction cooker and mashed. All processed samples were stored in a refrigerator at 4℃.

1.2 Main instruments and equipments

Main experimental instruments included K-type thermocouples (Omega Engineering, Stamford, USA), a data logger (34970A, Agilent Technologies Inc., USA), a circulation thermostat (Henan Brothers Instrument Equipment Co., Ltd., China), a vacuum packaging machine (Shanghai Yute Packaging Machinery Manufacturing Co., Ltd., China), a water bath (Jiaxing Zhongxin Medical Instrument Co., Ltd., China) and a induction cooker (Shanghai Pentium Enterprise Co., Ltd., China).

The HP equipment (HPP/600 MPa/5 L) was provided by Baotou Kefa High Pressure Technology Co. and added temperature detection and control unit, as shown in Fig. 1. The maximum processing pressure of the HP equipment was 600 MPa. Effective treatment volume was 5 L. Effective working temperature range was 4 ~ 80℃. The pressure medium was pure water. The pressurization rate of the HP equipment was about 110 MPa/min, the depressurization rate was 90 ~ 120 MPa/s. During the trial, adjust the temperature setting of circulation thermostat and intelligent temperature control instrument to reach the temperature of HP vessel and pressure transmission medium to the initial value. The sample and HP vessel temperature were measured using the K-type thermocouples. The online pressure and temperature data were collected by the data logger and recorded in computer.

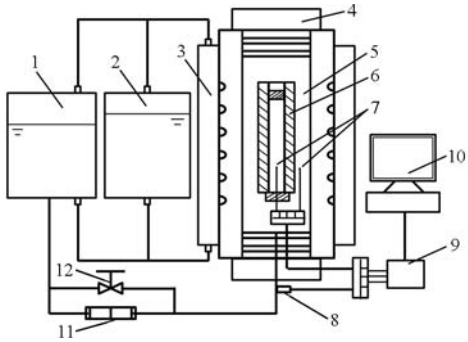

Fig. 1 Schematic diagram of high-pressure processing apparatus

1. HP medium reservoir 2. Circulation thermostat 3. Insulations 4. HP plug 5. HP vessel 6. Insulated chamber 7. Thermocouple 8. HP transducer 9. Data logger 10. Computer 11. HP pump 12. Release valve

A self-made insulated chamber (inner diameter 35 mm, outer diameter 80 mm, height 200 mm) was used in this experiment. The material was polyformaldehyde (low thermal conductivity, 0.23 W/(m·K), meets the requirements of the experiment for the heat preservation). Schematic diagram of the insulated chamber is shown in Fig. 2. The device was mainly composed of chamber, end

cover, piston, seal fitting and rubber ring. There was a hole (diameter 3 mm) used for installation of thermocouple in the center of the end cover and of the seal fitting. It mainly adapted the method of pressing-seal in view of that the thermocouple wire was difficult to glue with its sheath material of polytetrafluoroethylene according to the experimental requirements. Put the thermocouple wire through the lock nut and the filler, and then tightened the lock nut to compress the filler and clamp the thermocouple wire. So the thermocouple wire was sealed. The piston at the bottom of the chamber was used to transfer pressure. The equal area of two sides could realize constant pressure transmission which ensured that the pressure of sample in the chamber equaled the pressure of HP vessel during HPP.

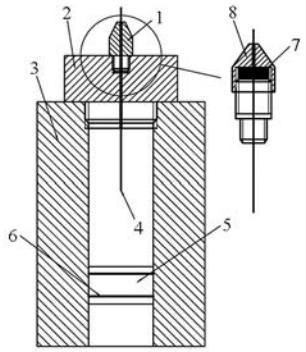

Fig. 2 Schematic diagram of insulated chamber

1. Seal fitting 2. End cover 3. Chamber 4. Thermocouple 5. Piston 6. Rubber ring 7. Filler 8. Lock nut

The sample sealed bags located in central of the insulated chamber, and its structure is shown in Fig. 3. Principle of thermocouple seal joint was similar as the seal fitting of the insulated chamber. Tightened lock nut to compress filler, and thus sealed the thermocouple. The seal joint was connected and sealed with bolt by thread connection. The polytetrafluoroethylene packing bag was located between the washers. The bag was sealed through increasing the pressure of the washers and narrowing the gap of washers and bags by gland nut. Adjusted the position of the thermocouple to make it locate in the heart of the packing bag when install the seal joint.

1.3 Experimental methods

1.3.1 Adiabatic compression heating experiment of water under high pressure

In order to check this experimental setup, water was used as a calibration sample, because physical properties of water are well characterized for the

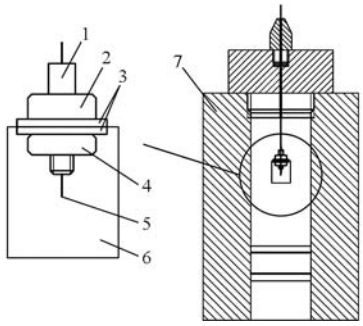

Fig. 3 Schematic diagram of sealed bags

1. Thermocouple seal joint 2. Bolt 3. Washer 4. Gland nut 5. Thermocouple 6. Polytetrafluoroethylene packing bag 7. Insulated chamber

pressure and temperature ranges used in this study and water is the main component of most food materials. Put the sample water in the insulated chamber and treated it under high pressure. Real-time pressure and temperature data were acquired by the data logger (once 1 s). An example of the experiment conditions is shown in Fig. 4. The HP vessel, the HP medium and the sample were preconditioned to a temperature of 20℃. The temperature of the sample water reached 25.4℃ under the pressure of 200 MPa. The temperature of the medium water in HP vessel rose slightly. But the increasing value was lower than that of the sample water in the insulated chamber as existing heat exchange with the outside. During the pressure-holding period, the temperature of sample water almost remained the same, but the temperature of water in HP vessel dropped continuously. The temperature of sample water and water in HP vessel both dropped sharply during depressurization. After that, the temperature of sample water dropped to the initial value. The experimental values of the adiabatic temperature increase of water were compared to those given by the NIST/ASME database[17]. No significant differences were found among experimental values and theoretical values. The fact that the temperature of water in HP vessel remained same during pressure-holding period and returned to the initial value after depressurization illustrated that the experimental transfer cylinder had great heat insulation effect.

1.3.2 Temperature change determination of materials under high pressure

The material samples were put in packing bags to ensure that the thermocouple located in center of the samples. The packing bag was sealed by thevacuum

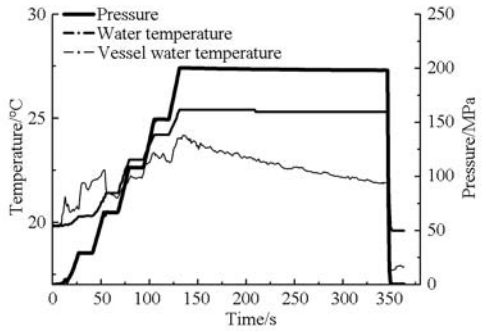

Fig. 4 Temperature-time and pressure-time profiles of water at an initial temperature of 19.8℃ and set pressure of 200 MPa during adiabatic compression experimental cycle

packaging machine. The insulated chamber was filled with the same sample as the pressure medium to avoid temperature gradient caused from different compression heating characteristics of sample and pressure medium which would affect the results.

Prior to experiments, the packing bag filled with sample to be tested, the same sample as pressure medium and the insulated chamber were equilibrated in a water bath to the same initial temperature ($T_0 \pm 0.5$)℃. And the temperature was monitored by the thermocouple in the packing bag during the pretreatment. When the initial temperature condition was met, the samples as pressure medium and the sealed packing bags filled with samples were transferred to the insulated chamber, and then tightened the end cover to seal it. The thermocouple within the insulated chamber was connected with thermocouple wire of temperature detection system. Finally, the insulated chamber was loaded inside the HP vessel for high pressure treatment. The pressure-holding time was set to 30 s. The temperature of samples was measured by thermocouple, the pressure of system was measured by pressure sensor, and the data were collected real-time by data logger and computer during the entire experiment (once per second).

The experiments were carried out at pressure of 100, 200, 300, 400 MPa and initial temperature of 15, 25, 35, 45℃. All the experiments were repeated three times, and the results were represented in the form of mean value ± standard deviation.

