

Running title: Engineering aspects of rate-related processes

Engineering aspects of rate-related processes in food manufacturing

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Many rate-related phenomena occur in food manufacturing processes. This review addresses four of them, all of which are topics that the author has studied in order to design food manufacturing processes that are favorable from the standpoint of food engineering. They include chromatographic separation through continuous separation with a simulated moving adsorber, lipid oxidation kinetics in emulsions and microencapsulated systems, kinetic analysis and extraction in subcritical water, and water migration in pasta.

Key words: Chromatographic separation, lipid oxidation, subcritical water, water migration, pasta

Food science, a subdivision of agricultural chemistry, consists of two main branches: the production of foods and food materials from farm, marine, and animal products, and understanding what happens to them in the body after they are consumed. Merging these branches is necessary if food science is to contribute to healthier living. Furthermore, a better understanding of the physiological processes in the body and the chemical properties of the raw materials used to make food is necessary in order to allow for efficient and large-scale food production.

Agricultural chemists rely on a number of methodologies to deepen their understanding of these issues. The author in particular has studied the basics of food production with the goal of improving the economics of the process, focusing specifically on improving efficiency and elucidating phenomena that relate to transport processes and chemical reaction engineering.

This article addresses four topics within this area of interest. The first involves liquid chromatographic separation, including continuous separation of two components, using simulated moving-bed adsorbers. This topic also includes the analysis of distribution and adsorption equilibrium between the liquid and solid (or resin and gel) phases. Retardation of lipid oxidation through microencapsulation is also addressed, including lipid oxidation kinetics in bulk and oil-in-water (O/W) emulsion systems. After this, food manufacturing applications of subcritical water, or pressurized water ranging in temperature from 100 to 374°C, are discussed. Finally, water migration in pasta is reviewed.

Liquid chromatographic separation

Liquid chromatography is a separatory and analytical method that relies on the difference in migration rates among solutes in a column packed with gel or resin. Although chromatography is typically operated in batch mode, continuous separation of two solutes can be realized by using a simulated moving-bed.

Continuous separation by a simulated moving-bed adsorber.

The chromatographic batch-type process is simple but has some disadvantages, in that it makes ineffective use of the whole adsorbent bed, consumes a large amount of desorbents, requires a large difference in the adsorption equilibria between the adsorbates, and operates discontinuously. Separation using a simulated moving-bed adsorber can overcome these disadvantages, although the

number of solutes is usually limited to just two. The process was originally developed by Universal Oil Products [1] and has been applied to, among others, the commercial separation of glucose and fructose in the production of high-fructose syrup. Overall, however, there are few designs that utilize this technique, which will be referred to as simulated moving-bed chromatography (SMBC) in this article.

Although simulated moving-bed operation does not include the real movement of the adsorbent particles, the operation can be easily understood in terms of a hypothetical moving-bed adsorber, which separates two solutes continuously by providing a counter-current of solid adsorbent to the direction of liquid desorbent flow. The strongly and weakly adsorptive solutes are designated here as A and B, respectively.

The bed, packed with gel or resin, is divided into four zones, labeled I to IV, that each perform a different primary function (Fig. 1). A mixture of A and B is continuously fed into the system; A is adsorbed mostly in II and carried to III and IV by the movement of the adsorbent particles, while B mostly passes through II and is almost completely withdrawn by a raffinate stream. Any amount of B that becomes adsorbed in II desorbs in III. However, most A that is adsorbed in II is desorbed in IV, joining the desorbent stream passing through the zone and getting extracted between III and IV. Meanwhile, any B remaining in the desorbent stream after II is adsorbed in I, moving back toward the point for raffinate extraction. Because the desorbent emerging from I is nearly pure, it can be recycled.

The actual movement of adsorbent particles is difficult to achieve. However, the counter-current movement of liquid and adsorbent can be simulated by periodically shifting the introduction and withdrawal points of the liquid streams against columns fixed in the direction of this flow; hence, the “simulated” moving-bed. We developed two mathematical models to calculate the concentration profiles of the two components in the adsorber [2]; one is an intermittent moving-bed model which expresses the actual mode of operation and enables the calculation of transient concentration changes, while the other is a continuous moving-bed model, based on the hypothetical movement described above, that can be used to calculate steady-state concentrations.

SMBC contains many operational variables, such as the total number of small columns N_t , number of columns in a given zone N_n (where n corresponds to I-IV), individual column length L_A , interval of transportation of introduction and withdrawal points T , and superficial velocity of liquid flow for a given zone in the fixed bed v_n . The parameter defined by Eq. (1) identifies the ratio of the amount of solute transported by the liquid phase to that transported by the adsorbent phase.

$$\beta_{nk} = u_n / [u_s(1 - \varepsilon_b)K_k] \quad (1)$$

where ε_b is the void fraction of the bed, K_k is the distribution coefficient of component k (where k corresponds to A or B), and u_n is the superficial velocity of liquid flow in the hypothetical moving-bed and is related to v_n by $u_n = v_n - \varepsilon_b L_A / T$. In order to obtain good separation, β_{nk} should be set in the manner shown in Table 1 [2]. Fig. 2 illustrates the effect of β_{nk} on separation. The β_{nk} values in Fig. 2(a) satisfy the criteria in Table 1, providing a good separation for glucose and fructose, which are weakly and strongly adsorptive to the adsorbent, respectively. On the other hand, a good separation was not obtained in Fig. 2(b), as these β_{nk} values do not satisfy the established criteria.

Unfortunately, the aforementioned operational variables are not useful in designing or constructing SMBCs. A simplified method has been proposed by which to determine the column length, their arrangement in the four zones, and operating conditions in cases where the adsorption isotherms of the two components are linear and independent of each other [3].

SMBC has been successfully applied to continuous separation of α -cyclodextrin and glucose [4] and continuous desalting of proteins [5]. It was also useful in the continuous separation of maltose and glucose, in which case the separation efficiency of this technique and that of batch-type chromatographic separation were compared [6]. Finally, SMBC has also been used to separate glucose-salt mixtures with non-linear and linear adsorption isotherms [7], as well as glycerol and sodium chloride mixtures that exhibited both linear and unfavorable adsorption isotherms [8].

Although SMBC usually consists of four zones, continuous separation of two components is, in principle, possible using only those three which correspond to II to IV in Fig. 1 [9]. A method for continuous separation of three components has also been proposed, in which the resin used to pack the columns alternates between two different kinds [10].

Continuous separation of multiple components can be achieved using rotating annular chromatography [11], but its separation efficiency is the same as that of conventional batch-type chromatography.

Reactive chromatographic operations.

We have developed a new process for producing high-fructose syrup containing more than 50% fructose using a system that combines selective column-based adsorption of fructose and immobilized glucose isomerase reactors [12]. As shown schematically in Fig. 3(a), the system is divided into three zones, I to III, by the introduction and withdrawal points of the liquid streams; these correspond to II to IV in the previously described SMBC system. An adsorbent that is more selective for fructose than glucose is packed into the adsorption columns. In addition, reactors and adsorption columns are arranged in an alternating pattern in I, while II and III contain only adsorption columns. The adsorbent particles move to the right through the bed, skipping the reactors. An equilibrium mixture of glucose and fructose introduced by a feed stream flows into the adsorption column in I, where fructose in the mixture is adsorbed and glucose content increases as a result. This solution leaves the adsorption column and is then introduced to the reactor, where glucose is converted to fructose. By alternating the mixture through adsorption columns and reactors, glucose is almost completely converted while the resulting fructose is almost completely adsorbed. Adsorbed fructose is then carried to II and III by the movement of the adsorbent particles; most of the fructose is then desorbed in III and joins the liquid stream passing through the zone, being recovered in the product stream.

Both the intermittent and continuous moving-bed models have been proposed for the calculation of concentration profiles in this system [12]. They are both similar to those used for SMBC, although they include reaction terms for the immobilized glucose isomerase; note that the β_{nk} criteria that were defined for SMBC apply here as well. Overall, this system was predicted to successfully produce high-fructose syrup, as shown in Fig. 3(b). In addition, since the curves in the figure were calculated using the continuous moving-bed model, they accurately express the experimental profiles. This system requires less desorbent than fixed-bed adsorber or simulated moving-bed processes in order to produce syrup with fructose content lower than 65%.

