



Investigation on Warming Capacity of Zeolite 3A and Water Reaction in Self-heating Cylinder to Warm up Beverages

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ARTICLE INFO	ABSTRACT
Article History: Received 2022/ 03/ 02 Accepted 2022/ 05/ 21 Keywords: Self-heating, Exothermic reaction, Kinetics, Simulation. DOI: 10.22034/FSCT.19.129.13 DOR: 20.1001.1.20088787.1401.19.129.1.8 *Corresponding Author E-Mail: azizit_m@modares.ac.ir	In recent years, changes in lifestyle and the need to provide and access food and beverages more easily and quickly have led to changes in food packaging. One of these changes is the advent of self-heating packaging, which allows the consumer to access hot food and drink in any place using various exothermic reactions, without the use of heating devices. In this study, a cylinder made of 316l stainless steel was used to heat 200 ml tea and low-fat pasteurized milk by using zeolite 3A and water reaction. As a result, the temperature inside the cylinder for the ratio of 9:1, after 95 seconds increased from 30.8 °C to 100.3 °C, and this amount of heat led to an increase in the temperature of tea from 26.8 °C to 29.3 °C in 488 seconds. Also, after 841 seconds, the milk temperature increased from 23.9 °C to 27.3 °C. Then, the heating of the cylinder containing this reaction inside the mentioned beverages was simulated and modeled using COMSOL Multiphysics software. It has been determined that the experimental data and simulated models were almost fitted.

1- Introduction

Consumer demand and market trends are constantly evolving in the direction of convenience foods, which require easier maintenance and should have new features [1]. Self-heating containers and cans made of aluminum and steel are heated using an exothermic reaction and have been commercially available for decades for tea, coffee and ready-to-eat foods, which are mainly popular in Japan [2]. The major limitation of this heating system is that the major part of the package space is engrossed by the heating device [3].

Zeolite is a natural or synthetic hydrated aluminosilicate with an open three-dimensional crystal structure in which water molecules are held in lattice cavities. Water can be removed by heating, and then zeolite can absorb other molecules in the right amount [4]. When zeolite is dehydrated, it stores energy as a chemical bond, and when hydrated, the same stored energy is released. Therefore, zeolite acts as a thermal energy storage system. Zeolite 3A is environmentally friendly as well as user-friendly. Zeolite can also be reused. It can be dehydrated after use and therefore can be reactivated to be reusable. This can make the self-heating food can reusable and reduce its effective cost compared to a disposable self-heating food can. Zeolite even immediately releases heat energy, which reduces the time required to heat food. It is noteworthy that zeolite is completely recyclable [5].

In 2015, Bohra et al. [5] conducted a study on the equilibrium reaction between zeolite and water and combined certain amounts of reactants. They concluded that the combination

of 28.34 g of the dried zeolite 3A sample at 500 °C with 16 ml of water could cause increase the temperature by 69 degrees.

The main problem with self-heating cans is that they are disposable and also limited to a specific type of beverage inside the package and the volume of the container. Therefore, the aim of this study was to make a reusable cylinder made of stainless steel in which reactive materials including zeolite and water were poured into it and thus the exothermic reaction took place inside the cylinder. The cylinder was then inserted into the beverage and heated it. This cylinder has advantages more than self-heating packaging; including portability, the ability to use it in different containers and most importantly its repeated usage for more than one time.

2- Materials and methods

2-1-Materials

In this study, industrial zeolite 3A in the form of pellets was prepared. As it is illustrated in figure 1, first of all, a cylinder made of stainless steel 316l with the dimensions listed in Table 1 was made.



Fig 1 Cylinder made of stainless steel 316l

Table 1 Cylinder dimensions

Full dimensions of the cylinder with lid (mm)	Total height	84
	Internal diameter	30
	External diameter	39
	Thickness	4.5
Dimensions of the cylinder without lid (mm)	Internal height	73
	External height	76
Lid dimensions (mm)	Internal height	11.8
	External height	17.5
	Internal diameter	38
	External diameter	45
	Thickness	3.5

2-2- Methods

In this reaction, by adapting to the findings of Bohra et al. in 2015 [5], a certain amount of zeolite 3A was placed in the laboratory furnace (S.R 81 model made by Pars Azma Iran Company) at 500 °C for 45 minutes to get dry and activate. Then, in order to reach the ambient temperature, without absorbing moisture, the sample was placed inside a desiccator.