1.3.3 Evaluation of adiabatic compression heating values of materials under high pressure

The test material samples actually experienced two reversible processes of adiabatic compression heating and adiabatic decompression cooling during HPP. The temperature change of decompression stage was used for compression heating value. The reason for this is that the HPP equipment had a relatively slower rate of pressurization which would cause heat exchange between the materials and external environment and affect the accuracy of results, while the decompression was faster (less than 5 s) and the heat loss could be ignored. The adiabatic compression heating values of test samples were evaluated using the following formula.

$$\delta = 100\frac{\Delta T}{\Delta p} = 100\frac{T_P - T_0}{p - p_0} \cong 100\frac{T_P - T_0}{p} \quad (1)$$

where δ is the adiabatic compression heating value of sample under high pressure, ℃/(100 MPa); T_P is the temperature of sample under high pressure, that is the initial temperature of decompression, ℃; T_0 is the temperature of sample under atmospheric pressure, that is the final temperature after decompression, ℃; p is the set pressure of treatment, MPa; p_0 is the atmospheric pressure, 0.1 MPa.

2 Results and discussion

2.1 Effect of pressure and food composition on adiabatic compression heating value

The behavior of adiabatic compression heating of material during HPP is a thermodynamic effect. It reflects the compressibility of material. Under compression, the internal energy of system increased as the material compressed quickly. It results in a rapid rise in temperature of the material. The adiabatic compression heating values of different materials under different pressures (100, 200, 300, 400 MPa) are shown in Tab. 1 (initial temperature was 25℃).

From Tab. 1, ethanol demonstrated the highest adiabatic compression heating value among the test materials at pressure of 100 MPa, up to (12.8 ± 0.2)℃/(100 MPa), decreasing with increasing pressure. The δ value of ethanol decreased to (9.0 ± 0.1)℃/(100 MPa) when the pressure increased to 400 MPa. Followed by high fat content materials of pork fat, colza oil and soybean oil, the δ value of these materials also shown a trend of decreasing with increasing pressure. Among them, the effect of pressure on the δ value of pork fat was more noticeable as it decreased from (10.7 ± 0.2)℃/(100 MPa)

Tab. 1 Adiabatic compression heating values of selected food materials at initial temperature of 25℃ and pressures from 100 MPa to 400 MPa

℃/(100 MPa)

Food materials	Pressure/MPa			
	100	200	300	400
Orange juice	2.6 ± 0.1	3.0 ± 0.1	3.1 ± 0.1	3.1 ± 0.1
Honey	3.5 ± 0.1	3.5 ± 0.1	3.4 ± 0.1	3.2 ± 0.1
Whole milk	3.0 ± 0.2	3.1 ± 0.1	3.3 ± 0.1	3.3 ± 0.1
Semi-skimmed milk	2.8 ± 0.1	2.9 ± 0.1	3.0 ± 0.1	3.1 ± 0.0
Skim milk	2.7 ± 0.1	2.8 ± 0.1	2.8 ± 0.1	2.9 ± 0.1
Yogurt	2.8 ± 0.1	3.1 ± 0.1	3.2 ± 0.1	3.3 ± 0.1
Soybean oil	10.2 ± 0.2	9.7 ± 0.2	8.9 ± 0.1	8.2 ± 0.1
Colza oil	10.6 ± 0.4	9.5 ± 0.1	9.3 ± 0.5	8.2 ± 0.1
Pork fat	10.7 ± 0.2	9.8 ± 0.1	8.6 ± 0.1	7.3 ± 0.1
Beef	3.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.6 ± 0.1
Chicken	3.0 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.3 ± 0.1
Mashed potato	2.6 ± 0.2	2.9 ± 0.1	3.7 ± 0.2	4.0 ± 0.1
Ethanol	12.8 ± 0.2	11.1 ± 0.2	10.1 ± 0.1	9.0 ± 0.1

(100 MPa) to (7.3 ± 0.1)℃/100 MPa(400 MPa). It could be also got that the high fat content materials had higher δ values than that of other materials. The reason is that the fat molecules are larger than water molecule and they are polarity unlike water linked by hydrogen bonds, hence the fat molecules are easier to be compressed. The law we got from our study was similar to that of PATAZCA et al[11]. and WANG et al[15]. However, the δ values in this study were higher than that of them under same pressure and initial temperature conditions. It may be related to the differences of the composition of selected fatty foods, the insulation devices, as well as the selection of temperature ranges (pressurization or de pressurization) for δ values evaluation. At the condition of 25℃, the δ value of colza oil was a little higher than that of soybean oil. It related to the difference of fatty acids types they contained. It was reported that[10] the adiabatic compression heating values of unsaturated fatty acids were higher than that of saturated fatty acids in fatty foods. This was determined by the compressibility of the two kinds of fatty acids. Composition of materials in this study is presented in Tab. 2[18]. It can be found that the unsaturated fatty acids content of colza oil (92.8%) was higher than that of soybean oil (84%), hence the δ value of colza oil was higher than that of soybean oil. But the phenomenon was not obvious at other initial temperatures, since it may be related to the differences of the types of unsaturated fatty acids they contained (the polyunsaturated fatty acids content of soybean oil was 59%, while the colza oil contained 28% polyunsaturated fatty acids).

Tab. 2 Composition of selected food materials %

Food materials	Major components/%					
	Water	Protein	Saturated fatty acids	Monounsaturated fatty acids	Polyunsaturated fatty acids	Carbohydrate
Orange juice	87.9	0.6	0	11.5		
Honey	25.0	0	0	75.0		
Whole milk	88.3	3.4	3.6	4.7		
Semi-skimmed milk	89.8	3.6	1.8	4.8		
Skim milk	91.6	3.4	0	5.0		
Yogurt	82.5	2.7	2.9	11.9		
Soybean oil	0	0	16.0	25.0	59.0	0
Colza oil	0	0	7.2	64.8	28.0	0
Pork fat	9.0	2.4	88.6	0		
Beef	76.3	20.2	2.3	1.2		
Chicken	70.0	19.3	9.4	1.3		
Mashed potato	79.8	2.0	0.2	16.5		
Ethanol	0					

At the condition of 25℃, the δ value of orange juice was about 3.0℃/(100 MPa), closing to that of water. The reason is that orange juice is a material of high water content (87.9%), hence its adiabatic compression heating characteristics is similar to that of water. The δ value of honey (carbohydrate content was 75%) was in the range of 3.2 ~ 3.5℃/(100 MPa). BALASUBRAMANIAM et al.[9] reported that the δ value of carbohydrate at temperature of 25℃ was 2.6 ~ 3.6℃/(100 MPa), closing to that of water. The δ value of mashed potato was about 2.6 ~ 4.0℃/(100 MPa), increasing with increasing pressure. It may be because the compression ratio of potato is large under high pressure. The δ value of milk (whole milk, semi-skimmed milk and skim milk) didn't vary significantly with increasing pressure, but it increased with the increase of fat content. From smallest to largest were skim milk, semi-skimmed milk and whole milk. It also illustrated that the materials with high fatty content is easier to be compressed. The δ value of yogurt

presented a rising trend with increasing pressure, which was a little different from that of milk. The reason may be that some energy was consumed at low pressure level to kill the microorganisms in yogurt, with the increase of pressure, the amount of microorganisms decreasing, corresponding energy consumed for kill the microorganisms reducing, so as the δ value increasing. The δ values of beef and chicken varied in the range of 3.0℃/(100 MPa) to 3.3℃/(100 MPa) on the whole, closing to that of water. This is because their water content is high. However, these values were higher than orange juice since beef and chicken contained rich protein except water. Fig. 5 is the temperature-pressure profiles of soybean oil and orange juice at initial temperature of 25℃ and pressure of 200 MPa during HPP. From the diagram, while the temperature of orange juice reached its initial temperature value immediately after pressurization, the cooling process of soybean oil was relatively slower, taking a long time (about 60 s) to reach steady state. It was a phenomenon of temperature delay. RASANAYAGAM[10] also reported the same phenomenon of temperature delay in fatty foods during HPP. Though the thermocouple used could have contributed some delays to experimental results since its response needed a certain time, the response time of K-type thermocouple used in this study was only hundreds milliseconds, and there were no significant phenomena of temperature delays in experiment results of other materials such as orange juice. So it could be ignored the effect of measuring time. This phenomenon should have a great relationship with composition of materials. Further researches on the effect of molecular structure on adiabatic compression heating are needed.

