Journal of
Engineering and
Applied Sciences

MEDWELL PUBLICATIONS SINCE 2000

Evaluation of Gallic Acid Retention in Onion Slices Drying under Different Temperature

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Key words: Air drying, degradation kinetics, gallic acid, onion drying, energy consumption

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Page No.: 2498-2504
Volume: 15, Issue 12, 2020
ISSN: 1816-949x
Journal of Engineering and Applied Sciences

Abstract: Onion is one of the most common seasoning ingredients that are useful for antioxidants. Drying is one of methods to prolong the storage life as well as preserve the ingredients. This research evaluated the effect of air temperatures on drying rate and onion quality. The onion was peeled and sliced into 1 mm thickness. It was then dried for 120 min under various temperatures ranging 40-70°C. As the response, the moisture and gallic acid content was observed at every 30 min. The data were used for calculating the kinetic parameters of drying rate and gallic acid degradation. Results showed that the drying rate of sliced onion can be well expressed using two term model. The model is very beneficial to predict effective drying time as well as energy consumption. Moreover, the gallic acid degradation can be classified as third order reaction that is meaningful to estimate the ingredients quality retention.

INTRODUCTION

Onion is one of the most common seasoning ingredients in several countries. Besides for culinary seasoning preparation, onion contains various beneficial chemical compounds such as fibers, vitamins, organic acids and antioxidants[1]. Gallic acid known as 3-5-trihydroxybenzoic acid is a phenolic compound contained in onion[2]. The compound is useful for human body as anti-allergies, antioxidants, anti-inflammation, anti-hyperglycaemic, anti-lipid peroxidative and anti-microbial[3, 4]. Gallic acid is sensitively influenced with the change of temperature. Thus, the proper post-harvest treatments and storage of onion are required to retain the compound.

One of the post-harvest treatments for onion is the drying, a process to evaporate water from the onion by introduction of heat[5, 6]. Previous study showed that the harvested onion contains moisture ranging 86-90%[7, 8]. With the higher moisture content, the onion is easily germinated. With the drying, the moisture in onion can be kept 10% or below in which prolong the storage life. However, the excessive thermal process can affect the stability of gallic acid and the others phenolic compounds[9]. So, the benefit as an antioxidant degrades.

Several studies showed that high temperature drying reduces vitamin C, phenolic contents, color and the other ingredients[10]. In addition, higher drying temperature needs the high thermal energy requirement[11]. However, low temperature drying results long drying time and some products cannot be fully dried due to the sorption isotherm characteristic. Hence, the scientific question is how to retain the active substance such as gallic acid with effective drying time and energy used.

One of the alternative to improve quality of onion is using air dehumidification dryer[12, 13]. Using air dehumidification, the driving force for drying can be enhanced[14]. So, the quality and nutrition in food product can be maintained as well as the faster drying time. This drying system showed a good result for onion[7, 8] as well as several agriculture products such as wheat[15], roselle[16], paddy[17]. However, the comprehensive observation involving drying time and ingredients retention such as gallic acid on different temperature has not been studied. This aspect is very meaningful for considering the proper temperature for onion drying and the other process treatment.

MATERIALS AND METHODS

Fresh onions namely Bima variety (*Allium cepa*) with moisture content 83-85% (wet basis) were obtained from local market in Semarang, Central Java, Indonesia. Gallic acid standard (purity 99.0% pa, Merck, Germany), Follin-Cioucalteureagen, $Na_2CO_3$2M and ethanol 96% were obtained from Merck, Germany and used for gallic acid content analysis in onion. The analysis was performed by Shimidzu Spectrophotometer UV-Vis (UV1800; Shimadzu Corporation, Kyoto, Japan).

The schematic research method was illustrated in Fig. 1 briefly, the methods consist of three main steps involving onion drying under different temperatures (40, 50, 60 and 70°C), observation (moisture and gallic acid content) and kinetic model development. The model was validated with experimental data and used to select the drying condition.

Onion drying: The fresh onion were peeled and sliced into approximately one mm using home scale slicer (Speedy mando, Tupperware, Indonesia). The sliced onion was then put at tray dryer with air dehumidified by zeolite. The schematic of tray dryer can be shown in Fig. 2 ambient air (temperature 30°C, relative humidity 75-80%) was passed dehumidification column contain with Zeolite 3A (provided by Zeochem) to reduce the humidity up to 10% (measured by KW0600561, Krisbow®, Indonesia presented as T-RH). The dry air was heated up to certain temperatures (supposed 40°C). The air was used for drying the sliced onion for 120 min. The linear velocity of air in pipe (ID 0.085 m) around 7 m sec^{-1} was measured by anemometer KW0600562, Krisbow®, Indonesia). This velocity resulted 0.54 m sec^{-1} drying chamber (Cross sectional area 0.15 m^2). As a response, the gallic acid concentration was observed every 30 min. The steps were repeated for air temperature 50, 60 and 70°C.