After cooling, according to Table 2, certain

amounts of zeolite were weighed in a beaker, by a laboratory scale (with a sensitivity of 0.01 made by Electronic Balance Iran) and then mixed with distilled water in certain proportions to obtain the final temperature value with the digital thermometer (TP101 model made in China). After adding distilled water, the beaker lid was closed with aluminum foil to reduce heat exchange with the environment.

Table 2 Ratio and amount of zeolite and water

Ratio	Amount of zeolite (g)	Amount of water (ml)
0.5 to 1	1.5	3
1 to 1	3	3
2 to 1	6	3
3 to 1	9	3
4 to 1	12	3
5 to 1	15	3
6 to 1	18	3
7 to 1	21	3
8 to 1	24	3
9 to 1	27	3

2-3-Investigating the heating of reactions inside the beverage

To investigate the heating of the reaction, 27 g of dried zeolite was weighed inside the cylinder and 3 ml of distilled water was added to it. The mixture was then stirred for 5 to 10 seconds and the cylinder lid was immediately closed. Then the cylinder was placed in a disposable 330 ml paper glass containing 200 ml of tea and 200 ml of low-fat pasteurized milk at room temperature. Then, by using the obtained data, a graph of temperature changes over time (kinetics) was drawn in Microsoft Excel 2019 software [6].

2-4- Performing simulation and modeling of heat transfer

At this stage, according to studies by Ho et al. in 2010 [7], the heat transfer from reactants to the cylinder and food samples was simulated and modeled with COMSOL Multiphysics 5.5 software [8].

For modeling in the software, the whole system after placing the cylinder inside the beverage, consisted of the following 3 parts:

-Inside the cylinder, which was the site of the exothermic chemical reaction.

-Cylinder body.

- Beverage.

In general, the theory of heat transfer in fluids and solids, follows Fourier's law:

$$(1) Q = \rho C_p \frac{\partial T}{\partial t} + \nabla \cdot q$$

$$(2) q = -k \nabla T$$

Where; ρ is density in kg/m³, C_p is heat capacity at constant pressure in J/(kg K), T is the temperature in Kelvin, t is time in seconds, q is heat flux in W/m², Q is the amount of heat produced in terms of W/m³ and k is the thermal conductivity in W/(m K).

Inside the cylinder (c), the reactants were mixed together and the chemical reaction took place:

$$(3) Q = \rho_c C_{p,c} \frac{\partial T_c}{\partial t} + \nabla \cdot q_c$$

In this Equation, the amount of heat generated (Q) is equal to the amount of heat generated by the reaction (Q_0):

$$(4) Q = Q_0$$

$$(5) Q_0 = -r \cdot H$$

Where r is the reaction rate in mol/(m³ s) and H is the enthalpy of reaction in J/mol.

After generating heat due to a chemical reaction, the heat was transferred to the cylinder body (s) (no heat was generated in the cylinder body):

$$(6) \rho_s C_{p,s} \frac{\partial T_s}{\partial t} = -(\nabla \cdot q_s)$$

In the cylinder body, heat transfer was done in the form of conduction. The general equation for this type of heat transfer is Equation (2), but this Equation was defined as a surface with a thickness:

$$(7) Q' = -kA \frac{\partial T}{\partial x}$$

In this Equation, Q' is the amount of heat transferred in terms of W, A is the area in terms of m^2 and x is wall thickness in terms of m.