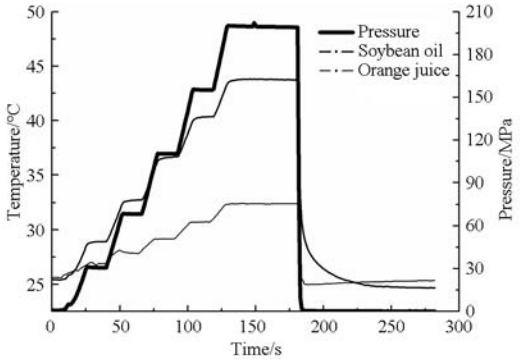

Fig. 5 Temperature-pressure profiles of soybean oil and orange juice at initial temperature of 25℃ and set pressure of 200 MPa during high-pressure processing

2.2 Effect of initial temperature on adiabatic compression heating value

Initial temperature is one of important factors that affect the adiabatic compression heating of materials during HPP. Effect of initial temperature on adiabatic compression heating of materials at pressure of 200 MPa was shown in Fig. 6.

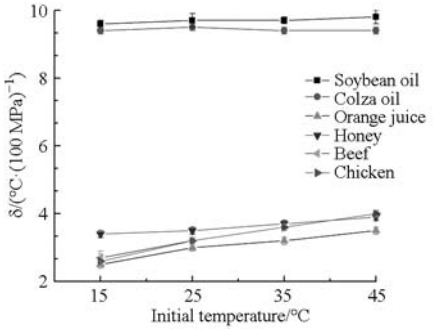

Fig. 6 Effect of initial temperature on adiabatic compression heating of food materials at 200 MPa

From the diagram, the δ values of soybean oil at different initial temperatures (15 ~ 45℃) almost remained same. The results of colza oil were similar to soybean oil. It illustrated that the δ values of fatty foods almost remained same with increasing initial temperature. PATAZCA et al.[10] researched the variation of vegetable oil at different initial temperatures (1 ~ 70℃) and found that the effect of initial temperature on δ values of vegetable oil was very small. The δ values of honey increased with increasing initial temperature, from 3.4℃/(100 MPa) to 3.9℃/(100 MPa) with initial temperature increasing from 15℃ to 45℃. It is because with the increase of initial temperature, the distance between materials molecules increased, resulting in easier to be compressed under high pressure. The more work was needed to compress molecules, the more internal energy transferred to, which shown increasing δ value. The results of orange juice were similar to honey. The δ values of orange juice were close to that of water since its major components are carbohydrate and water. The δ values of beef and chicken were almost the same and increased with increasing initial temperature. The reason was that the major component of beef and chicken was protein with δ value being similar to that of water. With increase of initial temperature, the spatial structure of protein becomes unstable and easier to be compressed, resulting in higher compression ratio under high pressure. More work was needed to

compress protein molecules, and more internal energy transferred to, so the δ value increased.

2.3 Prediction model of adiabatic compression heating value based on pressure and initial temperature

The insulated chamber used for this study can be approximately considered as an enclosed system with a piston pressurizing materials in the system. The energy balance equation of system can be obtained from the first law of thermodynamics

$$Q = W + \Delta U \tag{2}$$

where Q is the heat of system absorbing or releasing; W is the work of system; ΔU is the variation of system's internal energy.

The experiment could be approximately considered as an insulation process. The thermal energy $Q = 0$. The internal energy of system increased resulting from the work of system. That is $-W = \Delta U$. The external performance of internal energy increase is the temperature rise of material.

Some scholars deduced a formula for evaluating the reversible temperature variation of material under the condition of adiabatic based on the first law of thermodynamics[14]

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T\alpha}{\rho C_p} \tag{3}$$

where T is the thermodynamic temperature, K; α is the thermal expansion coefficient of material, K^{-1}; ρ is the density, kg/m^3; C_p is the specific heat at constant pressure, J/(kg·K).

For different materials, their thermal expansion coefficient, density and specific heat are different. For a specific material, the values of α, ρ and C_p are functions of pressure p and temperature T, hence its δ value is also a function of pressure p and temperature T. Eq. (3) can be expressed as

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T\alpha(p,T)}{\rho(p,T)C_p(p,T)} \tag{4}$$

Therefore, the δ value of a specific material under high pressure is mainly determined by treatment pressure p and initial temperature T_0.

In high pressure process, the final process temperature of material is the sum of the initial temperature and the adiabatic temperature increase. So it is necessary to know the adiabatic compression heating values of materials at different initial temperatures and pressures in order to reach the desired final process temperature. Establishing an appropriate mathematical model would contribute to predict the adiabatic compression heating values of materials at different conditions.

In an attempt to describe the adiabatic compression heating values of materials as a function of the initial temperature and pressure, data for each tested material was fitted to an empirical equation

$$\delta = \sum_{i=0,j=0}^{i+j\leq n} a_{ij} p^i T_0^j \tag{5}$$

where a_{ij} is the coefficients for material at a specific initial temperature and pressure (i, j represent i times of pressure p and j times of initial temperature T_0, respectively).

Eq. (5) was expanded to a third order model

$$\delta = a_{00} + a_{10}P + a_{01}T_0 + a_{11}PT_0 + a_{20}P^2 + a_{02}T_0^2 + a_{30}P^3 + a_{03}T_0^3 + a_{12}PT_0^2 + a_{21}P^2T_0 \tag{6}$$

The adiabatic compression heating values of orange juice, honey, whole milk, semi-skimmed milk, soybean oil, beef and ethanol at pressure of 100 ~ 400 MPa and initial temperature of 15 ~ 45℃ were fitted to the above equation. The parameters in the equation could be calculated. From Tab. 3, the regression coefficients fitted for those materials were 0.997, 0.987, 0.987, 0.989, 0.974, 0.985 and 0.987, respectively. It illustrated that the above equation could fit the adiabatic compression heating values of those materials under the condition well since the regression coefficients were high.

3 Conclusions

(1) The polyformaldehyde adiabatic pressure device designed for this study has a good insulation effect. The temperature of materials and the pressure could be real-time monitored during HPP with adding K-type thermocouple.

(2) The adiabatic compression heating values of materials were mainly affected by composition of materials, treatment pressure and initial temperature. The δ value of ethanol was the highest, followed by fatty materials (soybean oil, colza oil and pork fat). The δ values of protein materials (beef, chicken), carbohydrate materials (orange juice, honey) and milk (whole milk, semi-skimmed milk and skim milk) were close to that of water. The δ values of ethanol and fatty

Tab. 3 Regression coefficients for food materials from equation

Parameters	Orange juice	Honey	Whole milk	Semi-skimmed milk	Soybean oil	Beef	Ethanol
a_{00}	-1.753	3.334	-1.573	0.070	12.406	1.726	10.209
a_{10}	0.019	0.005	0.007	0.011	-0.008	-0.006	-0.044
a_{01}	0.229	-0.041	0.366	0.140	-0.080	0.124	0.366
a_{11}	-5.30×10^{-4}	1.45×10^{-5}	-1.96×10^{-4}	-1.84×10^{-4}	6.80×10^{-4}	1.74×10^{-4}	9.92×10^{-4}
a_{20}	-3.22×10^{-5}	-2.43×10^{-5}	-1.22×10^{-5}	-2.60×10^{-5}	-6.25×10^{-5}	2.08×10^{-5}	3.10×10^{-5}
a_{02}	-0.004	0.002	-0.010	-0.003	1.25×10^{-4}	-0.003	-0.006
a_{30}	8.33×10^{-9}	2.92×10^{-8}	8.33×10^{-9}	2.50×10^{-8}	9.58×10^{-8}	-1.25×10^{-8}	-4.17×10^{-9}
a_{03}	3.33×10^{-5}	-2.08×10^{-5}	1.08×10^{-4}	3.33×10^{-5}	2.92×10^{-5}	4.58×10^{-5}	4.17×10^{-6}
a_{12}	1.50×10^{-6}	-2.50×10^{-7}	1.00×10^{-6}	5.00×10^{-7}	-1.18×10^{-5}	-2.25×10^{-6}	-1.68×10^{-5}
a_{21}	7.00×10^{-7}	-2.50×10^{-8}	2.00×10^{-7}	2.00×10^{-7}	1.25×10^{-7}	-2.75×10^{-7}	1.75×10^{-7}
Regression coefficients	0.997	0.987	0.987	0.989	0.974	0.985	0.987

materials were affected by pressure significantly, decreasing with increasing pressure. The δ values of other materials were insensitive to pressure. The effect of initial temperature on the δ values of fatty materials was not significant, while the δ values of protein and carbohydrate materials increased with increasing initial temperature.