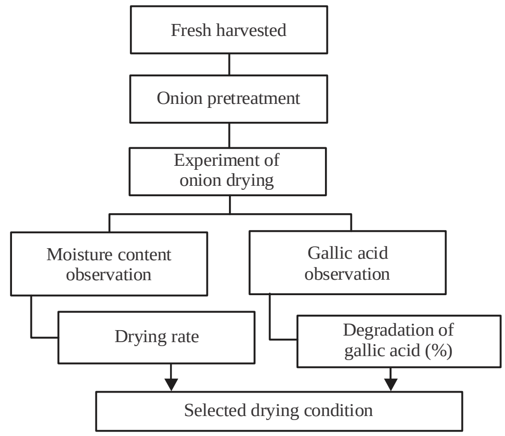

Fig. 1: The schematic diagram of research

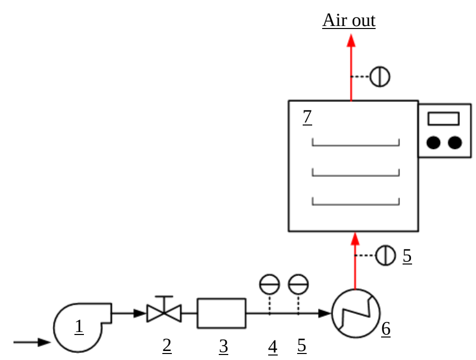

Fig. 2: The schematic of laboratory tray dryer system with air dehumidification: (1) Blower, (2) Valve, (3) Zeolite compartment, (4) Anemometer, (5) Temperature and Relative Humidity sensor (T-RH), (6) Heater, (7) Tray column dryer and (8) Thermo regulator

Determination of gallic acid content by Folin-Ciocalteu Colorimetric method: The gallic acid content was determined according to Folin-Ciocalteu Colorimetric method[18]. The 5 g dried onion was mixed by 100 mL extraction solvent (96% ethanol). This mixture was extracted with ultrasonic for 30 min and incubated in dark room for 30 min. The supernatants were used for gallic acid analysis.

The extract (0.1 mL) was mixed with 0.5 mL of 50% Folin-Ciocalteu reagent and 7.9 mL distilled water. The mixture was incubated at ambient/room temperature for 10 min. Then 1.5 mL of sodium carbonate solution (20%) was added and incubated at ambient temperature for 60 min. The absorbance of the solution was measured by a spectrophotometer (UV1800; Shimadzu Corporation, Kyoto, Japan) at 250 nm. The absorbance value of the sample was converted to mg gallic acid per 100 g of dry basis onion by interpolation with the absorbance values of gallic acid standard series in various concentration (50, 100, 200, 300, 400, 500, 600, 700 ppm).

Kinetic model of gallic acid degradation: The kinetic of gallic acid degradation was described by Eq. 1 as follow:

$$-\frac{dC}{dt} = kC^n \quad (1)$$

Where:
C = The concentration of gallic acid (mg GAE/100 g DW onion)
t = The drying time (min)
k = The constants of gallic acid degradation
n = The order reaction

The kinetic model order 0th, 1st, 2nd, 3rd and 4th were used to describe the kinetic of gallic acid degradation (Eq. 3-7). After integration, Eq. 1 changes based on the order as follow: nth order reaction:

$$C_t = [C_0^{(1-n)}-kt(1-n)]^{\frac{1}{(1-n)}} \quad (2)$$

Equation 2 can be written as follows: 0th order reaction:

$$C_t = C_0-kt \quad (3)$$

1st order reaction:

$$nCt = InC_0-kt \quad (4)$$

2nd order reaction:

$$\frac{1}{C_t} = \frac{1}{C_0}+kt \quad (5)$$

3rd order reaction:

$$\frac{1}{C_t^2} = \frac{1}{C_0^2}+2kt \quad (6)$$

4th order reaction:

$$\frac{1}{C_t^3} = \frac{1}{C_0^3}+3kt \quad (7)$$

The model was fitted to the experimental data using Sum of Square Error (SSE) for validity evaluation. The kinetic parameter, constants of gallic acid degradation can be correlated with drying temperatures using Arrhenius equation (Eq. 8):

$$\ln k = -\frac{Ea}{R}\frac{1}{T}+\ln k_0 \quad (8)$$

Where:
R = The universal gas constant (8.314 Joule/mol/K)
Ea = The activation energy (J mol^{-1})
k_0 = Frequency factor or Arrhenius constant
T = The absolute temperature (K)

The value of Arhhenius parameter, Ea and k_0 were used to predict the value of constants of gallic acid degradation in higher and lower drying temperatures.