Since most of the heat transfer from inside the cylinder to the beverage was done by the cylinder body, Fourier's law is written as follows:

$$(8) Q'_{cyl} = \frac{T_1 - T_2}{R_{cyl}}$$

$$(9) R_{cyl} = \frac{\ln(r_2/r_1)}{2\pi kL}$$

In these Equations, Q'_{cyl} is the amount of heat transferred in the cylinder body in terms of W, T_1 is the temperature inside the cylinder in terms of Kelvin, T_2 is the temperature outside the cylinder in terms of Kelvin, R_{cyl} is the conduction resistance of the cylinder, r_1 is the inner radius of the cylinder in terms of m, r_2 is the outer radius of the cylinder in terms of m and L is the length of the cylinder in terms of m.

The heat generated was then transferred to the beverage (f) (no heat was generated in the

beverage):

$$(10) \rho_f C_{p,f} \frac{\partial T_f}{\partial t} = -(\nabla \cdot q_f)$$

Because the heat transfer inside the beverage was in the form of convection, the heat flux relation (q) was written as follows:

$$(11) -n \cdot q = h(T_{ext} - T)$$

In this Equation, n is unit normal vector on the boundary wall, h is heat transfer coefficient in $W/(m^2 K)$, T is the temperature in the boundary wall (cylinder body) in Kelvin and T_{ext} is fluid temperature away from the boundary wall in Kelvin.

It should be noted that the simulation was performed in optimal and closed conditions and also heat loss was eliminated. Therefore, all disposable glass walls with bottom and top were closed and considered as thermal insulation:

$$(12) -n \cdot q = 0$$

All of these Equations were based on information obtained from the COMSOL Multiphysics software and the COMSOL Multiphysics 5.4 software manual entitled Heat Transfer Module, published in 2018, Ho et al. studies in 2010, and Bahrami studies in 2009 [7-10].

3- Results and discussion

3-1- Performing the chemical reaction

The results of combining different ratios of zeolite 3A and water can be seen in Table 3.

Table 3 Investigation of the composition of different ratios of zeolite and water

Ratio	Amount of zeolite (g)	Amount of water (ml)	Initial temperature (°C)	Final temperature (°C)	Temperature changes (°C)
0.5 to 1	1.5	3	27.6	41.7	14.1
1 to 1	3	3	26.1	36.9	10.8
2 to 1	6	3	26.5	59.3	32.8
3 to 1	9	3	27.9	72.1	44.2
4 to 1	12	3	28.1	73.0	44.9
5 to 1	15	3	27.9	75.1	47.2
6 to 1	18	3	31.8	99.4	67.6
7 to 1	21	3	31.5	99.8	68.3
8 to 1	24	3	29.3	104.5	75.2
9 to 1	27	3	29.3	104.3	75

As can be deduced from Table 3, the higher the zeolite content, the higher the temperature rise. These results were similar to the findings of Bohra et al. in 2015 [5], with the difference that in this project, less water was used. Therefore, the graph of kinetic of temperature changes (figure 2) was drawn for the last 4 ratios of zeolite and water in 45 minutes.

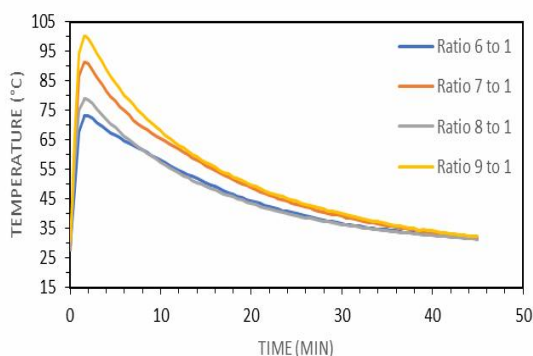


Fig 2 Kinetic of temperature changes in the reaction of zeolite and water

As shown in figure 2, the ratio of 6 to 1 in 105 seconds (1 minute and 45 seconds), which was more time than other samples, reached a maximum temperature of 73.4 °C from the initial temperature of 29.5 °C.

After that, the ratio of 7 to 1 reached the maximum temperature of 91.4 °C from the initial temperature of 28 °C in less time than the previous sample (96 seconds = 1 minute and 36 seconds).