(3) A mathematical model was established for predicting the adiabatic compression heating values of food materials based on pressure and initial temperature. It could be used for predicting rough adiabatic temperature changes of materials during actual HPP, and taking advantage of compression heating effects. This study has guiding significance for the optimization of high pressure processing.

References

[1] SU Guangming, ZHU Songming, HU Feifei, et al. Kinetics of polyphenoloxidase activation and inactivation in soybean paste koji by high pressure[J]. Transactions of the Chinese Society for Agricultural Machinery, 2015, 46(10): 257 - 265. (in Chinese)

[2] YI Jianyong, ZHANG Yan, LIAO Xiaojun, et al. Automatic high hydrostatic pressure equipment for food sterilization[J]. Transactions of the Chinese Society for Agricultural Machinery, 2011, 42(11): 113 - 117. (in Chinese)

[3] YU Yong, PAN Fang, SU Guangming, et al. Application of ultra high pressure on crop produces processing[J]. Transactions of the Chinese Society for Agricultural Machinery, 2015, 46(10): 247 - 256. (in Chinese)

[4] ZHU Songming, SU Guangming, WANG Chunfang, et al. Research and application on high-pressure processing of aquatic products[J]. Transactions of the Chinese Society for Agricultural Machinery, 2014, 45(1): 168 - 177. (in Chinese)

[5] ZHU S, NAIM F, MARCOTTE M, et al. High-pressure destruction kinetics of Clostridium sporogenes spores in ground beef at elevated temperatures[J]. International Journal of Food Microbiology, 2008, 126(1 - 2): 86 - 92.

[6] SHAO Y, ZHU S, RAMASWAMY H, et al. Compression heating and temperature control for high-pressure destruction of bacterial spores: an experimental method for kinetics evaluation[J]. Food and Bioprocess Technology, 2010, 3(1): 71 - 78.

[7] EVELYN, SILVA F V M. High pressure processing of milk: modeling the inactivation of psychrotrophic *Bacillus cereus* spores at 38 ~ 70℃ [J]. Journal of Food Engineering, 2015, 165: 141 - 148.

[8] AHN J, BALASUBRAMANIAM B V M. Inactivation kinetics and injury recovery of Bacillus amyloliquefaciens spores in low-acid foods during pressure-assisted thermal processing[J]. Food Science and Biotechnology, 2014, 23(6): 1851 - 1857.

[9] BALASUBRAMANIAM V M, TING E Y, STEWART C M, et al. Recommended laboratory practices for conducting high-pressure microbial inactivation experiments[J]. Innovative Food Science & Emerging Technologies, 2004, 5(3): 299 - 306.

[10] RASANAYAGAM V, BALASUBRAMANIAM V M, TING E, et al. Compression heating of selected fatty food materials during high-pressure processing[J]. Journal of Food Science, 2003, 68(1): 254 - 259.

[11] PATAZCA E, KOUTCHMA T, BALASUBRAMANIAM V M. Quasi-adiabatic temperature increase during high pressure processing of selected foods[J]. Journal of Food Engineering, 2007, 80(1): 199 - 205.

[12] BUZRUL S, ALPAS H, LARGETEAU A, et al. Compression heating of selected pressure transmitting fluids and liquid foods during high hydrostatic pressure treatment[J]. Journal of Food Engineering, 2008, 85

(3): 466 - 472.

[13] KNOERZER K, BUCKOW R, VERSTEEG C. Adiabatic compression heating coefficients for high-pressure processing—a study of some insulating polymer materials[J]. Journal of Food Engineering, 2010, 98(1): 110 - 119.

[14] KNOERZER K, BUCKOW R, SANGUANSRI P, et al. Adiabatic compression heating coefficients for high-pressure processing of water, propylene-glycol and mixtures—a combined experimental and numerical approach[J]. Journal of Food Engineering, 2010, 96(2): 229 - 238.

[15] WANG Biaoshi, LI Biansheng, ZENG Qingxiao, et al. Compression heating characteristics of foods during ultra high hydrostatic pressure processing[J]. Transactions of the CSAE, 2009, 25(2): 246 - 250. (in Chinese)

[16] WANG Biaoshi, LI Biansheng, ZENG Qingxiao, et al. Mathematical model for prediction of compression heating of foods processed with ultra-high hydrostatic pressure[J]. Modern Food Science and Technology, 2014, 30(8): 175 - 181. (in Chinese)

[17] HARVEY A H, LEMMON E W. NIST standard reference database 10: NIST/ASTM steam Properties (version 3.0)[S]. Applied Chemicals and Division National Institute of Standards and Technology, U. S. Department of Commerce, 2013.

[18] Zhou Caiqiong. Food Nutriology[M]. Beijing: Higher Education Press, 2011. (in Chinese)

doi:10.6041/j.issn.1000-1298.2016.03.028

超高压加工过程食品物料绝热压缩升温特性研究

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摘要: 为了掌握物料的绝热压缩升温特性,以便在超高压加工过程中合理利用绝热压缩升温效应,优化超高压加工工艺,通过特别设计的超高压下绝热压缩试验装置,测定了多种物料在不同压力(100 ~ 400 MPa)和初始温度(15 ~ 45℃)条件下的绝热压缩升温值。结果表明:在初始温度 25℃时,乙醇的绝热压缩升温值最大(12.8℃/(100 MPa)),且随压力的增大而减小,脂肪类物料的绝热压缩升温值(7.3 ~ 10.7℃/(100 MPa))较其他高含水率物料的(2.6 ~ 4.0℃/(100 MPa))要高,且随压力的增大而减小;高含水率物料的绝热压缩升温值随初始温度的升高表现出增大的趋势,而脂肪类物料的变化则不明显;建立了基于压力和初始温度的物料绝热压缩升温值的预测模型,对多种物料拟合得到的方程回归系数均在 0.97 以上。

关键词: 食品物料; 热效应; 超高压; 热力学
中图分类号: TS201.1　　**文献标识码**: A　　**文章编号**: 1000-1298(2016)03-0200-07

Adiabatic Compression Heating Characteristics of Selected Food Materials during High Pressure Processing

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Abstract: During high pressure processing (HPP), the work of compression always causes the food materials to undergo a reversible adiabatic temperature increase. This phenomenon results in non-uniform temperature distribution during processing. The compression heating can also influence the inactivation of bacteria, spore and enzyme. But knowledge in this filed is still very limited. In this study, adiabatic compression heating characteristics of food materials during HPP was investigated using a specially designed experimental setup. Selected liquid and solid food materials were studied at different pressure levels (100 ~ 400 MPa) and different initial temperatures (15 ~ 45℃). At 25℃ initial temperature, ethanol had the highest δ (adiabatic temperature increase up to 12.8℃/(100 MPa)) of the samples examined, and δ value was decreased with increasing pressure. Compared to high water content foods (2.6 ~ 4.0℃/(100 MPa)), fats and oils showed higher δ values (7.3 ~ 10.7℃/(100 MPa)), which were also decreased with increasing pressure. For high water content foods, δ values was increased with increasing initial temperature, but fats and oils had little or no effect of initial temperature. An empirical equation was established to predict the adiabatic temperature increase value during HPP at different pressure levels and different initial temperatures for food materials. The third-order polynomial was used to fit the δ values of orange juice, honey, whole milk, semi-skimmed milk, soybean oil, beef and ethanol. The regression coefficients of these equations were all above 0.97. This study provides useful information for the optimization of high pressure processing.