Because enzymes usually migrate faster than substrates and products in gel chromatographic columns, an enzyme reactor which could allow for continuous use without chemical or physical immobilization was successfully developed. Such a reactor successfully operated for an extended period, causing the hydrolysis of maltose to glucose using glucoamylase [13].

A theoretical method has been proposed for predicting the pulse responses in immobilized enzyme columns in which the irreversible [14], reversible, and consecutive [15] reactions are catalyzed. This method was applied for the determination of pyruvate, L-lactate, and glutamic pyruvic transaminase concentrations using an immobilized lactate dehydrogenase column [16].

Analysis of adsorption equilibrium.

Chromatographic separation is affected by both the adsorption equilibria, or distribution coefficients, and the intra- and interparticle diffusion coefficients of the solutes. Diffusion coefficients of saccharides and amino acids in cross-linked polymers have been measured previously [17].

Cation-exchange resin is commonly used for the separation of saccharides. Factors affecting this separation have been examined, and include divinylbenzene content [18-20], counter-ion form [19, 21], temperature [22], and solute concentration [23]. Water is usually used as the eluent in the separation of saccharides with cation-exchange resins, though the addition of alcohol can also be used, affecting distribution coefficients [24].

Maltooligosaccharides thermally degrade at about 200°C, while cation-exchange resins are stable until 350°C. Based on this fact, a thermogravimetric method under nitrogen atmosphere was developed to measure the distribution coefficients of saccharides in resins [25]. This method was effective, especially when the bulk solute concentration was high.

The intrinsic distribution coefficient of a solute for a given resin, K , is expressed in Eq. (2), based on equal chemical potentials for the solute in both the external solution and resin phases [26].

$$K = \gamma_0 \exp(-\Pi v_s / RT) \quad (2)$$

where Π is the swelling pressure of the resin, v_s is the partial molar volume of the solute, R is the gas constant, T is the absolute temperature, and γ_0 is the parameter reflecting both the steric effect of the resin matrix and the ratio of the activity coefficients of the solute between the phases. Eq. (2) indicates that the swelling pressure of the resin plays an important role in the distribution, a statement which also applies to ligand exchange. A model expressing the apparent distribution coefficient, K_{app} , which contains the effects of both K and the binding constant of the solute to the counter-ion of the cation-exchange resin, B , has been proposed and used to estimate the B values of some solutes [27]. A method to estimate the Π and B values simultaneously has also been developed [28], and has been applied for several solutes as well [29-31].

The distribution coefficients of maltooligosaccharides on a hydrophilic vinyl polymer gel have been measured [32]. Temperature dependence of the retention factor for some saccharides on hydrophobic resin was also analyzed based on Kirrhoff's law, while the enthalpy change for distribution was calculated [33]. Meanwhile, the temperature dependence of the distribution coefficients was determined for caffeine and vanillin on hydrophobic resin in aqueous systems [34], for hydrophobic solutes on porous divinylbenzene resin in methanol-water systems [35], and for hydrophobic solutes on porous methyl methacrylate resin in methanol-water systems [36].

Alkyl β -D-glucosides and n -alcohols have been separated by high-performance liquid chromatography on a porous gel of a trimethylolpropane trimethacrylate homopolymer using a mixture of water and either methanol or acetonitrile as the eluent; using the data generated from this experiment, a model for analyzing the elution characteristics of these solutes for various solvent compositions was proposed, based on the chemical potential of the solutes and eluents at the gel-eluent interface [37]. Methods for estimating the parameters of nonlinear Langmuir and Freundlich adsorption isotherms from pulse response curves have also been proposed, based on both the migration rate of the adsorbate at constant concentration and the mean residence time of the adsorbate in the bed [38].

Chromatographic methods for preparing peptide mixtures from protein hydrolysate have also been examined [39,40]. The adsorption isotherms of several dipeptides on activated carbon were measured, and the applicability of the Polanyi adsorption potential theory was examined [41].

Retardation of lipid oxidation by microencapsulation

Lipid oxidation affects the quality of food rich in lipids. Microencapsulation has been developed to retard or suppress this effect, and includes two steps: the preparation of O/W emulsions with a dense solution of encapsulating material, and their rapid dehydration. We have compared lipid oxidation kinetics in bulk, O/W, and microencapsulated systems.

Lipid oxidation in bulk samples and O/W emulsions.

Lipid autoxidation is a complicated process that proceeds through initiation, propagation, and termination steps. An equation that represents the entire process as a function of only the amounts of unreacted substrate and oxygen would be useful in predicting this process in various systems. Fig. 4 tracks the bulk autoxidation of the n -6 polyunsaturated fatty acids (PUFAs) ethyl γ -linolenate and ethyl arachidonate at 50°C and 75% relative humidity. Both processes can be expressed by an autocatalytic kinetic expression [42]:

$$dY / dt = kY(1-Y) \quad (3)$$

where Y is the fraction of the unoxidized substrate, t is time, and k is the rate constant. The k value

depended on oxygen concentration and is expressed by a Langmuir-Hinshelwood function of oxygen concentration. The inset of Fig. 4 applies the integrated form of Eq. (3) to the oxidation of the aforementioned compounds.

The same equation has been applied more generally to lipid oxidation by Özilgen and Özilgen [43]. The equation was applicable to other n-6 PUFAs and the first half of the process for n-3 PUFAs; the latter half of this process can be empirically expressed by first-order kinetics [42]. In addition, these rate expressions have also been applied to the autoxidation of polyunsaturated acylglycerols [44]. Furthermore, the entire oxidation process of *cis*-9 and *trans*-11 isomers of conjugated linoleic acid can be expressed by the autocatalytic rate expression, while the first and latter halves of the oxidation of the *trans*-10 and *cis*-12 isomers can be tracked by the autocatalytic expression and first-order kinetics, respectively [45].

The autoxidation of the ethyl esters of n-3 and n-6 PUFAs has been followed using thermogravimetry, calorimetry, and gas chromatography [46]. Thermogravimetric measurements indicated a 1:1 stoichiometry between n-6 PUFA and oxygen consumption throughout the process, while the stoichiometric coefficient between the n-3 PUFAs and oxygen was dependent on the fraction of the unoxidized substrate, with a value of 1:1 for $Y > 0.5$ and greater values as the reaction progressed. Calorimetric measurements gave identical results.

The oxidation of linoleic acid and methyl linoleate mixed with saturated fatty acids or the methyl esters of those acids, respectively, could be expressed by both the autocatalytic rate expression as well as that of the fatty acid alone. The rate constants for the linoleic acid mixtures were proportional to the molar fraction of linoleic acid alone [47], while the same applied to mixtures of methyl linoleate with methyl octanoate, laurate, or palmitate, given the independent evaporation of the additional compounds [48]. When two PUFAs or their esters were mixed, oxidation of the less oxidatively stable PUFA accelerated as its content in the mixture decreased, while oxidation of the more oxidatively stable PUFA slowed with decreasing content [49]. When two polyunsaturated acylglycerols were mixed, one would dilute the other, though the decomposition products would accelerate the process. However, a mixture of 1-monolinolein and either a saturated or monounsaturated acylglycerol followed the established autocatalytic kinetics; the rate constants were in fact greater than those predicted assuming that the acylglycerol acted merely as a diluent [50]. In addition, the oxidation rate constants of mono-, di-, and trilinoleoyl glycerols diluted with either 1-undecanol or hexadecane were measured [51]. These values were proportional to concentration for all substrates, suggesting that no intramolecular radical chain reaction between the residues occurred. Oxidation of oleoyl residue of its esters with ethylene glycol, glycerol, and erythritol was also kinetically analyzed [52].

The oxidation of linoleic acid in the presence of either L-ascorbic acid or saturated acyl L-ascorbate was also assessed [53]. The addition of the ascorbates lengthened the oxidation induction period, though the autocatalytic rate equation was still applicable overall. The addition of 1-pentyl, 1-hexyl, or 1-heptyl ferulate suppressed oxidation [54]; the greater effect of the alkyl ferulates is likely the result of their increased solubility in linoleic acid.