At the ratio of 8 to 1, contrary to expectations, the sample reached a maximum temperature of 79 °C from the initial temperature of 28.5 °C in 99 seconds (1 minute and 39 seconds), which was more time than the previous sample and lower maximum temperature was obtained.

Lastly, the best result was obtained in the ratio of 9 to 1, during which the sample reached a maximum temperature of 100.3 °C from the initial temperature of 30.8 °C in 95 seconds (1 minute and 35 seconds), which less time and maximum temperature were observed compared to the previous samples.

According to figure 2, the higher the ratio of zeolite 3A used to water, the less time was required to reach the maximum temperature and also the higher the maximum temperature was

obtained. However, due to the fact that the zeolite used in this study was of industrial type, despite repeated use and drying at the same temperature (500 °C), the results of repeating the combination of different ratios of zeolite and water, even if the sample was not used and re-dried, was not the same and as it is clear in the ratio of 8 to 1, the results were contrary to expectations and the temperature difference was observed.

Therefore, due to the limited volume of the cylinder, the maximum usable amount of zeolite was 27 g and thus a ratio of 9 to 1 was used to perform the next steps of the research.

3-2- Investigating the heat generation of the reaction within the beverage

Kinetic of temperature changes in food samples (tea and milk) in case of zeolite and water reaction in the cylinder is illustrated in figure 3.

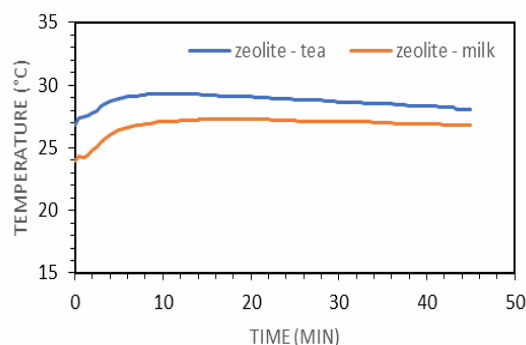


Fig 3 Kinetic of temperature changes of tea and milk in the zeolite reaction

As shown in figure 3, after placing the cylinder in the glass containing tea, the temperature of the beverage increased from 26.8 °C to 29.3 °C in 488 seconds (8 minutes and 8 seconds).

According to this figure, the milk temperature increased from 23.9 °C to 27.3 °C in 841 seconds (14 minutes and 1 second) which was a longer time than tea. Thus, temperature increase in tea and milk were 2.5 °C and 3.4 °C respectively.

Adsorbents, especially zeolites, can reach more than 100 °C in the adsorption process. On the other hand, since zeolites are legally food additives, the use of zeolites and water as reactants greatly reduces the risk of food contact [11].

Despite the temperature above 100 °C inside the

cylinder (figure 2), the beverage temperature did not increase significantly, probably due to the high rate of maximum temperature in the zeolite-water reaction, followed by a drop in temperature. Also, the temperature rose at a point and the temperature was not transferred to other parts.

In particular, if water is not distributed immediately, it first reacts only with particles adjacent to the zeolite granule, thus the mixture creates a barrier, which prevents further water distribution. Thus, heat production in turn decreases [12].

Another problem is the lack of heat transfer to the product for heating. As a rule, leakage of liquid reagent from its container and entry into the granular reactor is accompanied by volume change. Reagents take up less space, resulting in reduced points of contact with the container walls and also heating of the product. On the other hand, in natural types of zeolites, less water is absorbed, which is equivalent to the absorption of only 7 to 11 grams per 100 grams of natural zeolite. This decrease in water absorption is on the one hand due to their specific crystal structures and on the other hand due to inactive impurities of the natural product. However, natural items clearly have an advantage because their prices are significantly lower [11].

As shown in figure 3, the temperature of tea increased in a shorter period of time than milk. This was in contrast to the results of the Mahnoor Asghar's study in 2021 [13], which reported that milk has a higher boiling point than water, but when it comes to boiling, milk boils faster than water. This is due to the lower specific heat capacity of milk.

