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Research Article

Kinetics of Starch Degradation during Extrusion Cooking of Steady State Flow Konjac (*Amorphophallus oncophyllus*) Tuber Flour in a Single Screw Extruder

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Abstract

The presence of glucomannan in Konjac (*Amorphophallus oncophyllus*) tuber flour has promoted its various applications, especially in the food, drink, drug delivery and cosmetics. Starch is the main impurity of Konjac tuber flour. Although the common wet refining method may result in a high purity Konjac tuber flour, it is very tedious, time consuming and costly. This research aimed to study the kinetics of starch degradation in the extrusion cooking process of dry refining method to produce high quality Konjac tuber flour. In this research, Konjac tuber flour with 20% (w/w) moisture was extruded in a single screw extruder by varying screw speeds (50, 75, 100, 125, 150 and 175 rpm) and barrel temperatures (353, 373, 393, 413 and 433 K). The results showed that the starch extrusion cooking obeys the first reaction order. The reaction rate constant could be satisfactorily fitted by Arrhenius correlation with total activation energy of 6191 $J.mol^{-1}$ and pre-exponential factor of 2.8728×10^{-1} s^{-1}. Accordingly, thermal degradation was found to be the primary cause of starch degradation, which shared more than 99% of the energy used for starch degradation. Based on mass *Biot* number and *Thiele modulus* evaluations, chemical reaction was the controlling mechanism of the process. The results of this research offer potential application in Konjac tuber flour refining process to obtain high quality flour product.

Keywords: dry process; extrusion cooking; starch; reaction kinetics; glucomannan; refining

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1. Introduction

Due to its specific rheological and gelling properties, Konjac (*Amorphophallus oncophyllus*) flour is commonly used as a thickener, emulsifier, gelling agent, and stabilizer in many types of food, drink and cosmetic products [1]. This is because Konjac flour is rich in glucomannan content (50 to 70% w/w) and being a sustainable resource [2]. A premium quality konjac tuber flour should contain no less than 90% (w/w) of glucomannan. The impurities present in the crude Konjac tuber flour are usually orig-

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inated from the fragment of the tissue space [1], which primarily comprise starch, lipid, protein and ash [3]. However, starch is the most influential impurity that largely affects the pasting and rheological properties of Konjac tuber flour [4]. Whilst the commonly applied wet refining method may result in a high quality Konjac tuber flour, it is very tedious, time consuming and requiring high processing cost. Considering that the starch components (amylopectin and amylose) can be degraded to their smaller molecular components during extrusion cooking [5], extrusion cooking process can be a promising dry method for Konjac tuber flour refining. As the premium commodity from Konjac tuber flour, glucomannan exhibits very much higher water absorption capacity than the starch. If the extrusion process is carried out at higher moisture content, then the highly hydrophilic glucomannan will absorb water and result in an increase of its volume to more than 100 times leading to the formation of strong thick gel (hydrocolloid) [6]. This phenomenon may lead to thermomechanical degradation by extrusion.

Whereas, this research was aimed to degrade the starch in Konjac flour as the main impurity of Konjac flour to enrich the glucomannan content. A dry extruder can process tuber flour containing 16 to 20% moisture without additional drying of extrudates [7−8]. With 19.9 % w/w amylose content, Konjac tuber flour falls under normal starch category and its gelatinization temperature lies between 64.9 to 77.5 °C [9]. Based on his findings, Moad also suggested that the typical extrusion temperatures for low amylose starch are about 70−80 °C, while those for high amylose starch (> 50% w/w) can range 120−140 °C [10]. However, the use of high extrusion temperature (≥ 200 °C) and low moisture content (≤ 15%) should be averted to preserve the nutritional quality of the food product [11]. Adekola conducted an optimization of grain sorghum extrusion in a corotating twin-screw extruder using response surface analysis employing moisture contents of 15–25% w/w (w.b.), screw speed of 100–200 rpm, and barrel temperature of 100–160 °C. The quality of the extrudates was determined based on the extrudate properties, which include bulk density, residence time, solid density, moisture content, maximum stress, water solubility index (WSI), water absorption index (WAI), expansion index, extruder output, crispness and color. A number of trained panelists were selected to obtain their preference on the extrudates crispness and color. Based on this panel survey, Adekola suggested that the use of feed moisture content of 20% w/w (w.b.) and barrel temperature of 150 °C resulted in the best extrudate crispness and color quality [12].

An extruder could be regarded as a reactor, in which thermal and shear forces are applied to raw food materials [13]. The materials experience various structural, chemical, and nutritional changes, such as starch gelatinization and degradation, protein denaturation, lipid oxidation, formation of flavors and degradation of vitamins, antinutrients and other phytochemicals [14−15]. Indeed, these reactions are believed to influence the quality of the extruded products [11]. Unfortunately, most current research focuses on the influence of the extrusion conditions on the extent of these involving reactions, but very a few of them deal with the kinetics description.