The oxidation of methyl linoleate droplets with median diameters of 17 nm to 8.0 μm in O/W emulsions can be expressed by the autocatalytic rate expression; overall, the rate constant was lower for smaller oil droplets [55]. Generally, included surfactant molecules cover the surface of oil droplets and penetrate to the oil phase; in this study, the surfactant hydrophobic moiety was a lauroyl residue, a saturated acyl chain. This penetration apparently diluted the substrate, resulting in a decreased rate constant.

The effect of oil droplet size on oxidation in O/W systems was further examined for methyl linoleate, as well as for methyl α -linolenate, in an additional study [56]. The emulsions in this study had a mean droplet size of approximately 1 to 30 μm . The oxidation of methyl linoleate during the entire process and that of methyl α -linolenate during the first half of the process did not depend on droplet size, though the methyl α -linolenate rate accelerated for smaller droplet sizes during the second half of the process, at which point more oxygen was consumed.

It is not easy to duplicate experimental conditions for variously sized droplets; as a result,

studying the effects of droplet size can be very difficult. Therefore, additional research relied on computational simulations, where factors other than droplet size could be ignored [57]. Overall, size significantly affected the oxidation process when the oxidized molecules were gradually and randomly formed at regular intervals. Notably, oxidation was retarded for emulsions with smaller droplet sizes.

O/W emulsions of methyl linoleate with either ascorbic acid or acyl ascorbate were also studied when either the hydrophilic prooxidant 2,2'-azobis(2-aminopropane) dihydrochloride (AAPH) or the lipophilic prooxidant 2,2'-azobis(2,4-dimethylvaleronitrile) were added to the emulsion [58]. It was suggested that most of the ascorbic acid molecules in the emulsion were present in the water phase and suppressed AAPH-induced oxidation at the interface, while the dodecanoyl and hexadecanoyl ascorbates were thought to have been dissolved predominantly in the oil phase, contributing to the suppression of inherent oxidation.

Finally, (+)-catechin degradation in O/W emulsions with and without added ascorbic acid or acyl ascorbate has also been kinetically analyzed [59]. The first-order rate constant depended on the amount of the additive present; however, hexadecanoyl ascorbate addition had no effect on rate constant, regardless of amount. The rate constant with each ascorbate for smaller oil droplets was lower than that for larger droplets.

Oxidation of microencapsulated lipids.

Methyl linoleate, linoleic acid, and ethyl eicosapentaenoate were microencapsulated in saccharide and protein using a single-droplet drying method; their overall susceptibility to oxidation depended on the combination of the lipid and the encapsulating material [60]. Another study encapsulated two types of lipids rich in arachidonic acid in various saccharides, in which soluble soybean polysaccharide (SSPS) and gum arabic showed the best oxidation suppression [61]. SSPS microencapsulation was also effective at suppressing linoleic acid [62]. Further research fractionated SSPS into its low and high molecular weight components to examine their respective antioxidative and emulsifying properties, and indicated that the low molecular weight component in particular was responsible for the oxidative suppression of linoleic acid observed in the previous study [63].

Methyl linoleate was also encapsulated with gum arabic by drying with both hot air and freeze-drying [64]. Overall, relative storage humidity drove oxidation, with the freeze-drying sample oxidizing more slowly throughout. The effects of the drying method and relative humidity were also tested for linoleic acid samples that had been encapsulated in polysaccharides [65] and in gum arabic using a spray drying technique [66]. In the latter case, inlet air temperature played no effect, but the atomizer rotational speed affected both size and moisture content, leading to slower oxidation for larger microcapsules.

Because oxygen diffusion through dehydrated encapsulating material seems to affect oxidation rate, additional work has been completed to determine the apparent diffusion coefficient of oxygen for various potential materials, including dehydrated protein and saccharide films [67].

Oxidation in encapsulated lipids has two distinct features: rapid oxidation in the early stages of storage, and the leveling off of that oxidation over time. The conventional diffusion-oxidation model cannot account for this characteristic; however, another model, which considers the distribution of the free energy of activation for the rate constant of the oxidation kinetics, accurately predicted experimentally observed transient changes in the unoxidized substrate within the microcapsule [68, 69]. This difference in oxidation susceptibility was thought to be reflected in the free energy of activation, ΔG^\ddagger , while the distribution of ΔG^\ddagger was assumed to be Gaussian, with a standard deviation of σ and the mean value $\overline{\Delta G^\ddagger}$. The overall fraction of unoxidized lipid in a microcapsule at any time t , $\bar{Y}(t)$, can be expressed by Eq. (4).

$$\bar{Y}(t) = \frac{RT}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} \exp\left[-\frac{(RT/\sigma)^2 (\ln k - \ln \bar{k})^2}{2}\right] \frac{e^{-kt}}{(1-Y_0)/Y_0 + e^{-kt}} d(\ln k) \quad (4)$$

where \bar{k} is the rate constant corresponding to $\Delta\bar{G}^\ddagger$ and Y_0 is the initial value of Y . As shown in Fig. 5, this model works well for linoleic acid.

Separately, PUFAs were emulsified with cyclodextrins, dehydrated, and then autoxidized. Autoxidation of the encapsulated sample was allowed to proceed until the value of the unoxidized fraction reached its absolute minimal value Y_∞ . Thermogravimetric analysis of the encapsulated samples suggested that some of the PUFA molecules were trapped in the cyclodextrin cavity [70]. In a separate study, linoleic acid was encapsulated with varying weight ratios of saccharides through hot air drying. The weight ratio strongly affected the autoxidation process, with autoxidation suppressed for smaller values. Again, autoxidation leveled off at a fraction of Y_∞ of the unoxidized substrate. The dependence of this value on the weight ratio was analyzed with two- and three-dimensional percolation models, with the two-dimensional models accurately expressing the experimental dependence [71].

Later, linoleic acid was encapsulated with either gum arabic or maltodextrin by spray drying, with smaller droplets oxidizing more slowly [72]. These effects, as well as those of storage temperature and the oil/encapsulator weight ratio, were analyzed for a methyl linoleate and maltodextrin sample, also prepared by spray drying [73]. Overall, methyl linoleate oxidation was more retarded for smaller droplets and lower weight ratios. Percolation theory was then used to demonstrate the dependence of the level at which oxidation ceases on weight ratio. Finally, it was shown that lipid exposed on the surface more easily underwent oxidation.

Soottitantawat et al. [74] showed that the surface oil content for microencapsulated *d*-limonene was lower for smaller oil droplets. These effects were examined by simulated two- and three-dimensional percolation models, which showed that surface oil content decreased with general oil content and for smaller oil droplets, as shown in Fig. 6 [75]. A further study examined changes in surface oil content with respect to the droplet-to-microcapsule size ratios using a two-dimensional percolation model, and showed no significant effect [76]. Additional work found that low surface oil content is attainable when larger than or equal to the surface tension of the encapsulated lipid [77].

The fraction of extractable linoleic acid for saccharide microcapsules prepared by a single-droplet drying method was lower for lower oil-to-encapsulator weight ratios, and correlated fairly well with the fraction of easily oxidizable linoleic acid [78]. Autoxidation and solvent extraction of these microcapsules were also examined by freeze-drying [79].

An alternate experiment encapsulated linoleic acid and 6-*O*-palmitoyl L-ascorbate at various molar ratios within either maltodextrin or gum arabic. At higher ratios, the oil droplets were smaller and the oxidative stabilities were higher. 6-*O*-Capryloyl, caproyl, and lauroyl L-ascorbates were also tested; except for capryloyl L-ascorbate, all additives gave smaller particle diameters and decreased oxidation [80]. Meanwhile, the oxidation of arachidonic acid was successfully retarded by microencapsulation in gum arabic or SSPS, while the oxidation of the arachidonoyl moiety of 6-*O*-arachidonoyl L-ascorbate proceeded even more slowly given similar conditions [81].

Encapsulating linoleic acid in gum arabic or maltodextrin with 1-pentyl, 1-hexyl, or 1-heptyl ferulate had comparably higher antioxidative effects over ferulic acid [82]. The oxidatively suppressive effects of α -tocopherol on methyl linoleate in β -cyclodextrin microcapsules was also kinetically examined using the Weibull model [83]. Finally, fish oil was encapsulated with 6-*O*-decanoyl L-ascorbate in maltodextrin, gum arabic, and SSPS. Eicosapentaenoic and docosahexaenoic acids showed high oxidative stability, with the best performance observed first in SSPS and then in gum arabic [84].