Milk, on the other hand, is made up of a lot of water, but is essentially an emulsion that contains other molecules such as fat and protein. Because milk contains many non-volatile compounds, such as salts, fatty acids, sugars, proteins, etc., these molecules increase the boiling point of milk and therefore milk has a higher boiling point than water [13].

3-3- Heat transfer simulation and modeling

In order to simulate the heat transfer in the mentioned reaction, first, a shape of a glass containing a drink with a cylinder inside was

drawn, according to the dimensions mentioned before. In figure 4, the virtual image of the dimensions of the cylinder in a glass (containing 200 ml of drink) is illustrated.

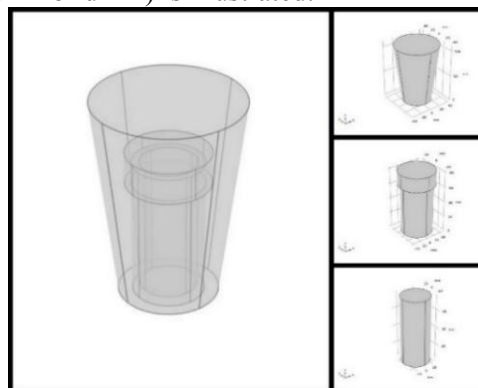


Fig 4 Virtual image of the glass and the cylinder before starting the process

Reaction rates and enthalpies of zeolite 3A and water reaction were required to simulate the heat transfer.

In 2015, Gabruš et al. reported the heat output of the reaction of zeolite 3A and water as 45.95 kJ/mol [14]. In 2016, Gaulke et al. achieved the reaction rate as $6.6 \times 10^3 \text{ m}^3/\text{mol s}$ [15].

In order to obtain the temperature inside the cylinder (reaction temperature), a point with coordinates (0,0,5) inside the cylinder was selected and the temperature was measured at that point during the simulation. This point was almost identical to the location of the thermometer during laboratory tests (near the bottom of the cylinder).

Since in this simulation the heat transfer was done in a closed environment without heat exchange with the surrounding environment, the time to reach the maximum temperature was faster than the results obtained in the laboratory. As can be seen in figure 5, during the simulation of the heat transfer due to this reaction in the tea container, after 7.68×10^{-4} seconds, the temperature inside the cylinder has increased from 25 °C to a maximum temperature of 99.66 °C. The temperature of the beverage also has reached from 25 °C to the maximum temperature of 42.21 °C in 9.61 seconds.

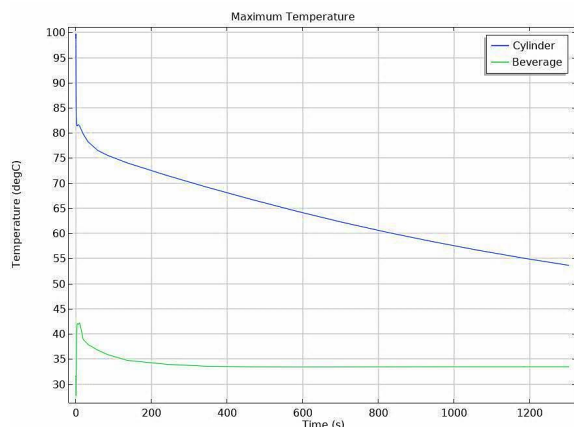


Fig 5 Simulated kinetic of temperature changes in cylinder and tea in 1200 seconds

By comparing the figures 2 and 3 with figure 5, it can be seen that the reaction behavior in both graphs was almost similar to each other and their difference was in the rate of reaching to maximum temperature and final temperature. The temperature of the beverage in the simulation increased rapidly and after some decrease, it was fixed, but the temperature of the beverage in the laboratory increased at a much slower rate and therefore differed from the simulation diagram. The difference between the experimental data and the proposed model might be due to the failure to calculate the heat loss.

By observing figure 6, the heat distribution in different parts of the cylinder and tea in 7.68×10^{-4} seconds (time-related to the maximum temperature inside the cylinder) is illustrated. As it can be seen, the maximum temperature was in the lower parts and slightly in the upper part of the cylinder. The temperature concentration at the bottom was probably due to the accumulation of reactants at the bottom of the cylinder.