FTIR analysis: FTIR analysis was used to observe the different of chemical composition in fresh onion and dried product. The analysis was conducted using Spectrometer (Frontier FT-IR 96681 from Perkin Elmer, America). All FTIR spectra were recorded from 4000-400 cm at a resolution of 4 cm^{-1}. The sample analysis was repeated three times.

Kinetic model of onion drying: The kinetic of onion drying (kd) was estimated using thin layer model namely two term (Eq. 9):

$$MR = a \exp(-k_{d1}t)+b \exp(-k_{d2}t) \quad (9)$$

The moisture ratio was calculated using Eq. 10:

$$MR = \frac{(M-M_e)}{(M_0-M_e)} \quad (10)$$

Where:
M = The moisture content at t, min
M_0 = The initial moisture content at 0, min
M_e = The equilibrium moisture content

The equilibrium moisture content was calculated using modified Henderson model[19], Eq. 11:

$$H_R = \exp(-3.6\times10^{-5}(T_c+10.87)M_e^{2.48} \quad (11)$$

Where:
HR = The relative humidity
T_c = The drying temperatures (°C)

The predicted drying time, from initial moisture content (84%, wet basis or 5.12, dry basis) to final moisture content (5%, wet basis or 0.52 dry basis) was calculated using Eq. 9. The value of kd was validated by moisture ratio reduction versus time from experiment.

RESULTS AND DISCUSSION

Effect of the drying temperature on gallic acid content: The phenolic compounds including the gallic acid can degrade with the change of condition such as light, pH, oxygen, temperature and time[9]. In this study, the stability of gallic acid in onion was observed during the drying process at different temperatures. The effect of drying temperature in gallic acid content was depicted in Fig. 3.

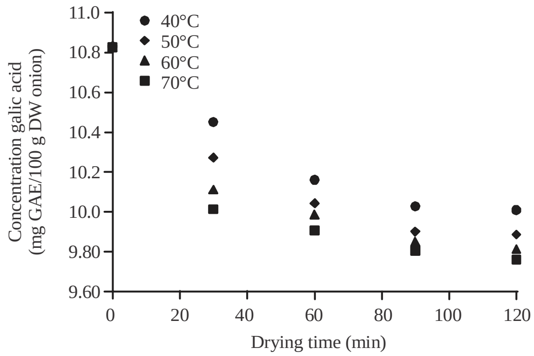

Fig. 3: Degradation of gallic acid (mg GAE/100 g DW onion) during heating at 40, 50, 60 and 70°C

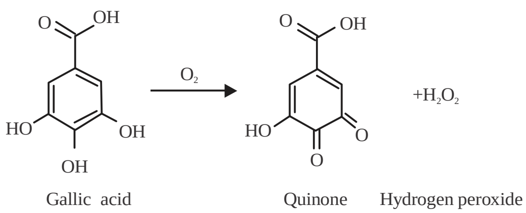

Fig. 4: Reaction of gallic acid thermal degradation[20]

Using the ANOVA test, the reduction of gallic acid content during the drying was significant ($p<0.05$). Heat treatment causes irreversible reaction of phenolic compound as illustrated in Fig. 4[9]. For example, the fresh onion contains gallic acid around 10.8 mg DW^{-1} gallic acid. After 120 min of drying, at air temperature 70°C the gallic acid content decreased about 10%, until 9.8 mg DW^{-1} gallic acid. While at 50°C and 60°C, the gallic acid content decreased was only 9%. The lowest degradation occurred at 40°C, amount 7%.

The thermal degradation of gallic acid in onion was lower than in the standard gallic acid. With direct heating, the gallic acid standard, degrades up to 15% at temperature 60°C for 220 min[21]. While in this research, the degradation of onion at drying temperature 60°C was only 9%. Perhaps, the pH or the presence of the other components such as water in onion can inhibits the degradation. Moreover, the onion layer can protect from the direct contact with heat.