The preparation of water-in-oil-in-water (W/O/W) emulsions by using an aqueous polymer as a trapping agent has also been investigated, and yielded powdery emulsions [85,86]. Microcapsules were successfully developed from W/O/W emulsions by drying with hot air or by freeze-drying the emulsion using a single-droplet [87] or spray-drying method [88].

Dispersion stability of O/W emulsions.

A model for estimating the stability of emulsions in cream layers has been developed that

measures the ratio of the kinetic energy of an emulsion particle to that of a molecule. By using Derjaguin–Landau–Verwey–Overbeek theory and Stokes' law, the kinetic energy of a particle needed for it to cross over a potential barrier was calculated by considering all the forces working on the particle. As such, the above ratio represents the empirically known effects of particle properties and the continuous phase on stability [89]. Note that adding neutral polymers to O/W emulsions destabilizes them; this can be explained by incorporating the depletion effect into this model [90].

Utilization of subcritical water in food manufacturing

Subcritical water, or compressed hot water, is water which maintains its liquid state above 100°C under pressure yet which remains below the critical point. Subcritical water is distinct from ambient water in that it has both a large ion product and a low relative dielectric constant, as shown in Fig. 7 [91]. The former property means that hydrogen and hydroxide ion concentrations are high, enabling subcritical water to act as either an acid or base catalyst, while the latter means that it can be used to extract hydrophobic substances.

Reactions in subcritical water.

A tubular reactor was used to track the hydrolysis of various disaccharides in subcritical water, including those consisting of two glucose residues, a glucose and fructose residue, and a glucose and galactose residue. Susceptibility to hydrolysis largely depended on the type of disaccharide, with the electrostatic potential charge of the glycosidic oxygen atoms contributing significantly [92]. Meanwhile, the rate of maltose decomposition could be approximated by first-order kinetics at early stages, but accelerated and deviated later on. The effluent pH decreased as reactor residence time increased, which had a corresponding effect on decomposition rate and glucose formation [93]. Furthermore, sucrose decomposition was found to be kinetically autocatalytic, with the rate being proportional to the product of the sucrose and acid concentrations; in this case, acid only contributed minimally [94].

The degradation kinetics of hexoses [95] and pentose and hexauronic acids [96] in subcritical water was analyzed by applying the Weibull equation. Sodium chloride accelerated hexose, but not sucrose degradation [97].

The hydrolysis of various trisaccharides consisting of glucose, galactose, and fructose residues proceeded consecutively, with one cleavage preceding the next [98]. Meanwhile, maltooligosaccharides with a degree of polymerization (DP) of 3 to 6 tended to hydrolyze the exo-site glycosidic bond more quickly than the endo-site one [99]. Fig. 8 shows changes in maltooligosaccharide concentration that occurred during the subcritical water treatment of maltohexaose.

The degradation processes of D-galacturonic acid and sodium galacturonate were also analyzed so as to estimate the activation energy and frequency factor of the reaction [100]. Meanwhile, the formation of glucurolactone during glucuronic acid treatment was monitored by ESI-TOF-MS and ¹H NMR. This degradation consisted of the reversible conversion of glucuronic acid to glucuronolactone and the irreversible degradation of both compounds [101]. Building on this, the antioxidative capacity of the degradation products of glucuronic and galacturonic acid were assessed, but did not exhibit any antioxidative activity for linoleic acid. However, the lyophilized degradation products did inhibit linoleic acid oxidation that had been initiated by AAPH in an aqueous dispersion, prolonging the induction period and decelerating oxygen consumption in the propagation period [102]. In addition, the degradation processes of *N*-acetyl-D-glucosamine and D-glucosamine obeyed first-order kinetics, with the main degradation product of the latter being 5-(hydroxymethyl)-furfural. This compound was a weak radical scavenger, although the decomposition product of *N*-acetyl-glucosamine was not [103].

The degradation processes of branched-chain amino acids were shown to obey first-order kinetics as well [104]. When glycyl-L-leucine and L-leucyl-glycine were treated in subcritical water, each initially formed the other, but then both gradually decomposed. Ring formation occurred

regardless, leaving *cyclo*-(glycyl-L-leucine) as one of the final products (Fig. 9) [105].

The hydrolysis of fatty acid esters with various acyl and alkyl chains also obeyed first-order kinetics. Steric hindrance was found to increase the activation energy of hydrolysis [106]. Meanwhile, the decomposition of monoacyl glycerols and their corresponding fatty acids was measured under heating conditions where the reaction temperature increased linearly from room temperature to 350°C at various rates. This data was then used to estimate the corresponding activation energies and frequency factors. Both sets of compounds obeyed first-order kinetics, while the monoacyl glycerols first broke down to the constituent fatty acids before decomposing further. Generally, both the activation energy and the frequency factor for these compounds were smaller for longer acyl chains [107].

Again, the degradation of 10 phenolic compounds and one flavanol were demonstrated to follow first-order kinetics. The degradation products were stable at high temperature and exhibited radical scavenging activity against DPPH [108].

The condensation reaction of angiotensin II and tartaric acid in water at 100–140°C proceeded without any added catalyst. One of the products was confirmed to be *N*-CO-tartarylangiotensin II by LC-MS, positive-ion MALDI-MS, and the fluorescamine method. Malic and succinic acids were also condensed with the peptide [109].

When mannose, fructose, and glucose were treated in subcritical water at 220°C, isomerization of mannose to fructose occurred most frequently, followed by mannose to glucose; no isomerization of glucose to mannose was observed [110]. Conversion of linoleic acid to its conjugated isomers also occurred, but in low yields [111]. Under subcritical aqueous conditions, primary and secondary alcohols promoted the conversion and isomerization of glucose to afford fructose and mannose with high and low selectivity, respectively [112].

Extraction with subcritical water.

Defatted rice bran has been treated in subcritical water at various temperatures, after which each extract was evaluated for yield, radical scavenging activity, molecular mass distribution, antioxidative activity, and carbohydrate, protein, total phenolic, and furfural content [113-118]. Fig. 10 shows some of these derived temperature-dependent values. Depending on the treatment temperature, the extracts exhibited emulsifying, emulsion stabilizing, forming, and/or antioxidative activity. In addition, one sample treated at temperatures between 150 and 180°C for 10 min was further treated at 250°C for 5 min, resulting in substances with emulsifying ability in the first-step treatment and antioxidative one in the second-step treatment [119]. More rapidly increasing temperature to the desired level was found to provide an even more favorable yield in a batch reactor, in addition to shortening treatment time [120].

Static and dynamic modes have also been tested at various treatment temperatures and flow rates in a packed column in order to determine the effect on protein, carbohydrate, and phenolic recovery [121]. Additional extracts were prepared after 5 min of treatment at 230°C in water and 40% (v/v) acetone, after which those substances soluble in acetone were fractionated from both. The antioxidative activities of the extracts and fractions were then tested against DPPH, hydroxyl and peroxy radicals, and hypochlorite and peroxy nitrile ions and were characterized using a 5-axe cobweb chart [122]. The mutagenicity of similar extracts prepared at various temperatures were also examined using the Umulac AT test, which showed no activity for both -S9 and +S9 [123]. Antioxidative performance for linoleic acid was then further tested for extracts prepared from 120 to 240°C. All extracts elongated the induction period in aqueous dispersions, but only the extract obtained at 240°C showed significant activity in bulk linoleic acid [124]. Additional extracts prepared after 7.5 min at 120, 150, and 180°C were combined with maltodextrin to encapsulate methyl linoleate. While the 120 and 150°C samples provided greater emulsion stability, the 180°C samples showed higher oxidative stability, as shown by the longer induction period [125].

Rice straw, corn stover, and sugar cane bagasse, all of which are agricultural waste, were treated with subcritical water at various temperatures for 10 min, yielding various amounts of reducing sugars and improving waste digestibility in cellulose and cellobiose tests [126]. Wheat bran [127],

defatted soy meal [128], okara [129], soy sauce cake [130], cereal residue [131], coconut meal [132], and kaffir lime peel [133] have all previously been treated with subcritical water, with their extracts having been characterized by, among other properties, yield, protein, carbohydrate, and total phenolic contents, and emulsifying, emulsion-stabilizing, and antioxidative ability. In addition, major flavoring compounds, including cinnamaldehyde, cinnamic acid, cinnamyl alcohol, and coumarin, were extracted from cinnamon bark; however, recovery was lower than it was for methanol, suggesting that these components might degrade in subcritical water [134].