Starch gelatinization in an extruder does not obey a common simple chemical reaction mechanism [16]. Extrusion cooking process involves three unique phenomena. First, extrusion cooking is basically a non-isothermal process, which hinders the implementation of a two-step method in finding the reaction kinetics parameters. Usually, the kinetic parameters are evaluated at a specific temperature and followed by finding the same parameters at various temperatures. Second, similar to the real plug flow reactor, the reactant and the product flow through the reaction channel in the extruder causing the residence time of the reactant and the product is distributed as a function of their axial position in the reaction zone. Hence, the extruder has the residence time distribution that is a narrow pulse around the mean residence time distribution. As a consequence, the residence time in an extruder is usually short and distributed, which causes it is very hard to accurately determine the rate of reaction. Third, intensive shear force sustained in an extruder, which causes the rate constant is not only depending on the temperature but also the shear stress. Therefore, all of these factors play a part in to the laboriousness and complexity of the reaction kinetic analysis for extrusion cooking [13]. Theoretically, the extent of a reaction is controlled by its reaction order, rate constant, and reaction time. The rate constant during extrusion of food materials is a function of many parameters, such as barrel temperature, moisture content, screw rotation speed and shear stress applied to the material. Obtaining the appropriate correlation between the rate constant and those factors could assist to optimize the extrusion to the desirable reactions, and simultaneously minimize the undesirable reactions [13].

Since starch is the major impurity of Konjac tuber flour, this research aims to study the kinetics of starch degradation in the hot extrusion of konjac tuber flour with 20% w/w moisture content as affected by barrel temperatures and screw rotation speeds. The results of this research are expected to function as an essential guidance in controlling the extrusion process for konjac tuber flour dry refining method and estimating the product quality.

2. Materials and Methods

2.1 Materials

The crude Konjac tuber flour used in this research was purchased from P.T. Prima Agung Sejahtera – Surabaya (Indonesia) with average particle size of 80 mesh (approximately 1.77×10^{-4} m). The initial moisture content of the flour samples was quantified by vacuum drying at ambient temperature to dryness. All of the chemicals and reagents used for analysis were of analytical grade (purity ≥ 98% w/w) products of Sigma Aldrich and procured from an authorized chemical store in Semarang-Indonesia. All the chemicals were directly used without pretreatments.

2.2 Extrusion Cooking

The Konjac tuber flour extrusion was conducted in a single screw extruder (Figure 1) [17]. The extruder design was similar to the C.W. Brabender Model 2802 with 1.0 m barrel length, 0.1 m barrel diameter and 0.0375 m average screw channel depth over the active volume. To facilitate dry refining process, the Konjac tuber flour feed was conditioned to 20% (w/w) moisture content by spraying a predetermined amount of distilled water as a fine mist on the flour in a Patterson V-blender. This flour moistening procedure was done several times to ensure its reproducibility. It was confirmed that the standard deviation was ± 0.82% (w/w) wet basis. The extruder was operated at various screw speeds (50, 75, 100, 125, 150, and 175 rpm) under steady state flow condition. The average residence time of the moistened Konjac tuber flour driven by each screw speed was measured by performing cold extrusion with the assistance of color tracer. The establishment of the steady state condition was determined by a constant torque needed to turn the screw and by a regular extrusion rate. The feed zone barrel temperature was then set at 353 K (slightly above the gelatinization temperature), whereas the compression and die zone temperatures were varied from 353 K to 433 K by adjusting the electrical resistance band heaters. Samples were withdrawn from the exit point of the extruder die every 2 seconds for starch content analysis. Prior to analysis, the extrudate was frozen in liquid nitrogen and then promptly ground in a Waring Blender followed by finer comminution in a coffee grinder. The starch and soluble sugar were separated from glucomannan by wind-sifting method.

2.3 Analytical Methods

The starch content of raw and extruded konjac tuber flour was calculated from total sugar content obtained from acid hydrolysis method, which includes hydrolysis of konjac tuber flour using concentrated hydrochloric acid solution, neutralization using caustic soda solution, and total sugar analysis using Lane-Eynon method involving copper sulfate, alkaline tartrate and sugar standard solutions [18]. The Kjeldahl method was used to obtain the total nitrogen content for protein determination