Key words: food material; thermal effect; high pressure processing; thermodynamics

收稿日期: 2015-12-26　修回日期: 2016-01-14
基金项目: 国家自然科学基金项目(31171779)
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引言

超高压加工(High pressure processing,HPP)技术是指将密封于弹性容器内的食品物料(农产品或生物材料)置于水或其他流体作为传压介质的压力系统中,经 100 MPa 以上压力处理,在常温或低温下达到杀菌、抑酶和改善理化特性的一种新技术[1-4]。在对物料进行超高压加工时,外界压力通过压缩物料做功产生能量的转换,致使物料出现升温现象,即物料的压缩升温(Compression heating),如果物料与外界没有热交换,则出现绝热压缩升温(Adiabatic compression heating),不同的物料具有不同的绝热压缩升温特性。在超高压加工过程中,低酸性食品中的细菌芽孢在常温下会对高压(达到 1 000 MPa)表现出较强的抗性,适当提高超高压处理温度可以对这些微生物起到很好的杀灭作用[5-8]。此外,在超高压处理过程中,物料、传压介质、高压容腔内壁往往会因不同的压缩升温特性产生温度梯度,致使温度分布不均匀,这会给超高压加工带来影响[9]。合理利用物料的绝热压缩升温特性可以有效提高超高压加工的效果。

近年来,国内外学者对超高压下不同物料和传压介质的压缩升温特性进行了一定程度的研究。RASANAYAGAM 等[10]对脂肪、植物油等的绝热压缩升温值进行了研究,发现脂肪类物料的压缩升温值要高于水,而初始温度也会对压缩升温值产生影响。PATAZCA 等[11]对奶酪、鳄梨等食品物料在不同压力和初始温度条件下的绝热压缩升温值进行了研究,并建立了物料的绝热压缩升温值关于压力和初始温度的预测模型。BUZRUL 等[12]和 KNOERZER 等[13-14]考虑到绝热装置和传压介质会使超高压处理过程中温度分布不均匀,测试了不同绝热材料和不同传压介质的绝热压缩升温值。国内学者王标诗等[15-16]在模拟较小热损失条件下对超高压下的食品升温值进行了研究并建立了预测模型。

目前国内的超高压设备功能不够完善,缺乏能在超高压下有效工作的温度检测与调控设备,制约了超高压加工过程中物料热特性的研究。本文通过自制的聚甲醛绝热传压装置,在现有超高压设备上加装测温及控温装置,实时检测高压腔内温度和压力,研究多种物料在不同压力和温度下的绝热压缩升温特性。

1　材料与方法

1.1　材料

无水乙醇(分析纯,国药集团化学试剂有限公司),橙汁、蜂蜜、牛奶(全脂、半脱脂和脱脂)、酸奶、大豆油、菜籽油、猪肥肉、牛肉、鸡肉和土豆购于当地沃尔玛超市,聚四氟乙烯包装袋。液体物料无需处理,肉类经绞肉机绞碎,土豆经电磁炉煮熟后捣碎成土豆泥,处理后样品存放在 4℃冰箱内待用。

1.2　主要仪器与设备

主要试验仪器有 K 型热电偶(美国 Omega Stamford 公司);数据采集仪(34970A 型,美国 Agilent 公司);恒温循环器(河南兄弟仪器设备有限公司);真空包装机(上海余特包装机械制造有限公司);水浴锅(嘉兴市中新医疗仪器有限公司);电磁炉(上海奔腾企业有限公司)。

试验采用的超高压处理设备(HPP)由包头科发高压科技有限责任公司提供,并通过改造加装温度检测和控制单元,如图 1 所示。设备的最大工作压力为 600 MPa,有效处理容积为 5 L,有效工作温度为 4 ~ 80℃,传压介质为纯净水。该设备的增压速率约为 110 MPa/min,卸压速率为 90 ~ 120 MPa/s。试验过程中,通过调节恒温循环器和智能温控仪的温度设置使高压容腔与传压介质的温度达到需要的初始值。试验样品和传压介质的温度通过 K 型热电偶测量。加工过程中的压力和温度数据通过数据采集仪由计算机记录。

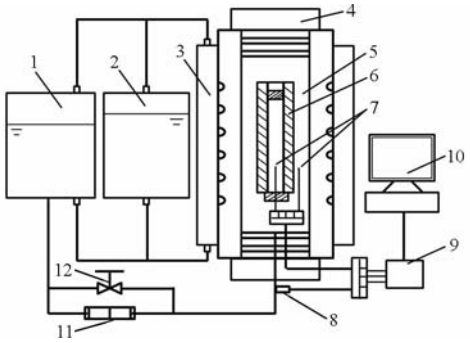

图 1　超高压试验装置示意图

Fig. 1　Schematic diagram of high pressure processing apparatus

1. 传压介质容器　2. 恒温循环器　3. 保温夹层　4. 高压堵头　5. 高压腔　6. 绝热套筒　7. 热电偶　8. 压力传感器　9. 数据采集仪　10. 计算机　11. 倍加器　12. 卸压阀

试验采用自制的绝热套筒(内径 35 mm,外径 80 mm,高度 200 mm),材料为聚甲醛(导热系数较低,为 0.23 W/(m·K),满足试验对于保温效果的要求)。图 2 为绝热套筒的示意图。该装置主要由腔体、端盖、活塞、密封接头、橡胶圈构成。端盖与密封接头中央开有通孔(孔径 3 mm)以便安装热电偶。根据试验要求,热电偶线的护套材料为聚四氟乙烯,不易胶黏,故主要采用压紧密封。热电偶线从压帽和填料中央穿过,拧紧压帽使填料不断压缩,从而夹

紧热电偶线,实现热电偶线的密封。腔体底部的活塞主要起到压力传递作用,活塞两侧面积相等,可以实现等压传递,保证了在超高压加工过程中,腔体内试样的压力与高压容腔的压力相等。

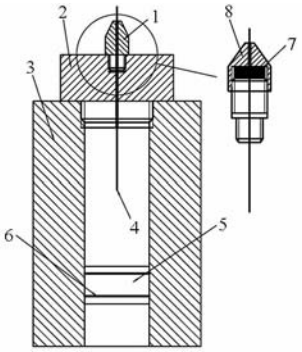

图 2 绝热套筒结构示意图

Fig. 2 Schematic diagram of insulated chamber

1. 密封接头 2. 端盖 3. 腔体 4. 热电偶 5. 活塞 6. 橡胶圈 7. 填料 8. 压帽

样品密封包装袋位于绝热套筒中央,其结构如图 3 所示。热电偶密封接头与绝热套筒的密封接头原理类似,也是通过拧紧压帽来挤压填料,从而实现热电偶的密封。密封接头通过螺纹连接形式与螺栓连接并密封。包装袋(聚四氟乙烯)位于上下垫片之间,通过压紧螺母增大上下垫片的压力,缩小垫片与包装袋的间隙,实现包装袋的密封。安装密封接头时,调整热电偶的位置使之位于包装袋中心。

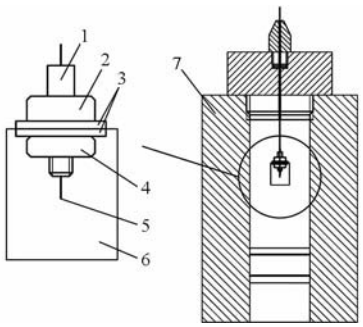

图 3 密封包装示意图

Fig. 3 Schematic diagram of sealed bags

1. 热电偶密封接头 2. 螺栓 3. 垫片 4. 压紧螺母 5. 热电偶 6. 聚四氟乙烯包装袋 7. 绝热套筒

1.3 试验方法

1.3.1 水在超高压下绝热压缩升温试验

为了检验本试验装置的有效性,用水作为校准试样,因为在本研究使用的压力和温度范围内,水的属性是已知的,而且水是大多数物料的主要成分。将水作为处理样品置于绝热套筒中在超高压下处理,通过数据采集仪实时采集压力和温度数据(每秒一次)。图 4 所示为本试验条件下的结果。高压容腔、传压介质和样品预处理使其温度达到 20℃,处理压力为 200 MPa 时,样品水的温度达到 25.4℃。高压腔内作为传压介质的水的温度略有上升,但因与外界存在热交换,其温度上升值低于绝热套筒中的水。保压过程中,样品的温度基本不变,而腔内水温则持续下降。卸压时,样品水温和腔内水温都迅速下降,样品水温降至初始温度水平。将水的绝热压缩升温试验值与 NIST/ASME 数据库[17]给出的值对比,试验值与理论值之间没有显著差异。保压阶段绝热套筒内的水温基本保持不变,卸压时恢复到初始温度水平,说明本试验采用的传压套筒有着良好的绝热效果。

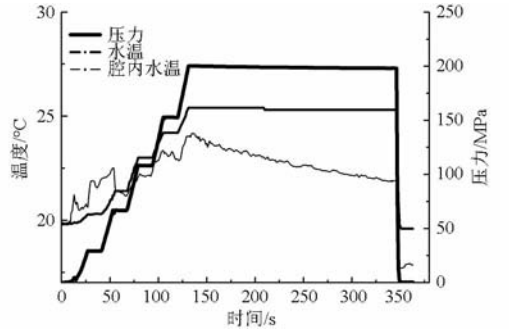

图 4 水在超高压下绝热压缩升温试验的温度-时间和压力-时间曲线(初始温度 19.8℃,压力 200 MPa)