Defatted rice bran has also been treated with an aqueous ethanol solution under subcritical conditions to recover materials with antioxidative activity. The 20% (v/v) ethanol extract was more efficient than identical treatments with just water based on total and constituent yield, DPPH radical scavenging activity, and antioxidative activity against bulk linoleic acid [135]. Similar oxidative testing revealed 80% (v/v) acetone extracts to be more efficient than both subcritical water and 40% (v/v) acetone [136]. An additional study found a 50% (v/v) acetone extract to provide the best DPPH radical scavenging ability when compared to water, 50% (v/v) ethanol, ethanol, and acetone, all of which had been treated at 230°C for 5 min [137]. Similarly obtained extracts were further subjected to acetone solubilization, which suggested that DPPH radical scavenging activity depended on total phenolic content; the fraction isolated from the 40% (v/v) acetone extract showed the highest activity [138].

In an additional study, rice straw was separated into the leaf and the upper, middle, and lower parts of the stem, all of which were treated with subcritical water at 140–260°C. The stem extracts were all very similar to each other but different from the leaf extracts. Higher temperature extracts exhibited higher radical scavenging ability overall [139]. Another case treated rice straw stems with subcritical water, ethanol, and a mixture of the two from 170 to 230°C, in which case higher general and carbohydrate yields were achieved for higher ethanol content and higher temperature [140]. Further work subjected the stems to subcritical water treatment at 260°C for anywhere from 0 to 20 min, after which the extracts obtained after 5 min were subjected to an additional treatment for anywhere from 0 to 60 min. The extended treatment gave lower total phenolic and carbohydrate content, radical scavenging ability, and metal chelating ability over time, while correlations were observed between total phenolic content and radical scavenging ability and between total carbohydrate content and metal chelating ability for all conditions [141]. Finally, the stems were subjected to subcritical fluid treatment at 230°C using ethanol and acetone with a complete range of dilution in water. The highest general and carbohydrate yields were achieved with subcritical 20% (v/v) organic solvents, while the highest phenolic content was obtained with subcritical 80% (v/v) acetone. In addition, the highest radical scavenging ability was achieved with subcritical 60% (v/v) ethanol and 80% (v/v) acetone [142].

The solubility of saturated fatty acids with even numbers of carbon atoms ranging from 8 to 18 was measured in water at temperatures ranging from 60 to 230°C under either 5 or 15 MPa. While pressure had no significant effect, fatty acid solubility did increase with temperature. At temperatures higher than about 160°C, the molar solubility was logarithmically related to the reciprocal of the absolute temperature for each fatty acid, indicating the formation of a regular solution [143]. The solubility of oleic and linoleic acids in water was also measured in the same temperature range at 15 MPa. Values were overall similar, and again demonstrated a logarithmic relationship; negative slopes of the logarithms above 150°C were constant [144].

Based on this increased solubility, a novel method for preparing finely dispersed O/W emulsions was proposed. Octanoic acid, already dissolved in water at high temperatures, was combined with an aqueous solution of a surfactant and cooled. This resulted in median oil droplet diameters of 100 nm or less, even for low surfactant concentrations [145]. Another study prepared an octanoic acid emulsion using a rotor/stator homogenizer, after which the emulsion was passed through a stainless steel tube immersed in an oil bath at 220°C and for a residence time of 60 s. Mixing the resulting solution with low levels of surfactant produced a finely dispersed emulsion, with droplet diameters of about 40 nm [146].

Water migration in pasta

Pasta is widely eaten not only in Western countries, but also in Asian countries, including Japan. It is usually distributed dry in order to improve its storage stability and make it easier to transport, and is consumed after sorption by cooking in boiling water. Water migration in both the drying and cooking processes has been experimentally examined, and a method for accurately measuring the moisture profile in pasta has been developed.

Drying of pasta.

The drying of durum wheat semolina dough was measured by thermogravimetry in temperature and relative humidity ranges of 30–90°C and 0–80%, respectively, in order to better understand the process for any arbitrary conditions. It was demonstrated that the period during which constant drying was observed is integral in accurately predicting the drying curve. The rate in this period, as well as the mass transfer coefficient measured by thermogravimetric analysis, was successfully related to the tested variables [147]. The effects of these variables were also examined using thermogravimetry and differential scanning calorimetry (DSC) in an additional study in which temperature was increased at a rate of 0.2 to 1.0°C/min. The conclusion temperature of the endothermic peak in DSC and the temperature of the inflection point of the drying curve were located near the glass transition curve [148].

Sheet-like and cylindrical pasta shrinkage both showed slight anisotropy. The Young's modulus of the dumbbell pasta specimen did not depend on the drying conditions. However, the modulus decreased with moisture content and became almost constant at values lower than 0.17 kg-H₂O/kg-d.m., suggesting that the glass transition affected the mechanical properties [149]. A further study showed that the moisture sorption and desorption isotherms of durum semolina for a temperature range of 30–80°C were well expressed by the Guggenheim-Anderson-de Boer equation; while the desorption isotherm could be overlaid with the sorption one at any temperature, a slight hysteresis was observed [150]. Meanwhile, the partial molar volume of water sorbed to durum wheat flour was measured by dilatometry, which showed that the volume increased with moisture content and reached a constant value of about 17.5 cm³/mol at 0.2 kg-H₂O/kg-d.m. [151].

Water sorption of pasta.

The temperature dependency of equilibrium moisture content and initial sorption rate in spaghetti indicated that the former is limited by starch gelatinization and the latter is governed by diffusion through pores, a process independent of starch gelatinization [152]. Later on, the water sorption kinetics of spaghetti dried under different conditions were further measured at various cooking temperatures. The maximum temperature during drying affected the enthalpy change of water sorption to a greater degree than the starch gelatinization temperature, but had no effect on the activation energy at the initial sorption rate [153]. Additional studies took place for temperature ranges of 20–90°C in 1.83 mol/L NaCl and at 80°C in 1.83 mol/L LiCl, KCl, NaBr, and NaI. The Hofmeister ion series is an index for ion effects on the equilibrium of sorption. In this case, the apparent diffusion coefficient did not correlate with the crystal radius of the salts, but did with the Stokes radius of the hydrated ions [154].

The surface smoothness of spaghetti prepared using dies showed a direct relation to the die material, with smoothness decreasing, in order, from Teflon, polypropylene, polycarbonate, aluminum, and bronze. The die material did not affect the gelatinization temperature, but the hypothetical quantity of momentarily sorbed water, used to characterize initial water intake, was higher for rougher surfaces [155].

An image processing method was developed to measure pasta moisture profiles during rehydration based on the fact that sample color brightness increases with moisture content. Fig. 11 shows the moisture distribution in spaghetti cooked for different amounts of time [156]. The moisture profile was unique in shape and suggested that various phenomenon play a role in rehydration, including water penetration into small holes and cracks on the surface, water diffusion into the bulk, and structural relaxation of the gluten matrix. The moisture content of pasta under

conditions where water diffusion plays a negligible effect was estimated by extrapolating average moisture content for increasingly smaller diameters. The values for imaginary, infinitely thin pasta gradually increased with cooking time in a manner similar to that of pasta made only of gluten; this suggested that the swelling of starch by fast gelatinization was restricted by the gluten network and that the relaxation of this network is what controlled the kinetics of pasta rehydration [157]. In a separate study, moisture distribution was studied in spaghetti prepared at three different maximum temperatures and cooked to an average moisture content of 1.71 kg-H₂O/kg-d.m; the high temperature spaghetti showed the highest values at both the surface and in the center, while the highest temperature sample showed the lowest [158].

An additional method was proposed which estimated the gelatinization temperature of starch-containing foods by observing the water sorption curve for steady increases in temperature, and was subsequently applied to dried noodles [159].