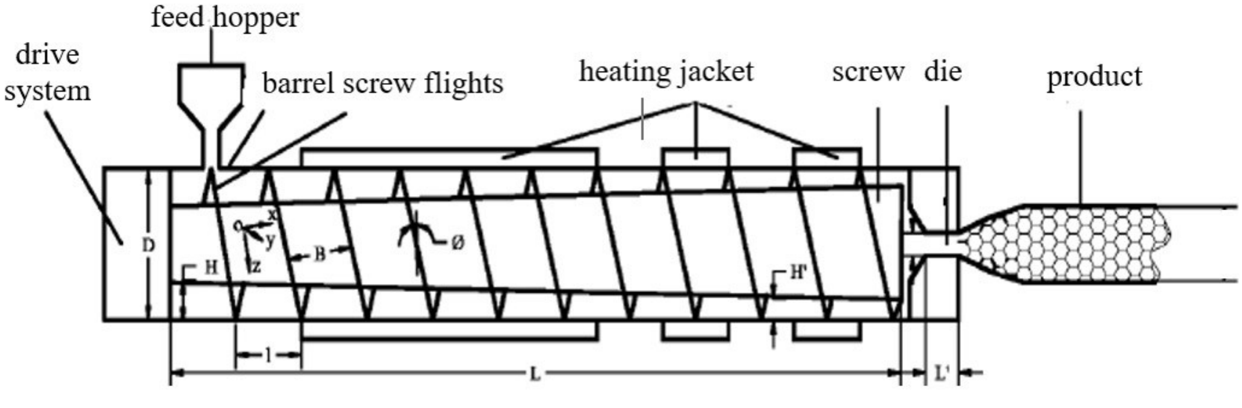

Figure 1. The typical cross sectional of single screw extruder [17].

[19]. The protein content was then estimated by multiplying the nitrogen conversion factor of 5.7, as proposed by the U.S. Food Chemicals Codex (FCC) and European Commission [20]. The moisture, ash, fat and dietary fiber contents were quantified following the AOAC Method 934.01, 920.153, 948.15 and 991.43, respectively [21]. The reducing sugar of the sample was determined using phenol-sulfuric acid colorimetry [22]. Subsequently, the glucomannan content was calculated based on the reducing sugar content of the extrudate and raw Konjac flour sample solution according to the method previously described by Chua *et al.* [23]. This quantitative analysis of glucomannan was accurate enough as long as the speed of sulfuric acid addition directly over the liquid surface was precise to obtain consistent results. This suggestion is related to the fact that rapid addition of sulfuric acid provided sufficient heat to break all of the glycosidic bonds in the complex carbohydrate. Soluble sugars were quantified by high performance liquid chromatography (HPLC) according to a protocol used by Berrios *et al.* [24].

2.4 Mathematical Modeling

During extrusion, the starch experience pyroconversion, which involves thermal treatment of a dried starch with or without addition of acid. It contributes two mechanisms of starch structural modification, which include partial depolymerization through hydrolysis and repolymerization. The cleavage of glycosidic bond can be performed by dry roasting of starch either alone using natural moisture (10-20%) or in the existence of acid as a catalyst [25]. Hydrolysis of starch results in a range of starch fractions with various chain length (low conversion). The second mechanism exhibits a recombination of these starch fragments that can be regarded as transglycosidation and repolymerization. Transglycosidation employs the transfer of portions of glucan chains to hydroxyl groups on the same or different chains to develop a branch point. This is a highly branched carbohydrate polymer and is more soluble (high conversion). Repolymerization or reversion happens with existence of acid as a catalyst at high temperatures and low-moisture content. This further creates high molecular weight and more branched structure [25]. However, in the absence of acid as catalyst, the complicated reactions between starch (*S*) of a given chain length and water (*W*) molecules to form dextrins (*D*), which are mixtures of polymers of *D*-glucose units linked by α-(1-4) or α-(1-6) glycosidic bonds, can be simplified to:

$$C_6H_{11}O_5\left[C_6H_{10}O_5\right]_p C_6H_{11}O_6+\left(\frac{p-q}{2}\right)H_2O \rightarrow \frac{(p+2)}{(q+2)}C_6H_{11}O_5\left[C_6H_{10}O_5\right]_q C_6H_{11}O_6 \tag{1.a}$$

$$S+aW \rightarrow D \tag{1.b}$$

However, no generous model has been reported to predict the degree of starch degradation during extrusion cooking process. Lund and Wirakartakusumah reported that the reaction between starch and water molecules is not an elementary reaction. Therefore, the overall reaction rate can be generally expressed as [26]:

$$-\left(\frac{dC_S}{dt}\right)=k_r.C_S^n.C_{Ws} \tag{2}$$

where k_r, C_S, C_{Ws}, t, and n are apparent reaction rate constant, starch concentration in the extrudate, water concentration in the starch granule surface, time and reaction order, respectively. The starch granules can be assumed to shrink in size as the reaction take places. The rate of water molecules transfer from the bulk water system (either in the form of moisture or water vapor) can be represented by:

$$-\left(\frac{dC_{Ws}}{dt}\right)=K_{la}\cdot\left(C_{Wb}-C_{Ws}\right) \tag{3}$$

where K_{la} and C_{Wb} are respectively the moisture mass transfer rate constant and saturated water concentration in the bulk reaction system. Based on Equation (1.b), *a* moles of water are required to react with one mole of starch. Eliminating C_{Ws} and rearrangement of Equation (2) and Equation (3) should result:

$$-\left(\frac{dC_S}{dt}\right)=\frac{C_{Wb}}{\frac{1}{k_r.C_S^n}+\frac{a}{K_{la}}} \tag{4}$$