The decrease in the phenolic compounds during drying could be attributed to the binding of polyphenol with other compounds (protein) or to alteration in the chemical structure of polyphenol which cannot be extracted or determine by available method[13]. On the other hand, polyphenol can be oxidized by with oxygen from air forming Quinone and Hydrogen Peroxide[22]. This reaction was represented in Fig. 4[20].

There were some absorbance changes based on FTIR analysis (Fig. 5). After drying process the absorbance of

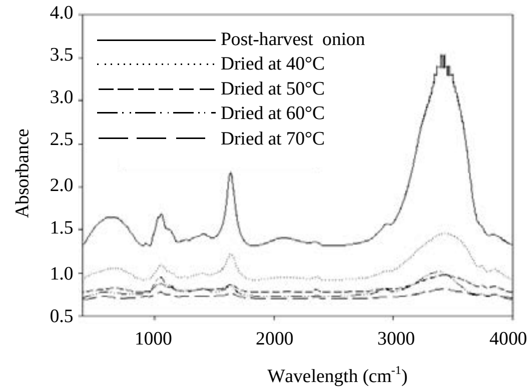

Fig. 5: FTIR spectra of fresh and dried onion at frequency of 400-4000 cm^{-1}

OH peak (wavelength 3400 cm^{-1}) in fresh onion was decreased. The absorbance is directly proportional to the concentration[18]. The gallic acid content can be indicated by lower of OH peak. It will be concluded that the gallic acid are converted into Quinone as represented (Fig. 4). The degradation increases with the increase of temperature.

Kinetics of gallic acid degradation at different temperature: Degradation of gallic acid used 0-4th order kinetics models. The models were fitted to experiment data. The parameters validity were evaluated by Sum of Square Error (SSE). The value of k, constant of gallic acid degradation and the SSE values were listed in Table 1. The minimum SSE value was showed in the third-order kinetic model. This was new finding since the usual kinetic model for gallic acid degradation is the kinetic first model such as in pure gallic acid[23] and yacon[24]. The different raw materials of gallic acid resulted the different kinetic model of gallic acid degradation.

Degradation parameters such as half-life and activation energy were shown in Table 2 for third order reaction. The half life for 3rd order reaction can be calculated as follow:

$$h = \frac{3}{2kC_0^n} \quad (12)$$

As the drying temperature increased, the value of constant of gallic acid degradation also increased from 7.32×10^{-6}-1.03×10^{-5}. The result indicated that the higher drying temperature, the degradation of gallic acid in onion is faster. The kinetic data were then used for estimating Arrhenius parameters such as Activation Energy (E_a) (as expressed in Eq. 9). The activation energy for the gallic acid degradation in onion was 10.052 kJ mol^{-1}. While in Activation Energy (E_a) for the gallic acid degradation in yacon was lower, 8.68 kJ mol^{-1}[24].

Table 1: The value of k and SSE for kinetic model

	40°C		50°C		60°C		70°C	
Reaction order	k	SSE	k	SSE	k	SSE	k	SSE
0	8.4×10^{-3}	0.08	9.78×10^{-3}	0.17	1.05×10^{-2}	0.25	1.08×10^{-2}	0.35
1	7.81×10^{-4}	0.07	9.24×10^{-4}	0.15	1×10^{-3}	0.23	1.05×10^{-3}	0.33
2	7.73×10^{-5}	0.07	9.11×10^{-5}	0.14	9.89×10^{-5}	0.22	1.02×10^{-4}	0.30
3	7.32×10^{-6}	0.06	8.85×10^{-6}	0.12	9.73×10^{-6}	0.20	1.03×10^{-5}	0.28
4	8.13×10^{-7}	0.08	9.4×10^{-7}	0.13	9.53×10^{-7}	0.19	1.01×10^{-6}	0.28

Table 2: Degradation kinetic parameters of gallic acid degradation at 40, 50, 60 and 70°C

T (°C)	h	Ea (kJ mo^{-}l^{1})	$k_0\times10^{-6}$
40	1751.85	10.05	3.60
50	1448.99		
60	1317.94		
70	1245.00		

Table 3: Kinetic parameters of drying at 40, 50, 60 and 70°C

T (°C)	a	k_{d1}	b	k_{d2}	SSE
40	0.90	0.02	0.23	0.05	0.07
50	0.90	0.03	0.23	0.10	0.06
60	0.90	0.03	0.23	0.10	0.09
70	0.80	0.07	0.23	0.07	0.03