Fig. 4 Temperature and pressure-time profiles of water at an initial temperature of 19.8℃ and set pressure of 200 MPa during adiabatic compression experimental cycle

1.3.2 物料在超高压下温度变化的测定

将待测物料样品置于包装袋中,保证热电偶置于样品中央,再用真空包装机热封。绝热套筒内装入同种样品作为传压介质,以避免在超高压处理过程中传压介质和样品因不同的压缩升温特性产生温度梯度而影响试验结果。

试验开始前,将装有待测样品的密封包装袋、作为传压介质的同种样品和传压套筒同时置于一定温度的水浴锅中平衡,通过包装袋内的热电偶对温度变化进行监测,使其达到试验所需初始温度(T_0 ± 0.5℃)。达到初始温度时,迅速将作为传压介质的样品和装有样品的密封包装袋转移至绝热套筒腔体中,拧紧套筒端盖将其密封。将绝热套筒内的热电偶与超高压温度检测系统的热电偶线相连。最后,将绝热套筒置于高压容腔内进行超高压处理,保压时间设置为 30 s。整个过程中样品的温度可由热电偶测量,系统压力由压力传感器测量,并通过数据采集仪和计算机实时采集(每秒一次)。

试验处理压力为 100、200、300、400 MPa。初始温度为 15、25、35、45℃。所有试验重复 3 次,结果以“平均值 ± 标准差”形式表示。

1.3.3 物料在超高压下绝热压缩升温值的计算

被测物料样品在超高压处理的整个过程中实际

上是经历了绝热压缩升温和绝热降压减温 2 个可逆的过程。因为本试验采用的超高压设备增压速度相对较慢，过程中物料与外界环境不可避免会发生热交换，引起样品内部温度变化，从而影响试验结果的准确度，而设备的卸压速度较快（5 s 以内），可以不计这一温度变化。因此，试验中均采用样品在卸压过程中的温度变化作为最终测试结果。被测样品的绝热压缩升温值计算公式为

$$\delta = 100\frac{\Delta T}{\Delta p} = 100\frac{T_P - T_0}{p - p_0} \cong 100\frac{T_P - T_0}{p} \quad (1)$$

式中　δ——样品在超高压下的绝热压缩升温值，℃/(100 MPa)

T_P——样品在超高压下的温度，即卸压开始时的温度，℃

T_0——样品在常压下的温度，即卸压结束后的温度，℃

p——设定的处理压力，MPa

p_0——常压，取 0.1 MPa

2　结果与分析

2.1　压力和物料成分对绝热压缩升温的影响

物料在超高压加工过程中的绝热压缩升温是热力学效应，其反映了物料的压缩特性。在压力作用下，物料被快速压缩致使系统内能增加，结果使得物料的温度快速上升。不同物料在不同压力（100、200、300、400 MPa）下的绝热压缩升温值如表 1 所示（初始温度 25℃）。

表 1　物料在不同压力下的绝热压缩升温值（初始温度 25℃）

Tab.1　Adiabatic compression heating values of selected food materials at initial temperature of 25℃ and pressures of 100 ~ 400 MPa　℃/(100 MPa)

物料	压力/MPa			
	100	200	300	400
橙汁	2.6 ± 0.1	3.0 ± 0.1	3.1 ± 0.1	3.1 ± 0.1
蜂蜜	3.5 ± 0.1	3.5 ± 0.1	3.4 ± 0.1	3.2 ± 0.1
全脂牛奶	3.0 ± 0.2	3.1 ± 0.1	3.3 ± 0.1	3.3 ± 0.1
半脱脂牛奶	2.8 ± 0.1	2.9 ± 0.1	3.0 ± 0.1	3.1 ± 0.0
脱脂牛奶	2.7 ± 0.1	2.8 ± 0.1	2.8 ± 0.1	2.9 ± 0.1
酸奶	2.8 ± 0.1	3.1 ± 0.1	3.2 ± 0.1	3.3 ± 0.1
大豆油	10.2 ± 0.2	9.7 ± 0.2	8.9 ± 0.1	8.2 ± 0.1
菜籽油	10.6 ± 0.4	9.5 ± 0.1	9.3 ± 0.5	8.2 ± 0.1
猪肥肉	10.7 ± 0.2	9.8 ± 0.1	8.6 ± 0.1	7.3 ± 0.1
牛肉	3.2 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.6 ± 0.1
鸡肉	3.0 ± 0.1	3.2 ± 0.1	3.2 ± 0.1	3.3 ± 0.1
土豆泥	2.6 ± 0.2	2.9 ± 0.1	3.7 ± 0.2	4.0 ± 0.1
乙醇	12.8 ± 0.2	11.1 ± 0.2	10.1 ± 0.1	9.0 ± 0.1

由表 1 可知，在所研究的物料中，乙醇在 100 MPa 压力下的绝热压缩升温值最大，达到（12.8 ± 0.2）℃/(100 MPa)，并随着压力的增大而减小，当压力增至 400 MPa 时，其绝热压缩升温值已降低至（9.0 ± 0.1）℃/(100 MPa)。其次是猪肥肉、菜籽油、大豆油这几种高脂肪含量的物料，它们的绝热压缩升温值也表现出随着压力的增大而减小的趋势。其中，压力对猪肥肉的绝热压缩升温值的影响比较明显，从（10.7 ± 0.2）℃/(100 MPa)（100 MPa 时）减小至（7.3 ± 0.1）℃/(100 MPa)（400 MPa 时）。从中也可以看出，脂肪含量较高的物料，其绝热压缩升温值明显高于其他类物料，这是因为脂肪分子相对较大并且是非极性的，不同于水分子之间有氢键相连，因而更容易被压缩。研究得到的规律与 PATAZCA 等[11]和王标诗等[15]的研究类似。而在相同压力和初始温度条件下测得绝热压缩升温值，本试验结果比其报道的结果要高，这可能与选取的脂肪类食品组成成分、采用的绝热装置以及计算时选取的温度变化区间（增压或卸压）不同有关。在 25℃条件下，菜籽油的绝热压缩升温值略高于大豆油，这与它们所含脂肪酸的类型不同有关。有文献报道[10]，在脂肪类食品中，不饱和脂肪酸的绝热压缩升温值比饱和脂肪酸的绝热压缩升温值高，这是两类脂肪酸的压缩性决定的。所研究的物料的组成成分如表 2 所示[18]，从中可以看出菜籽油的不饱和脂肪酸含量（92.8%）大于大豆油的（84%），因此其绝热压缩升温值大于大豆油的绝热压缩升温值。但在其它初始温度条件下这一现象却并不明显，这可能与它们所含的不饱和脂肪酸的类型有关，大豆油的多不饱和脂肪酸含量为 59%，而菜籽油的多不饱和脂肪酸含量为 28%。

表 2　物料的组成成分

Tab.2　Composition of selected food materials　%

物料	主要成分					
	水分	蛋白质	饱和脂肪酸	单不饱和脂肪酸	多不饱和脂肪酸	碳水化合物
橙汁	87.9	0.6	0	11.5		
蜂蜜	25.0	0	0	75.0		
全脂牛奶	88.3	3.4	3.6	4.7		
半脱脂牛奶	89.8	3.6	1.8	4.8		
脱脂牛奶	91.6	3.4	0	5.0		
酸奶	82.5	2.7	2.9	11.9		
大豆油	0	0	16.0	25.0	59.0	0
菜籽油	0	0	7.2	64.8	28.0	0
猪肥肉	9.0	2.4	88.6	0		
牛肉	76.3	20.2	2.3	1.2		
鸡肉	70.0	19.3	9.4	1.3		
土豆泥	79.8	2.0	0.2	16.5		
乙醇				0		