Although starch gelatinization in an extruder involves remarkably complex chemical reaction mechanisms, if the water mass transfers in both external and internal portions of starch granules are rapid enough compared to the starch-water reaction, Zhao *et al.* suggested that the overall reaction kinetics of an extrusion cooking of food material can be simplified into the following equation [13]:

$$-\frac{dC_S}{dt}=kC_S^n \tag{5}$$

in this regard, $k = k_r.C_{Wb}$. Integrating equation (5) with respect to reaction time results in:

$$-\int_0^t k_0 dt=\left(C_S-C_{S0}\right) \qquad \text{for n = 0} \tag{6.a}$$

If the rate of starch-water reaction and water mass transfer are close to each other or water diffusion process is not a limiting mechanism, a zeroth order reaction will satisfactorily represent the overall mechanism. Bhattacharya and Hanna reported that the kinetics of corn starch gelatinization during extrusion in a single-screw extruder with moisture between 17.8% to 42.2% (dry basis) and temperatures between 116 to 164 °C followed a pseudo-zeroth-order reaction kinetics. The reaction rate constants were observed to be higher for waxy corn than for high amylose corn starch and increased with increasing temperature [27].

$$-\int_0^t k_1 dt = \ln\left(\frac{C_S}{C_{S0}}\right) \qquad \text{for n =1} \qquad (6.b)$$

Lai and Kokini observed that starch gelatinization during extrusion obeys a first order reaction [28]. In line with their research findings, Lund and Wirakartakusumah (1984) suggested that the gelatinization kinetics for rice starch in high-moisture systems follow first-order reaction kinetics when the temperature is greater than 67 °C [26]. Burros *et al.* (1987) reported that corn starch gelatinization at high temperature (110 to 140 °C) and low moisture (25%) was lower (approximately 0.8) than that in excess water, which exhibiting first-order kinetics [29]. Accordingly, they proposed that a mass transfer limitation of the first-order reaction in a restricted water environment that caused gelatinization depending on transport of the available water to and into starch granules.

$$-\int_0^t k_2 dt = \frac{1}{1-n}\left(C_S^{1-n} - C_{S0}^{1-n}\right) \qquad \text{for n} \neq 1 \qquad (6.c)$$

For extrusion of starch, the degree of conversion (X_s) of the fraction of the starch which is fully cooked (f) increases during extrusion process [30]. For the case of plug flow reactor, the reaction time can be replaced with average residence time (t), and hence equations (6.a), (6.b) and (6.c) can be rewritten as:

$$X_S = \frac{k_0.t}{f.C_{S0}} \qquad \text{for n = 0} \qquad (6.d)$$

$$X_S = \frac{1-e^{-k_1.t}}{f} \qquad \text{for n =1} \qquad (6.e)$$

$$X_S = \frac{k_2.C_{S0}.t}{\left(1+k_2.C_{S0}.t\right).f} \qquad \text{for n = 2} \qquad (6.f)$$

$$X_S = \frac{1-\left(1-0.2.f.k_3.C_{S0}^{-0.2}.t\right)^5}{f} \qquad \text{for n = 0.8} \qquad (6.g)$$

Starch extrusion implicates both thermal and shear energies. When the extrusion cooking is conducted at low temperature (close to gelatinization temperature), the shear energy is dominant in causing starch degradation in the starch melt conveying channel of the extruder [31]. Biliaderis suggested that the applied temperature for starch extrusion cooking should be higher than its phase transition temperature usually obtained from differential scanning calorimetry (DSC) analysis [32]. If not, the starch phase transition would not take place.

To model the starch extrusive conversions in a single-screw extruder, Qu and Wang suggested that extrusion of starch follows a first order reaction so that the overall rate constant k_1 is equal to the summation of shear induced rate constant k_S, thermally induced rate constant k_T, and the shear and thermal interaction term [33].

$$k_1 = k_T + k_S + \left(k_T k_S\right)^{1/2} \qquad (7)$$

In a shearless environment, the relationship of k_T with temperature obeys the Arrhenius equation, whereas for k_S, an Arrhenius type of relationship is used to represent the rate constant:

$$k_T = k_{T,0}.\exp\left({}^{-\Delta E_T}\!/_{RT}\right) \qquad (8.a)$$

$$k_S = k_{S,0}.\exp\left({}^{-\Delta E_S}\!/_{t.v}\right) \qquad (8.b)$$

where k_{T0} and k_{S0} are the pre-exponential factors of k_S and k_T, respectively. Similarly, the E_T and E_S are the activation energies needed for thermal shearless condition and shear conversion processes, respectively. Accordingly, T, ΔE_T, and R are the absolute reaction temperature, activation energy and universal gas constant. In the shear conversion rate constant correlation, τ is the shear stress and v is the molar volume of anhydroglucose unit [34].

$$v = \frac{16200}{\left(A_S.\rho_S + \left(100 - A_S\right).\rho_W\right)} \qquad (9)$$

where As, ρ_s, and ρ_w are the mass percentage of starch and density of starch and water, respectively.