Table 4: Drying time and gallic acid degradation at drying 40, 50, 60 and 70°C

T (°C)	Drying time (min)	Gallic acid degradation (%)
40	158.28	11.30
50	123.85	10.79
60	107.06	10.33
70	52.00	5.730

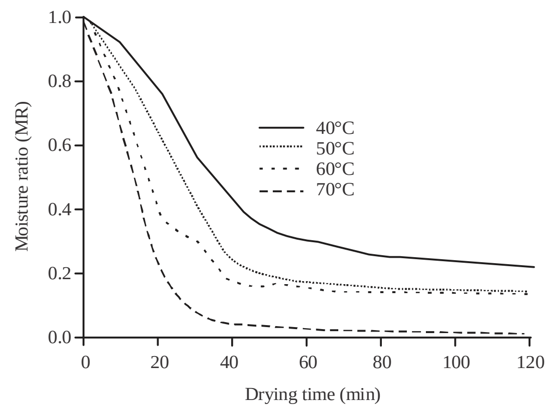

Fig. 6: Moisture ratio during drying at 40, 50, 60 and 70°C

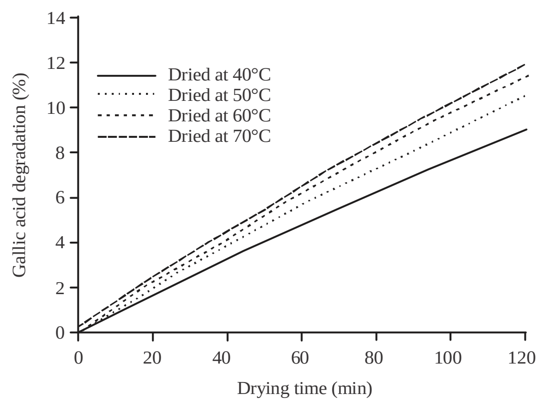

Fig. 7: Predicted of Gallic acid degradation (%) during the drying time

Kinetics of drying at different temperature: The moisture content during the drying process was observed. The moisture content was converted into dimensionless moisture, namely moisture ratio and it was depicted in Fig. 6. The higher drying temperature resulted the lower moisture ratio. Increasing the drying temperature 10°C from temperature 40-50°C resulted moisture ratio 1.67 times lower.

The kinetic parameter of the drying was then calculated using two term model (Eq. 9) from the moisture ratio data. The kinetic parameter from two term model was listed in Table 3. The kinetic parameter was then used to obtain the estimated drying time. The drying time was listed in Table 4. The higher drying temperature leads the higher driving force for the drying and higher drying rate[25]. So, the drying time was shorter as the result of this research.

The kinetic parameter of gallic acid degradation in Table 2 and kinetic parameter of drying in Table 3 were used to estimate the gallic Acid degradation along the drying process (Fig. 7). Selection of the proper drying condition is important to minimize the drying time and maintain the nutrition such as gallic acid.

Selected drying condition: The selection of drying condition was important to get the proper condition with short drying time and high nutrition such as gallic acid. The comparison of each drying temperature was listed in Table 4. As the parameter, the drying time and gallic acid degradation were calculated. At drying temperatures 70°C, the drying time was 3 times faster than in drying temperatures 40°C. Since, the faster drying times the gallic acid degradation in 70°C was lower than in 40°C. Drying at 70°C for 52 min can be option to retain the gallic acid content and short drying time.

CONCLUSION

The post-harvest onion contains gallic acid around 10.8 mg DW^{-1} gallic acid. The kinetic parameter of the drying was estimated using two term model. The drying temperature affects the gallic acid degradation. The thermal degradation of gallic acid in onion was lower than that of the gallic acid isolated the others food products. The presence of the other components such as water and onion layer can inhibit gallic acid degradation. At higher drying temperatures, the kinetic of the drying was higher so the drying time can be shorter and the degradation can be lower. gallic acid degradation resulted quinone and hydrogen peroxide in which followed to the third order kinetic model. The activation Energy (E_a) for the gallicacid degradation in onion was 10.05 kJ mol^{-1} and frequency factor was . The kinetic parameter of drying and kinetic parameter of gallic acid degradation can be used for drying condition selection. The drying at temperature 70°C for 52 min was selected as the favourable drying condition.

ACKNOWLEDGEMENTS

This study was supported by Research and Community Service Centre, Diponegoro University under Research and International Publication Grant 2019.

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