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Table 1. β_{nk} values necessary to obtain high separability in SMBC

Zone n	I	II	III	IV
β_{nA}	< 1	< 1	< 1	> 1
β_{nB}	< 1	> 1	> 1	> 1

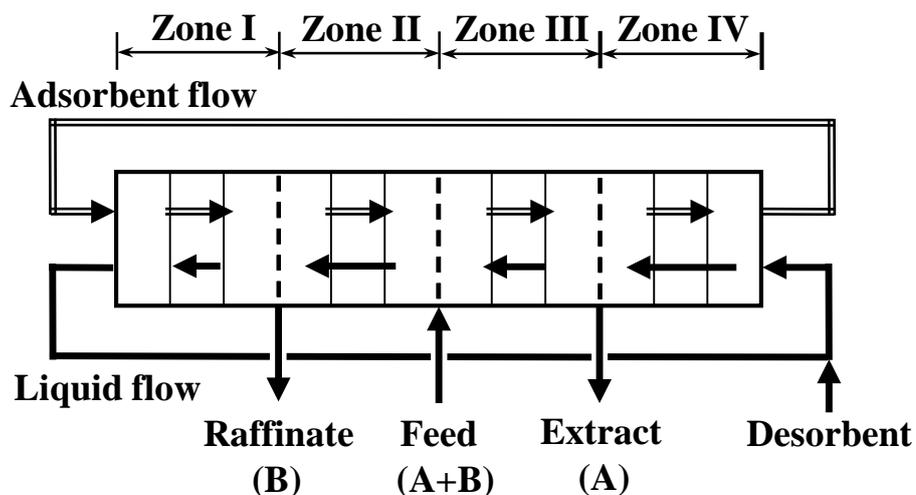


Fig. 1. Schematic representation of a simulated moving-bed adsorber.

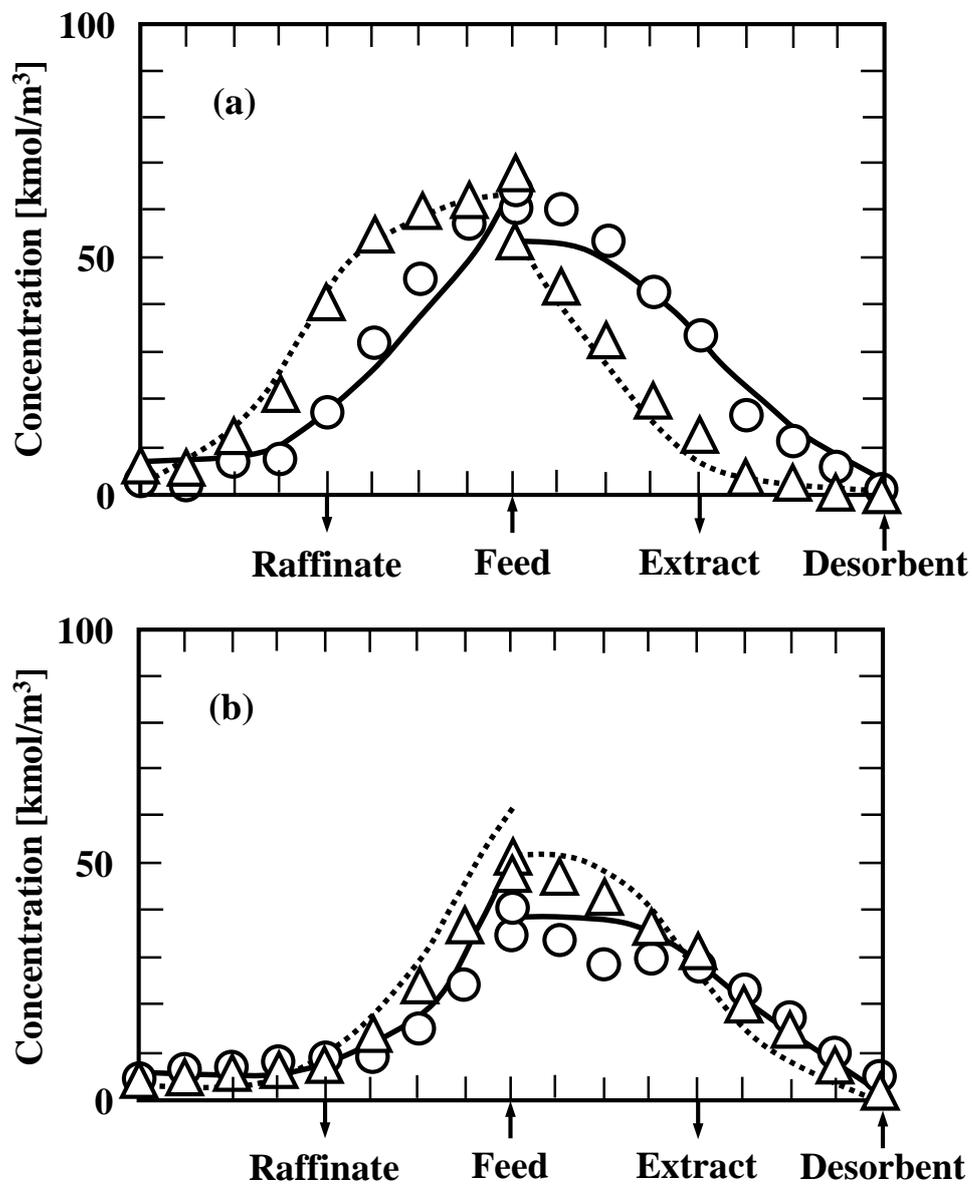


Fig. 2. Concentration profiles of glucose (○) and fructose (△) at a steady state under conditions where the criteria for β_{nk} are (a) satisfied and (b) unsatisfied. The solid and broken curves were calculated for glucose and fructose, respectively.

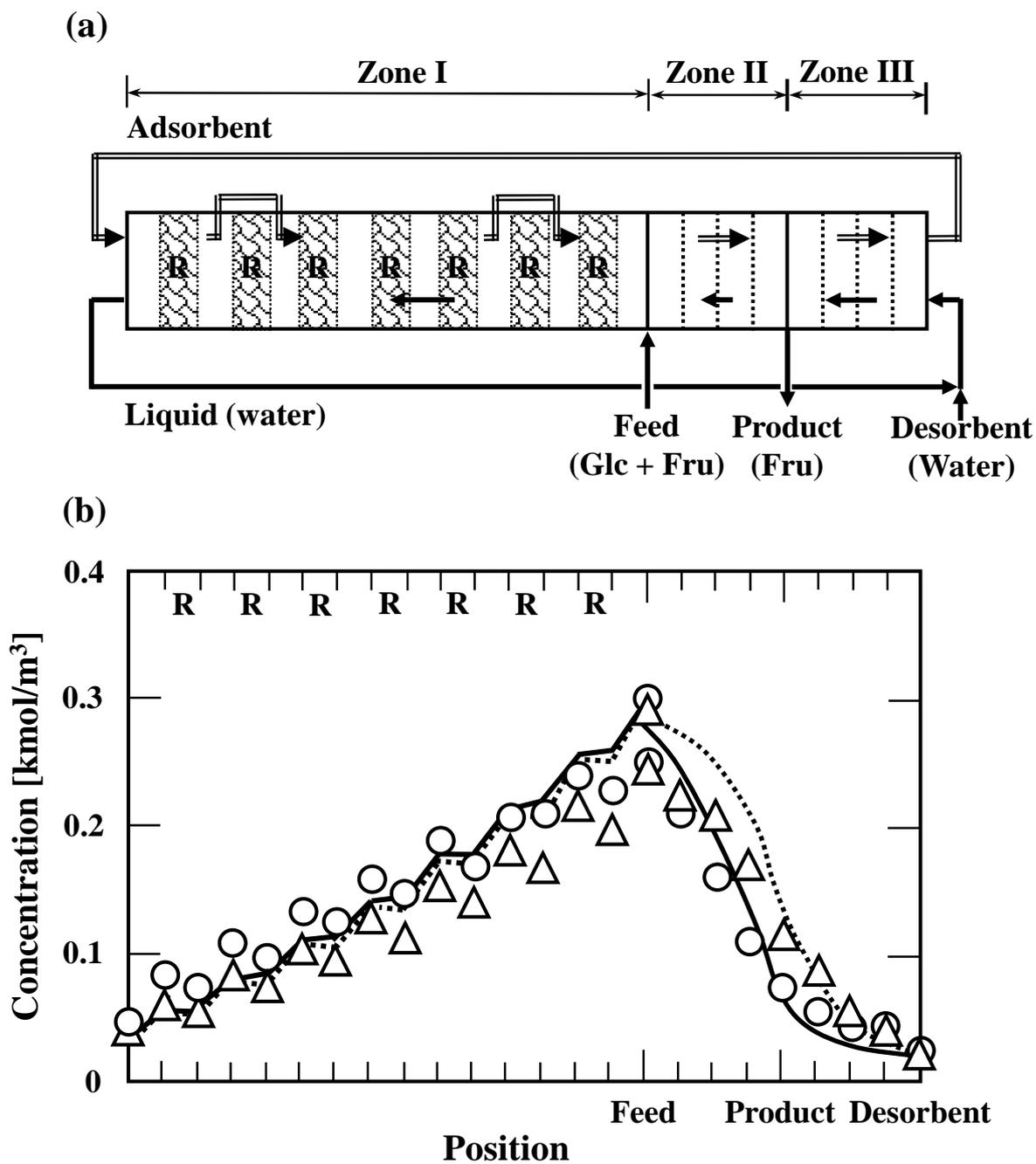


Fig. 3. (a) Schematic representation of a system combining adsorption columns and immobilized glucose isomerase reactors for producing high-fructose syrup. (b) Concentration profiles of glucose (○) and fructose (△) at a steady state for the presented system.