The shear-stress sustained by the starch molecules can be estimated from their apparent viscosity (η) and shear rate (γ):

$$\tau = \eta.\gamma \qquad (10)$$

Assuming that the starch melt is a non-Newtonian fluid, Diosady *et al.* successfully used the following equation to estimate the apparent viscosity (N.s.m^{-2}) of wheat starch during extrusion cooking [30]:

$$\eta = 78.5.\gamma^{-0.49}\exp\left(\frac{2500}{T} - 7.9M\right) \qquad (11)$$

where M is the moisture fraction of the feed. For a single-screw extruder, if the screw section is fully filled with starch melt and no slip takes place at the interfaces between the starch melt and channel bottom, and between the starch melt and barrel inner surface, the velocity of the starch melt with respect to screw is zero at the bottom of channel and $\pi D\omega$ at the screw tip. Taking an assumption that the starch melt is in a simple shear flow and the screw channel depth is much smaller than the screw radius, Zhao *et al.* used the following correlation to estimate the effective shear rate (γ, s^{-1}) within the fully-filled screw channel [13]:

$$\gamma = \frac{\pi D\omega}{60H} \qquad (12)$$

where D, ω, and H are respectively the barrel diameter (m), rotating speed (rpm), and average screw channel depth over the active volume (m). Another alternative equation was proposed by Cai and Diosady to correlate the apparent reaction rate constant with temperature and shear stress (τ) [16].

$$k_1 = k_0.\exp\left(-\left(\Delta E_T - \beta.\tau\right)/RT\right) \qquad (13)$$

where k_0 and β are the pre-exponential factors and activation volume for the respective bond scission. From Equation (13), it is clear that when $\tau = 0$, Equation (13) simplifies to an equation for a shearless environment, which is Equation (8.a). This suggests that starch gelatinization in the extruder is basically a thermal process and the effect of shear stress in the extruder mainly contributes to the rate constant by "activating" chemical bonds so that starch is more vulnerable to thermal influence. Mass *Biot number* (B_{im}) and *Thiele modulus* (ϕ_n) were then used to justify the mechanisms that control the overall reaction [35].

$$B_{im} = \frac{K_{la}.R}{D_{eff}} \qquad (14)$$

Thorell and Wadsö reviewed that a generally used consideration is that if $B_{im} << 0.1$, the mass diffusion is relatively fast and the external resistances should control the whole process. In contrast, a value of $B_{im} >> 50$ indicates that diffusivity is relatively slow compared to convective mass transfer and therefore the effect of external resistance is negligible. If the mass *Biot* number is $0.1 << B_{im} < 50$, the reaction rate should govern the process [36]. Diffusivity coefficient of water in gelatinized starch can be estimated using an equation proposed by Karathanos *et al.* [37]:

$$\ln D_{eff} = 10.882 - \frac{2851}{T} - 0.3122\times\ln P - 1.5111\times MC \qquad (15)$$

In the above equation D_{eff} is the effective diffusivity of water (m^2/s), T is the absolute temperature in Kelvins, P is the pressure in atmospheres, and MC is the moisture content, dry basis. The solid-liquid mass transfer coefficient in a screw extruder can be satisfactorily predicted using [38]:

$$\frac{K_{la}}{a_b} = 2.3\times10^{-6}.N^{0.5} \qquad (16)$$

where K_{la}, a_b and N are the solid-liquid mass transfer coefficient (m.s^{-1}), surface area of barrel per unit volume of empty barrel (m^{-1}) and screw speed (s^{-1}). The Thiele modulus evaluated by:

$$\phi_n^2 = \frac{R^2 k_n.C_S^{n-1}}{D_{eff}} \qquad (17.a)$$

where R, Cs and n are the radius or flour particles (m), water concentration in the flour particles (g/g) and reaction order. For, first order reaction involving spherical particles, the Thiele modulus can be estimated using:

$$\phi_1 = \frac{R}{3}\left(\frac{k_1}{D_{eff}}\right)^{1/2} \qquad (17.b)$$

According to Weisz's criteria, if the *Thiele modulus* is large (much higher than 3), internal diffusion usually controls the overall rate of reaction and the surface reaction is very fast in which water molecules are consumed very near to external surface of the starch granule. On the other hand, when the value of *Thiele modulus* is small (less than 0.3), the surface reaction is usually the rate-controlling mechanism and a significant amount of the water molecules easily diffuse into the starch granules interior without reacting. Therefore, if $0.3 \leq \phi \leq 3$, a more detail analysis is needed to examine the effect of mass transfer on the reaction rate [39].