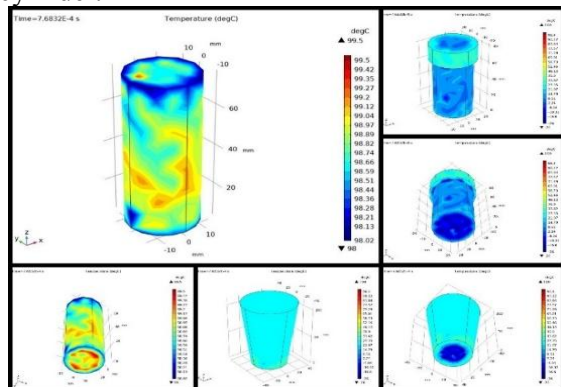


Fig 6 Heat distribution at the maximum temperature inside the cylinder (tea)

Figure 7 also shows the heat distribution in different parts of tea and the cylinder in 9.61 seconds (time-related to the maximum temperature of the beverage).

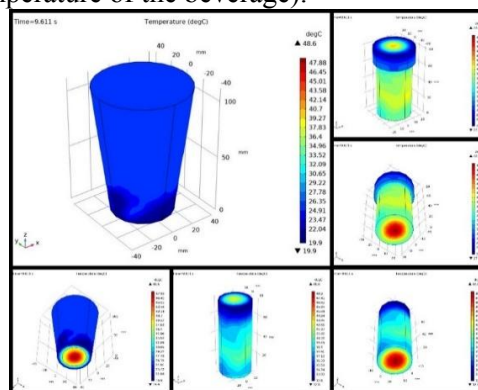


Fig 7 Heat distribution at the maximum temperature of the beverage (tea)

Kinetic of temperature changes in milk container which was simulated by software, is illustrated in figure 8. The temperature inside the cylinder has reached from 25 °C to the maximum temperature of 99.68 °C in 7.68×10^{-4} seconds. The temperature of the beverage also increased from 25 °C to 42.44 °C in 9.61 seconds.

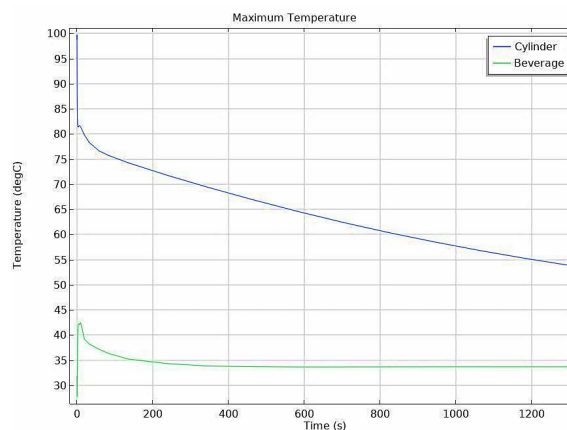


Fig 8 Simulated kinetic of temperature changes in cylinder and milk in 1200 seconds

By comparing figures 2 and 3 with figure 8, the reaction in both graphs showed the same behavior and according to the reasons mentioned, there was a difference in the graphs related to the beverage.

In figures 9 and 10, the heat distribution is illustrated in 7.68×10^{-4} seconds (time-related to the maximum temperature inside the cylinder) and 9.61 seconds (time-related to the maximum temperature of the beverage), in the different

parts of the cylinder and milk. In these figures, as before, the temperature concentration was observed in the lower parts of the cylinder and the beverage and slightly in the upper part of the cylinder.