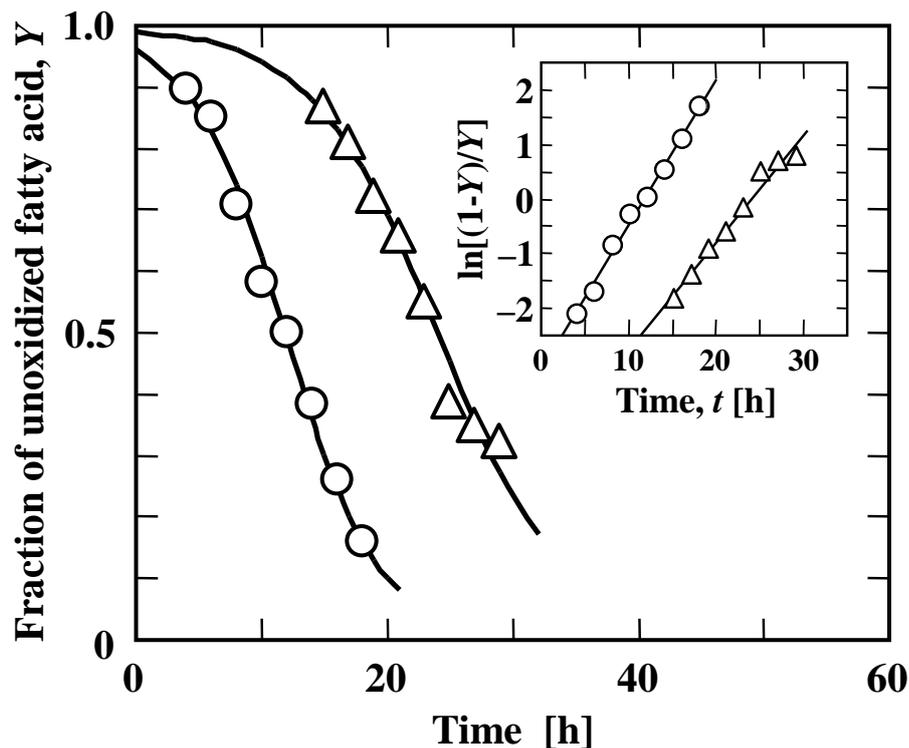


Fig. 4. Bulk oxidation of ethyl γ -linolenate (Δ) and ethyl arachidonate (\circ) at 50°C and 75% relative humidity. Inset: Applicability of the autocatalytic kinetic equation.

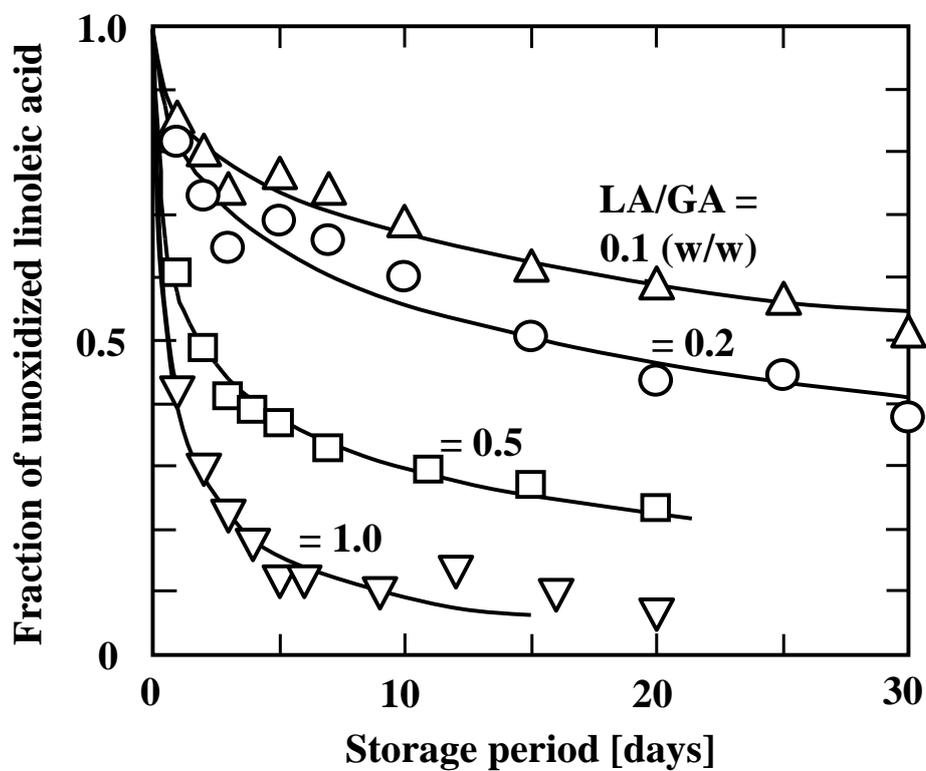


Fig. 5. Changes in the fraction of unoxidized linoleic acid encapsulated in gum arabic at weight ratios of 0.1 (Δ), 0.2 (\circ), 0.5 (\square), and 1.0 (∇). The temperature and relative humidity during storage were 37°C and 12%, respectively. The curves were calculated by Eq. (4).

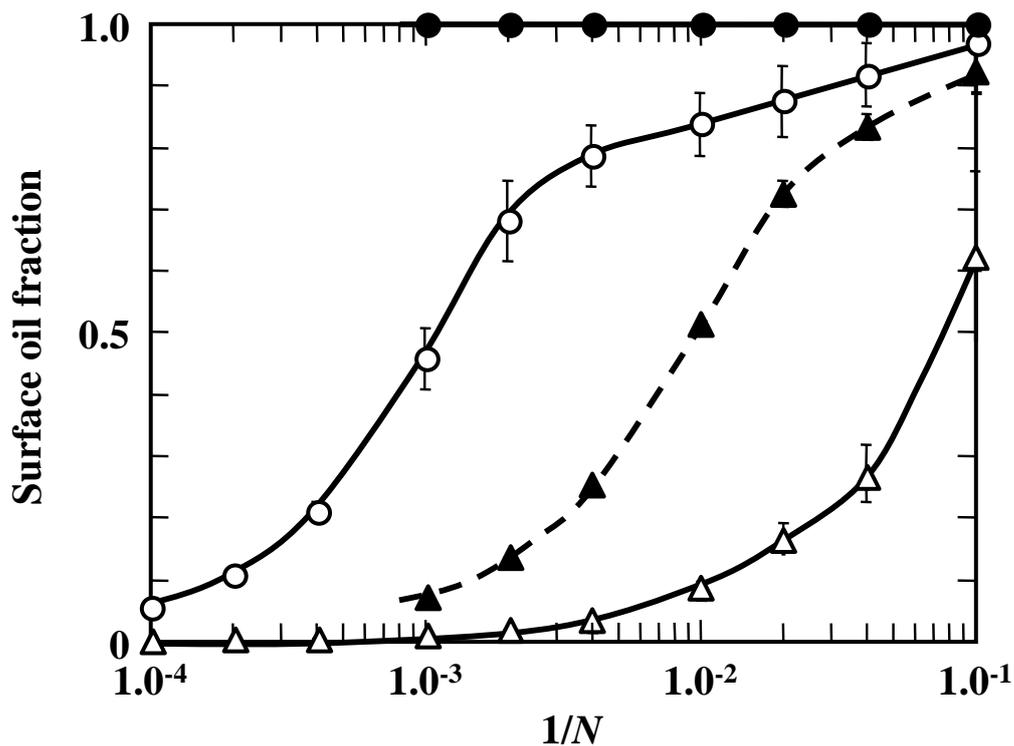


Fig. 6. Effect of oil droplet size, expressed by $1/N$, on the surface oil content of the microcapsule. N is the number by which a side of square and cube is divided in the two- and three-dimensional percolation models, respectively. Oil fractions were 0.35 (\triangle , \blacktriangle) and 0.6 (\circ , \bullet). The open and closed symbols indicate two- and three-dimensional percolation models, respectively.