3. Results and Discussion

3.1 Chemical Characteristics of Crude Konjac Tuber Flour

The crude Konjac tuber flour used in this research contained glucomannan (50.62%), starch (21.62%) soluble sugar (4.27%), protein (6.53%), fat (2.02%), ash (4.84%), fiber (0.44%) and moisture (9.67%). Based on triplicate analytical work, the standard deviation of each measurement was ± 0.22, which confirm the reproducibility of the procedure. The flour met the criteria of the general quality standard for crude Konjac tuber flour in the commercial market [2]. To widen the utilization of Konjac tuber flour in various industrial applications, an effort to improve its glucomannan content by removing of its impurities through extrusion cooking process has been performed. A kinetics study of the extrusion cooking of the Konjac tuber flour is the focus of the current research.

3.2 Reaction Order of Konjac Tuber Flour Extrusion Cooking

The profiles of starch degradation in term of degree of conversion (X_S) at various mean residence times and reaction orders at 373 K are depicted in Figure 2. The zeroth order reaction exhibited unacceptable prediction of the starch degradation as the X_S values exceeded 1.0 at residence times beyond 40 s. Another unacceptable approach is that that the fraction of fully cooked starch (*f*) was only 0.4913, whereas the extrusion was conducted fairly above the gelatinization of Konjac tuber flour. The 0.8th reaction order exhibits a relatively good estimation, especially in the beginning of the process (up to 30-minute average residence time). Unfortunately, it demonstrates wider deviation to the experimental data at longer average residence times than first reaction order. In addition, the use of zeroth, first or second reaction orders are more common application in chemical engineering field rather than 0.8th reaction order. Although the second order reaction fitted the experimental data quite well (average of absolute errors of 1.7158 %), this approach was not plausible because this viewpoint resulted in a complete conversion of starch (X_S = 1) while the fraction of fully cooked starch (*f*) was only 0.6255 at the longest residence time (approximately about 61 s). Cai and Diosady observed that gelatinization of wheat starch initially follows a pseudo-second order rate law, but soon it reverses to a pseudo-first order reaction [16]. From this point of view, the first order reaction was regarded as the most suitable approach to the reaction order of starch extrusion cooking, with average of absolute errors of 1.2241%. Burros *et al.* studied the kinetics of corn meal gelatinization at high temperatures (80–140 °C) and low moisture contents (13.4–31.5 % w/w) in a differential scanning calorimetry (DSC) analyzer, and the reaction order was obtained was to be approximately 0.8, which suggested a diffusional limitation of a first order reaction [29]. They conducted a series of experiment to study the kinetics of gelatinization and melting of starch without inclusion of shear but with designated modifications to improve heat transfer rate using DSC (Perkin-Elmer DSC-4) by sealing 5 mg of corn meal in the volatile sample pans and adjusting the scan rate of 2.5 °C.min^{-1} for possible use with Perkin-Elmer stainless-steel high-pressure cells if such cells had been needed to hold pressure at 165 °C. However, no information was given on the gas used in their experiments. It was reported that the use of volatile sample pans was adequate for the low moisture samples at high temperature. Ibanoglu and Ainsworth also reported that the rate of gelatinization of wheat starch in Tarhana during extrusion using a co-rotating twin-screw extruder follow a reaction order of 0.8, which is fairly close to first order reaction [40]. Under this limited water condition, gelatinization depends on the migration of available water molecules to the starch granules and water into the starch granules. The reaction order decreased slightly due to the reduction of moisture content, which support the assumption that moisture diffusion plays a significant role in starch gelatinization. However, in an extruder where shearing and bulk mixing exist, the convective mass transfer should assist in the reduction of mass transfer limitation of diffusion alone in differential scanning calorimetry (DSC). These findings demonstrate that starch gelatinization is not an elementary reaction; a series of reactions may be involved in this process so that only lumped reaction kinetics can be obtained because the reaction mechanism of gelatinization is not well-understood [26,40].