在25℃条件下,橙汁的绝热压缩升温值约为3.0℃/(100 MPa),与相同条件下水的绝热压缩升温值接近,这是因为橙汁是高含水率(87.9%)的物料,其绝热压缩升温特性与水相似。蜂蜜(含碳水化合物75%)的绝热压缩升温值在3.2~3.5℃/(100 MPa)变化,BALASUBRAMANIAM等[9]报道了碳水化合物在25℃时的绝热压缩升温值为2.6~3.6℃/(100 MPa),与水的绝热压缩升温值类似。土豆泥的绝热压缩升温值在2.6~4.0℃/(100 MPa),且随压力的增大而增大,这可能是因为它在高压下的压缩率比较大。牛奶(全脂、半脱脂和脱脂)的绝热压缩升温值随压力的增加变化不明显,但随着脂肪含量的增加,其绝热压缩升温值δ呈递增趋势,从小到大依次为脱脂牛奶、半脱脂牛奶、全脂牛奶,这也说明了脂肪含量高的物料更容易被压缩。酸奶的绝热压缩升温特性与牛奶略有不同,其绝热压缩升温值随压力的增大呈现出上升的趋势。原因可能是在超高压处理过程中,在低压阶段,压力对酸奶中的微生物产生杀灭作用,消耗了部分能量,随着压力的增大,酸奶中的微生物减少,杀灭微生物所消耗的能量也相应减少,从而表现出绝热压缩升温值的增大。牛肉和鸡肉的绝热压缩升温值总体在3.0~3.3℃/(100 MPa)变化,与水接近,这是因为其含水率较高。但因为牛肉和鸡肉中还含有丰富的蛋白质,故其绝热压缩升温值高于橙汁。图5为在初始温度25℃下,大豆油和橙汁经200 MPa高压处理过程中温度随压力变化的曲线。从图中可以看出,在压力瞬间释放时,橙汁的温度也瞬间回复到初始温度水平,但是大豆油的降温过程却相对缓慢,需要经过较长时间(60 s左右)才能到达平稳状态,即出现了温度延迟现象。RASANAYAGAM[10]对油脂类食品在超高压下处理时的这种类似的温度延迟现象也进行过报道。尽管热电偶响应需要一定时间,由此会给试验结果带来一定的延迟,但试验采用的K型热电偶响应时间只有几百毫秒,且从其它物料如橙汁的试验结果看出并未有显著的温度延迟现象,所以可以忽略测量时间对该现象的影响,这种现象应该与物料的组成成分有较大关系,需要进一步研究物料组分分子结构对绝热压缩升温的影响。

2.2 初始温度对绝热压缩升温的影响

物料在超高压处理过程中的影响绝热压缩升温的因素中,初始温度是其中重要因素之一。在200 MPa压力条件下,初始温度对物料的绝热压缩升温的影响如图6所示。

从图中可知,大豆油在不同初始温度条件下(15~45℃)的绝热压缩升温值基本不变,菜籽油的

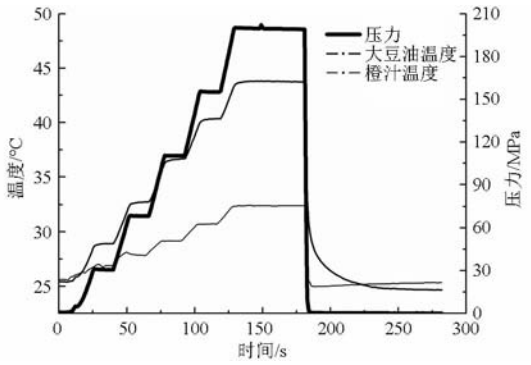

图5 大豆油和橙汁在超高压处理过程中温度-压力曲线(初始温度25℃、压力200 MPa)

Fig. 5 Temperature-pressure profiles of soybean oil and orange juice at initial temperature of 25℃ and set pressure of 200 MPa during high pressure processing

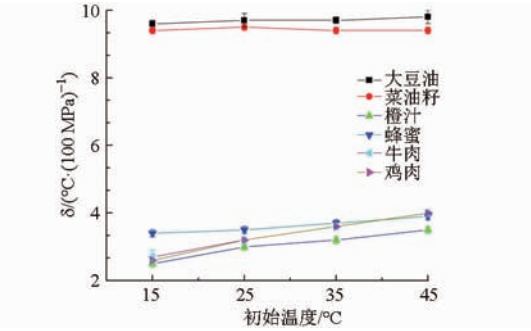

图6 初始温度对物料绝热压缩升温值的影响(压力200 MPa)

Fig. 6 Effect of initial temperature on adiabatic compression heating of food materials at 200 MPa

情况与大豆油类似,说明随着初始温度的升高,脂肪类物料的绝热压缩升温值基本不变。PATAZCA等[10]研究了植物油在不同的初始温度条件下(1~70℃)的绝热压缩升温值变化情况,结果发现初始温度对植物油的压缩升温值影响很小。蜂蜜的绝热压缩升温值随着初始温度的升高而增大,在初始温度为15℃时是3.4℃/(100 MPa),当初始温度增加到45℃时,达到了3.9℃/(100 MPa)。这是由于随着初始温度的升高,物料分子间的距离逐渐变大,在超高压下变得更容易被压缩,压缩分子需要做的功更多,由此转化的内能更多,从而表现出绝热压缩升温值的增大。橙汁的情况与此类似,其主要成分为碳水化合物和水,压缩升温值同样与水接近。牛肉与鸡肉的绝热压缩升温值基本相同,而且都随初始温度的升高而增大,这是因为它们的主要成分都是蛋白质,而蛋白质的绝热压缩升温特性与水相似。随着初始温度的升高,蛋白质分子的空间结构变得不稳定,更容易被压缩,致使其在超高压下具有更高的压缩率,对其分子压缩做功更多,转化的热能也就更多,表现为压缩升温值的增大。

2.3 基于压力和初始温度的物料绝热压缩升温预测模型

试验中采用的绝热套筒可以近似看成一个密闭系统，通过活塞来给系统内的物料加压。由热力学第一定律可得系统的能量平衡方程

$$Q = W + \Delta U \tag{2}$$

式中　Q——系统吸收或释放的热量

W——系统做功

ΔU——系统内能变化量

试验过程近似看成一个绝热过程，系统热能 $Q \approx 0$，系统做功导致系统内能增加，即 $-W = \Delta U$。系统内能变化的外在表现就是物料的温度升高。

一些学者基于热力学第一定律推导出了物料在绝热条件下的可逆温变公式[14]

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T\alpha}{\rho C_p} \tag{3}$$

式中　T——热力学温度，K

α——物料的热膨胀系数，K^{-1}

ρ——密度，kg/m^3

C_p——恒压热容量，J/(kg·K)

对于不同的物料来说，其热膨胀系数、密度和热容量不同。对于一种特定的物料来说，α、ρ 和 C_p 均是压力 p 和温度 T 的函数，其绝热温变实际上是压力 p 和温度 T 的函数，即式(3)可以表示为

$$\frac{\mathrm{d}T}{\mathrm{d}p} = \frac{T\alpha(p,T)}{\rho(p,T)C_p(p,T)} \tag{4}$$

因此，特定物料在超高压下的绝热压缩升温值主要是由处理的压力 p 和温度 T_0 决定的。

在超高压加工过程中，物料最终的处理温度是初始温度与升温值的和，所以为了达到加工所需的温度，就必须掌握物料在不同初始温度和压力条件下的绝热压缩升温值。建立合适的数学模型有助于合理预测物料在不同条件下的绝热压缩升温值。

为了得到物料的绝热压缩升温值关于初始温度和压力的函数关系，测试数据用来拟合经验公式

$$\delta = \sum_{i=0,j=0}^{i+j\leqslant n} a_{ij} p^i T_0^j \tag{5}$$

式中　a_{ij}——物料在特定初始温度和压力下的常数（i、j 分别表示压力 p 的 i 次项和温度 T_0 的 j 次项）

展开到三阶模型

$$\delta = a_{00} + a_{10}p + a_{01}T_0 + a_{11}pT_0 + a_{20}p^2 + a_{02}T_0^2 + a_{30}p^3 + a_{03}T_0^3 + a_{12}pT_0^2 + a_{21}p^2T_0 \tag{6}$$

压力 100 ~ 400 MPa、温度 15 ~ 45℃时，通过上述方程对橙汁、蜂蜜、全脂牛奶、半脱脂牛奶、大豆油、牛肉和乙醇的绝热压缩升温值进行拟合，从而可以求出方程中的参数。由表 3 可知，对这几种物料拟合得到方程的回归系数分别为 0.997、0.987、0.987、0.989、0.974、0.985 和 0.987，回归系数较高说明上述方程能够较好地拟合这些物料在此条件下的绝热压缩升温值。