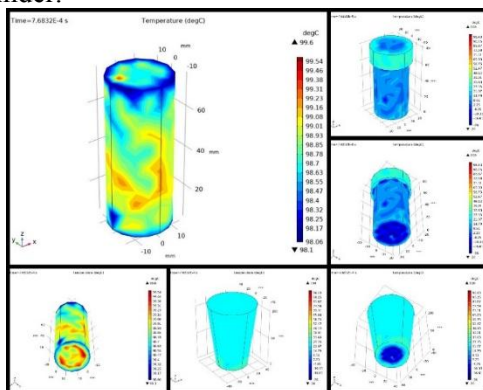


Fig 9 Heat distribution at the maximum temperature inside the cylinder (milk)

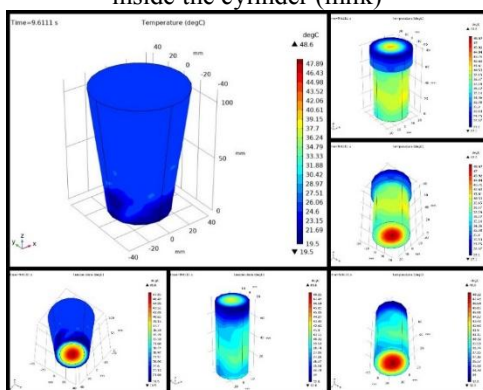


Fig 10 Heat distribution at the maximum temperature of the beverage (milk)

4- Conclusions

Today, life is moving faster than in the past, so the self-heating packages have made it possible to provide access to hot and ready-to-eat foods and beverages at any place and any time without the use of heating devices. In this study, by using a stainless steel cylinder with 27 g of zeolite 3A and 3 ml of distilled water, the temperature inside the cylinder increased from 30.8 °C to 100.3 °C in 95 seconds (1 minute and 35 seconds). This amount of heat led to an increase in tea temperature from 26.8 °C to 29.3 °C in 488 seconds (8 minutes and 8 seconds). Also, after 841 seconds (14 minutes and 1 second), the milk temperature increased from 23.9 °C to 27.3 °C.

Therefore, despite the temperature above 100 °C inside the cylinder, the beverage temperature did

not increase significantly. It has been determined that the experimental data and simulated models were almost fitted.

According to the obtained results and also the innovation in using this device to heat the beverage, more research is needed to increase the final temperature of the drink.

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بررسی ظرفیت گرمایشی واکنش ژئولیت ۳A و آب در سیلندر خود گرم شونده جهت گرم کردن نوشیدنی‌ها

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چکیده

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خود گرم شونده،

واکنش گرمازا،

سینتیک،

شبیه سازی.

در سال‌های اخیر، تغییر در سبک زندگی و نیاز به تهیه و دسترسی راحت‌تر و سریع‌تر به مواد غذایی و نوشیدنی‌ها منجر به تغییراتی در بسته‌بندی مواد غذایی شده است. یکی از این تغییرات، ظهور بسته‌بندی‌های خود گرم شونده است که به مصرف‌کننده اجازه می‌دهد بدون استفاده از دستگاه‌های گرمایشی، به غذا و نوشیدنی گرم در هر مکانی دسترسی پیدا کند. در این مطالعه، از سیلندر ساخته شده از فولاد ضد زنگ ۳۱۶L برای گرم کردن ۲۰۰ میلی‌لیتر چای و شیر پاستوریزه کم‌چرب با استفاده از واکنش ژئولیت ۳A و آب استفاده شد. در نتیجه، دمای داخل سیلندر برای نسبت ۱:۹، پس از ۹۵ ثانیه از ۳۰/۸ درجه سانتی‌گراد به ۱۰۰/۳ درجه سانتی‌گراد افزایش یافت و این مقدار گرما منجر به افزایش دمای چای از ۲۶/۸ درجه سانتی‌گراد به ۲۹/۳ درجه سانتی‌گراد در مدت زمان ۴۸۸ ثانیه گردید. همچنین، پس از گذشت ۸۴۱ ثانیه، دمای شیر از ۲۳/۹ درجه سانتی‌گراد به ۲۷/۳ درجه سانتی‌گراد افزایش یافت. سپس نحوه گرمایش سیلندر حاوی این واکنش در نوشیدنی‌های ذکر شده با استفاده از نرم افزار COMSOL Multiphysics شبیه‌سازی و مدل‌سازی شد و مشخص گردید که داده‌های تجربی و مدل‌های شبیه‌سازی شده تقریباً مشابه بودند.

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