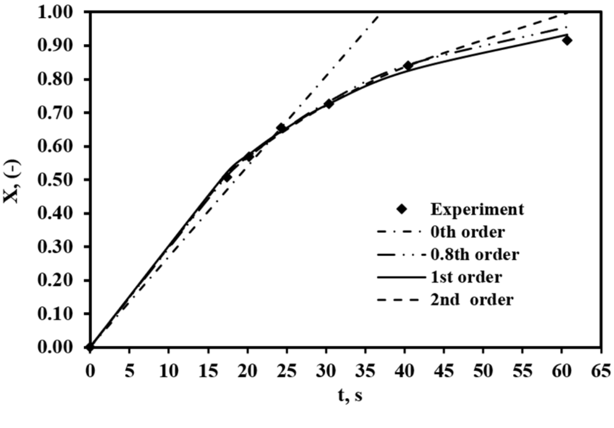

Figure 2. Profile of starch conversion at various mean residence time

3.3 Effect of Temperature and Screw Speed on Reaction Rate Constants

Figure 3 depicts the profile of the degree of starch conversion (Xs) at various temperatures obtained from experiments and mathematical modeling. The reaction rate constants of the Konjac tuber flour extrusion cooking at temperatures ranged from 353 to 433 K obtained in this work are tabulated in Table 1. In starch-water systems with limited water content, no gelatinization may happen under the heating regime, especially when the water content is lower than 30% w/w [41]. However, in extrusion systems, starch gelatinization may take place at water contents between 2% and 28.5% (w/w) [42]. As expected, the use of a higher extrusion temperature caused a speedy starch degradation as indicated by a higher value of reaction rate constant. This phenomenon is in good accordance with gelatinization of waxy corn starch at low moisture content (20 % w/w) observed by Wang *et al.* [43]. It was also proven that under these experimental conditions, all of the starch granules were melted as shown by the fraction of cooked starch values were unity. According to van der Goot *et al.*, an increase of extrusion temperature reduces the melt viscosity and subsequently reduces the degree of mechanical breakdown. As a consequence, an improvement in the degree of thermal degradation would be achieved [44].

For the extruder geometry and operating conditions (screw rotation speeds varied from 50 to 175 rpm) used in this work, all of the nominal shear rates were below 25 s^{-1} (Table 2). Figure 4. presents the linear correlation between reaction rate constant and temperature from which the total activation energy can be obtained. Thus, the activation energies from thermal and shear effects were evaluated using Equation (13). These values were one order of magnitude lower than the average shear rates calculated for the extrudate material in the die section [5]. Both activation energies from thermal and shear effects required for starch deg-

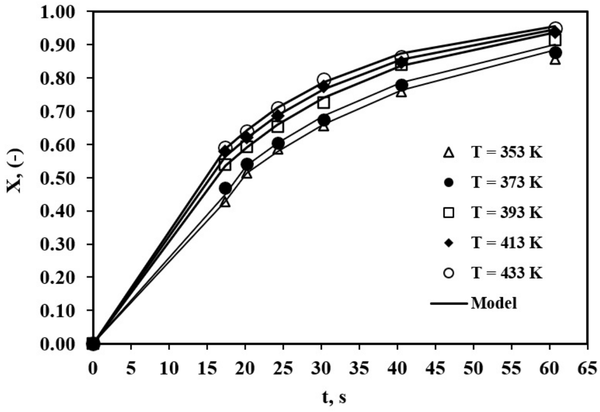

Figure 3. Effect of temperature on starch conversion.

Table 1. Reaction rate constant (k_1), effective diffusivity (D_{eff}), mass transfer coefficient (K_{la}) and other kinetics physical parameters at various temperature.

Temperature, (K)	353	373	393	413	433
Fraction of cooked starch, ($g.g^{-1}$)	0.9989	1.0000	1.0000	1.0000	1.0000
Experimental reaction rate constant, (s^{-1})	0.0351	0.0384	0.0425	0.048	0.0511
Estimated reaction rate constant, (s^{-1})	0.0351	0.0393	0.0434	0.0476	0.0517
Average absolute errors, %	1.3259				
R^2, -	0.9921				
Activation energy from thermal, $J.mol^{-1}$	6222.6906	6213.7617	6207.9659	6204.2741	6201.4243
Activation energy from shear, $J.mol^{-1}$	32.0032	23.0737	17.2792	13.5836	10.7364
Shear stress, ($N.m^{-2}$)	16837.85	11531.10	8207.09	6036.86	4568.30
Viscosity, ($N.s.m^{-2}$)	965.2270	661.0185	470.4704	346.0622	261.877
Activation volume × 10^3, ($m^3.mol^{-1}$)	1.9007	2.0001	2.1054	2.2506	2.3502
Effective Diffusivity × 10^{10}, ($m^2.s^{-1}$)	17.8105	17.8182	17.8251	17.8314	17.8370
Mass transfer coefficient × 10^4, ($m.s^{-1}$)	1.9700	1.9711	1.9712	1.9713	1.9715
Biot number, (-)	9.7940	9.7901	9.7866	9.7839	9.7817
Thiele Modulus, (-)	0.1310	0.1390	0.1440	0.1531	0.1579

radation decreased as the extrusion temperature increased are presented in Table 1. This is primarily due to the reduction of the viscosity of the molten starch, which induce the decline of shear stress. Accordingly, the activation volume for the scission of α-(1-4) or α-(1-6) glycosidic bonds increased. The activation volumes ranged between 1.9807 to 2.3502×10^{-3} $m^3.mol^{-1}$, which are consistent with that reported by Cai and Diosady who observed that the activation volume for corn starch extrusion was 1.784×10^{-3} $m^3.mol^{-1}$ [16]. This might suggest that the effects of shear on the starch gelatinization in the extrusion of Konjac tuber flour was minimal. Under this circumstance, it could be assumed that the starch degradation was occurring primarily in the fully melted starch along the length of the screw channel due to the superposition of thermal stresses on mechanical effects. As a consequence, the shear effect on rate constant (k_1) was negligible and equation (8.a) could be safely utilized for the calculation of reaction rate constant of starch extrusion in this work.