表 3　通过经验方程得到的回归参数

Tab.3　Regression coefficients for food materials from equation

参数	橙汁	蜂蜜	全脂牛奶	半脱脂牛奶	大豆油	牛肉	乙醇
a_{00}	−1.753	3.334	−1.573	0.070	12.406	1.726	10.209
a_{10}	0.019	0.005	0.007	0.011	−0.008	−0.006	−0.044
a_{01}	0.229	−0.041	0.366	0.140	−0.080	0.124	0.366
a_{11}	-5.30×10^{-4}	1.45×10^{-5}	-1.96×10^{-4}	-1.84×10^{-4}	6.80×10^{-4}	1.74×10^{-4}	9.92×10^{-4}
a_{20}	-3.22×10^{-5}	-2.43×10^{-5}	-1.22×10^{-5}	-2.60×10^{-5}	-6.25×10^{-5}	2.08×10^{-5}	3.10×10^{-5}
a_{02}	−0.004	0.002	−0.010	−0.003	1.25×10^{-4}	−0.003	−0.006
a_{30}	8.33×10^{-9}	2.92×10^{-8}	8.33×10^{-9}	2.50×10^{-8}	9.58×10^{-8}	-1.25×10^{-8}	-4.17×10^{-9}
a_{03}	3.33×10^{-5}	-2.08×10^{-5}	1.08×10^{-4}	3.33×10^{-5}	2.92×10^{-5}	4.58×10^{-5}	4.17×10^{-6}
a_{12}	1.50×10^{-6}	-2.50×10^{-7}	1.00×10^{-6}	5.00×10^{-7}	-1.18×10^{-5}	-2.25×10^{-6}	-1.68×10^{-5}
a_{21}	7.00×10^{-7}	-2.50×10^{-8}	2.00×10^{-7}	2.00×10^{-7}	1.25×10^{-7}	-2.75×10^{-7}	1.75×10^{-7}
回归系数	0.997	0.987	0.987	0.989	0.974	0.985	0.987

3　结论

(1)设计的聚甲醛传压装置在超高压下有着良好的绝热效果，通过加装 K 型热电偶可以实现超高压加工过程中物料的温度和所受压力数据的实时监测。

(2)物料在超高压下的绝热压缩升温值主要受物料组分、处理压力和初始温度的影响。所测样品中，乙醇的绝热压缩升温值最大，脂肪类物料（大豆油、菜籽油、肥肉）次之。蛋白质类（牛肉、鸡肉）、碳水化合物类（橙汁、蜂蜜）以及牛奶（全脂、脱脂、半脱脂）的绝热压缩升温值与水的接近。乙醇、脂肪类物料的绝热压缩升温值受压力影响明显，随着压力的增大而减小。其他物料的绝热压缩升温值对压

力不敏感。脂肪类物料的绝热压缩升温值受初始温度的影响不大,蛋白质类和碳水化合物类的绝热压缩升温值随着初始温度的升高而增大。

(3)建立了食品物料的绝热压缩升温值基于压力和初始温度的数学模型。在实际使用超高压技术加工这些食品物料时,可以预测物料大概的绝热温变过程,更好地利用其压缩升温效应,对于优化超高压加工工艺有指导意义。

参 考 文 献

1 苏光明,朱松明,胡菲菲,等. 超高压对酱曲多酚氧化酶激活和钝化作用动力学研究[J]. 农业机械学报, 2015, 46(10): 257 - 265.
SU Guangming, ZHU Songming, HU Feifei, et al. Kinetics of polyphenoloxidase activation and inactivation in soybean paste koji by high pressure[J]. Transactions of the Chinese Society for Agricultural Machinery, 2015, 46(10): 257 - 265. (in Chinese)

2 易建勇,张燕,廖小军,等. 智能化超高压食品灭菌设备[J]. 农业机械学报, 2011, 42(11): 113 - 117.
YI Jianyong, ZHANG Yan, LIAO Xiaojun, et al. Automatic high hydrostatic pressure equipment for food sterilization[J]. Transactions of the Chinese Society for Agricultural Machinery, 2011, 42(11): 113 - 117. (in Chinese)

3 于勇,潘芳,苏光明,等. 超高压技术在粮食产品加工中的应用[J]. 农业机械学报, 2015, 46(10): 247 - 256.
YU Yong, PAN Fang, SU Guangming, et al. Application of ultra high pressure on crop produces processing[J]. Transactions of the Chinese Society for Agricultural Machinery, 2015, 46(10): 247 - 256. (in Chinese)

4 朱松明,苏光明,王春芳,等. 水产品超高压加工技术研究与应用[J]. 农业机械学报, 2014, 45(1): 168 - 177.
ZHU Songming, SU Guangming, WANG Chunfang, et al. Research and application on high-pressure processing of aquatic products[J]. Transactions of the Chinese Society for Agricultural Machinery, 2014, 45(1): 168 - 177. (in Chinese)

5 ZHU S, NAIM F, MARCOTTE M, et al. High-pressure destruction kinetics of Clostridium sporogenes spores in ground beef at elevated temperatures[J]. International Journal of Food Microbiology, 2008, 126(1 - 2): 86 - 92.

6 SHAO Y, ZHU S, RAMASWAMY H, et al. Compression heating and temperature control for high-pressure destruction of bacterial spores: an experimental method for kinetics evaluation[J]. Food and Bioprocess Technology, 2010, 3(1): 71 - 78.

7 EVELYN, SILVA F V M. High pressure processing of milk: modeling the inactivation of psychrotrophic *Bacillus cereus* spores at 38 ~ 70℃[J]. Journal of Food Engineering, 2015, 165: 141 - 148.

8 AHN J, BALASUBRAMANIAM B V M. Inactivation kinetics and injury recovery of Bacillus amyloliquefaciens spores in low-acid foods during pressure-assisted thermal processing[J]. Food Science and Biotechnology, 2014, 23(6): 1851 - 1857.

9 BALASUBRAMANIAM V M, TING E Y, STEWART C M, et al. Recommended laboratory practices for conducting high-pressure microbial inactivation experiments[J]. Innovative Food Science & Emerging Technologies, 2004, 5(3): 299 - 306.

10 RASANAYAGAM V, BALASUBRAMANIAM V M, TING E, et al. Compression heating of selected fatty food materials during high-pressure processing[J]. Journal of Food Science, 2003, 68(1): 254 - 259.

11 PATAZCA E, KOUTCHMA T, BALASUBRAMANIAM V M. Quasi-adiabatic temperature increase during high pressure processing of selected foods[J]. Journal of Food Engineering, 2007, 80(1): 199 - 205.

12 BUZRUL S, ALPAS H, LARGETEAU A, et al. Compression heating of selected pressure transmitting fluids and liquid foods during high hydrostatic pressure treatment[J]. Journal of Food Engineering, 2008, 85(3): 466 - 472.

13 KNOERZER K, BUCKOW R, VERSTEEG C. Adiabatic compression heating coefficients for high-pressure processing—a study of some insulating polymer materials[J]. Journal of Food Engineering, 2010, 98(1): 110 - 119.

14 KNOERZER K, BUCKOW R, SANGUANSRI P, et al. Adiabatic compression heating coefficients for high-pressure processing of water, propylene-glycol and mixtures - a combined experimental and numerical approach[J]. Journal of Food Engineering, 2010, 96(2): 229 - 238.

15 王标诗,李汴生,曾庆孝,等. 超高静压下食品压致升温规律的研究[J]. 农业工程学报, 2009, 25(2): 246 - 250.
WANG Biaoshi, LI Biansheng, ZENG Qingxiao, et al. Compression heating characteristics of foods during ultra high hydrostatic pressure processing[J]. Transactions of the CSAE, 2009, 25(2): 246 - 250. (in Chinese)

16 王标诗,李汴生,曾庆孝,等. 超高静压下食品压致升温的预测及数学模型建立[J]. 现代食品科技, 2014, 30(8): 175 - 181.
WANG Biaoshi, LI Biansheng, ZENG Qingxiao, et al. Mathematical model for prediction of compression heating of foods processed with ultra-high hydrostatic pressure[J]. Modern Food Science and Technology, 2014, 30(8): 175 - 181. (in Chinese)

17 HARVEY A H, LEMMON E W. NIST standard reference database 10: NIST/ASTM steam Properties (version 3.0)[S]. Applied Chemicals and Division National Institute of Standards and Technology, U.S. Department of Commerce, 2013.

18 周才琼. 食品营养学[M]. 北京: 高等教育出版社, 2011.