The activation energy for starch extrusion obtained in this work is 6191 $J.mol^{-1}$, while the pre-exponential factor of the Arrhenius correlation obtained in this work is 2.8728×10^{-1} s^{-1}. The activation energy obtained in this study is in excellent agreement with Senouci and Smith who reported that the activation energy for extrusion of potato starch was 7150 $J.mol^{-1}$ when they studied the extrusion of potato starch at 80–140 °C and moisture content 18–42% (w.b.) in a twin screw-extruder using screw speed of 50–250 rpm (shear rate 21–74 s^{-1}) [45]. The temperature, screw speed and moisture content ranges applied in this study fell in the same range of parameters used by Senouci and Smith [46]. In addition, both studies also used tuber starches as the raw material. However, the activation energy for starch extrusion obtained in this work is approximately twofold of the activation energy for starch gelatinization during the extrusion of Tarhana, a traditional Turkish wheat flour-yoghurt mixture in a co-rotating twin-screw extruder reported previously by Ibanoglu and Ainsworth, which was 3325 $J.mol^{-1}$ [32]. Wang *et al.* reported that the activation energy for starch gelatinization of *Amioca* (a waxy corn starch) at 20% moisture content was 141.33 $kJ.mol^{-1}$ [43], while Burros *et al.* obtained that the activation energies for corn meal gelatinization at high temperatures (80–140 °C) and low moisture contents (13.4–31.5 % w/w) ranged between 99.8 to 328.9 $kJ.mol^{-1}$ [29]. The difference of these two reports with the activation energy obtained in this work is most probably due to the difference of the botanical sources of the starch, which mean the difference in the composition and type of amylose and amylopectin. In addition, starch molecules need more energy to initiate gelatinization during the heating process in the limited water system, because water molecules play their role as plasticizer agents of polymeric carbohydrate molecules. Coral *et al.* also found the same finding that enthalpy of gelatinization increased when the moisture content of the maize flour decreased, but it decreased when the flour granule size increased [46]. This phenomenon is also in good accordance with Ibanoglu and Ainsworth who conducted the extrusion process at a higher moisture content (50% (w/w)) that promotes easier gelatinization process to occur. Whereas this work employed a lower moisture content (20% (w/w)), which obviously require the crystallites

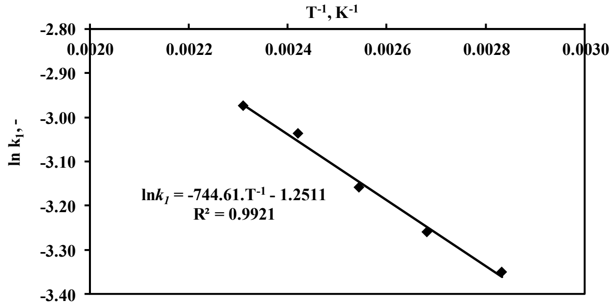

Figure 4. Correlation between reaction rate constant and temperature.

Table 2. The estimated physical parameters measurement.

screw rotation speed, rpm	axial velocity of starch melt, $m.s^{-1}$	average residence time, s	shear rate, s^{-1}
50	0.0164	60.7108	6.9778
75	0.0247	40.4738	10.4667
100	0.0329	30.3554	13.9556
125	0.0412	24.2843	17.4444
150	0.0494	20.2369	20.9333
175	0.0577	60.7108	24.4222

of the starch to undergo melting process upon continuous heating [40].

The mass *Biot* numbers obtained from mathematical modeling tabulated in Table 1 range from 9.7817 to 9.7940. Because mass *Biot* numbers are significantly higher than 0.1, but lower than 50, then the reaction rate should be the controlling mechanism [36]. The values of *Thiele* modulus obtained in this study are small (less than 0.3). Therefore, the *Thiele* modulus value confirm that the surface reaction on the starch granules is the rate-controlling mechanism. Under this situation, a significant amount of water molecules easily diffuse into the starch granules interior without reacting. This finding is in good conformation with mass *Biot* number analysis [39].

4. Conclusion

A kinetics study of starch degradation in a single screw extruder has been performed. The starch extrusion cooking was found to follow the first reaction order. Under the operating condition used in this study, the thermal degradation was found to be fairly predominant over the shear degradation, which shared more than 99% of the energy used for starch degradation. The reaction rate constant satisfactorily fitted the Arrhenius correlation with activation energy of 6191 J.mol^{-1} and pre-exponential factor of is 2.8728×10^{-1} s^{-1}. Based on mass *Biot* number and *Thiele modulus* evaluations, chemical reaction on the starch granules surface was the controlling mechanism of the extrusion process. The kinetics parameters acquired in this study can be used to predict the degree of starch degradation in Konjac tuber flour during extrusion cooking for the its refining optimization.

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