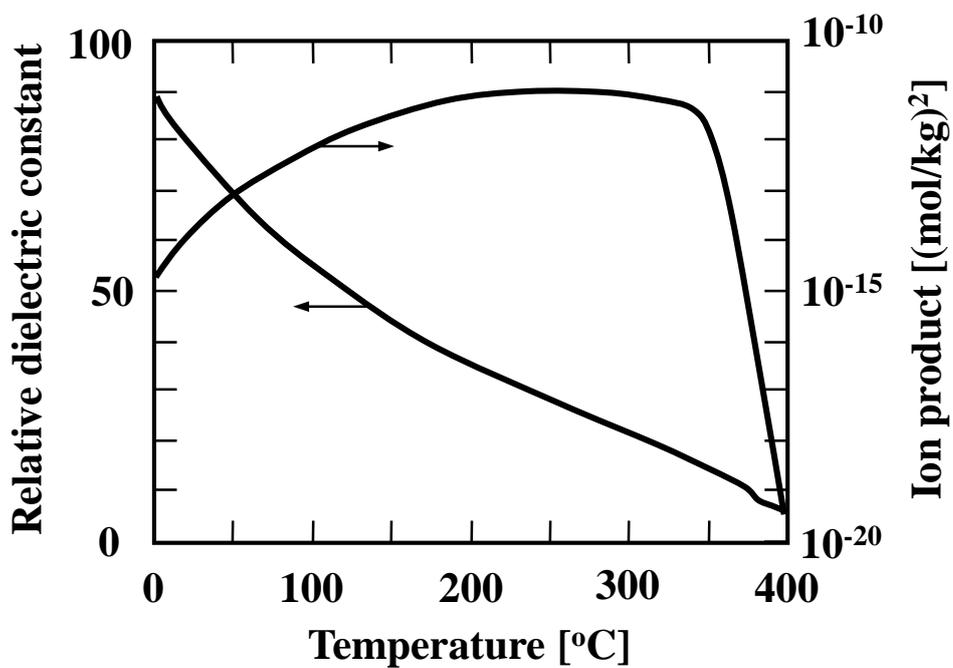


Fig. 7. Temperature dependencies of the relative dielectric constant and ion product of water.

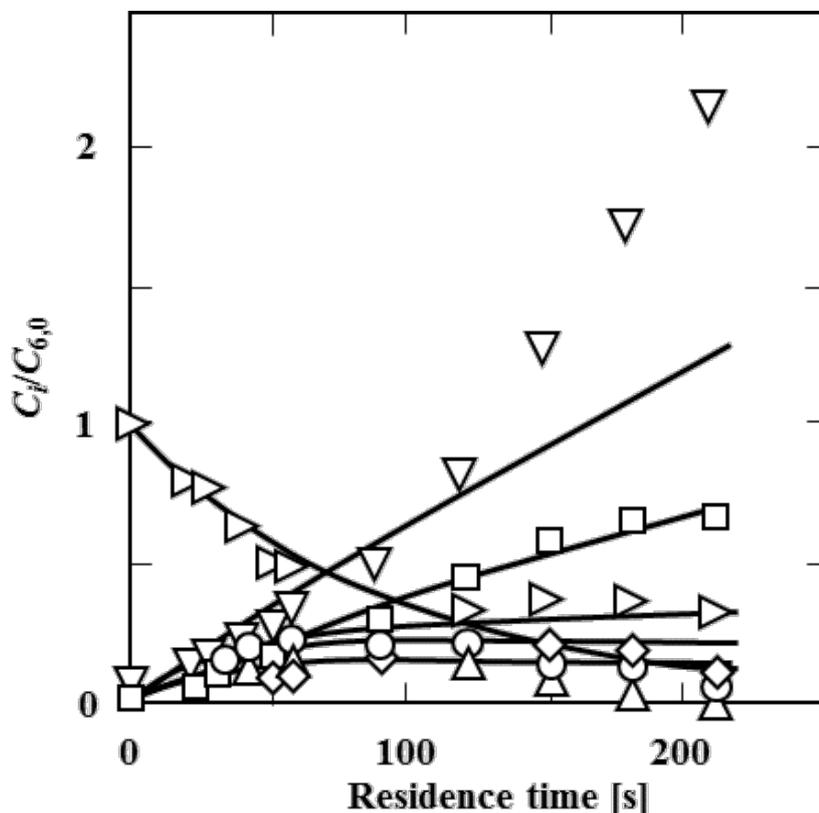


Fig. 8. Hydrolysis of maltohexaose at 220°C and 10 MPa. The residence and reaction times correspond to each other given the use of a tubular reactor. Maltohexaose (\triangleright), maltopentaose (\circ), maltotetraose (\diamond), maltotriose (\triangle), maltose (\square), and glucose (∇) concentrations are all provided. Subscript i (where $i = 1-6$) indicates the degree of polymerization of the maltooligosaccharide, while $C_{6,0}$ is the maltohexaose concentration in the feed solution.

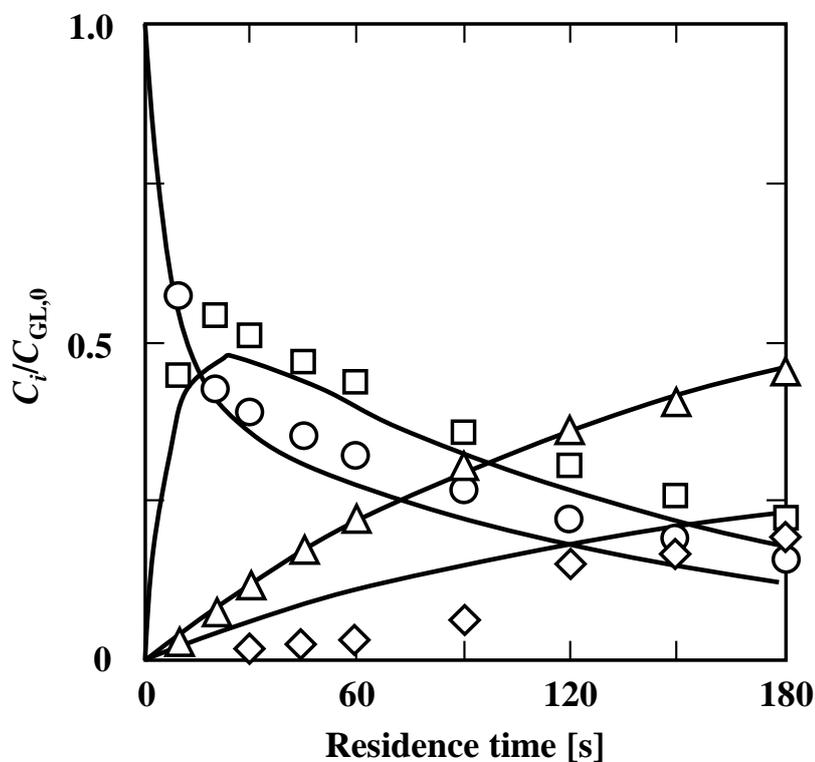


Fig. 9. Molar fractions of glycyl-L-leucine (\circ), L-leucylglycine (\square), glycine (\diamond), and *cyclo*-glycyl-L-leucine (\triangle) for the degradation of glycyl-L-leucine at 220°C and under different residence times. Subscript i indicates the substrate and the products, while $C_{GL,0}$ is the concentration of glycyl-L-leucine in the feed solution.

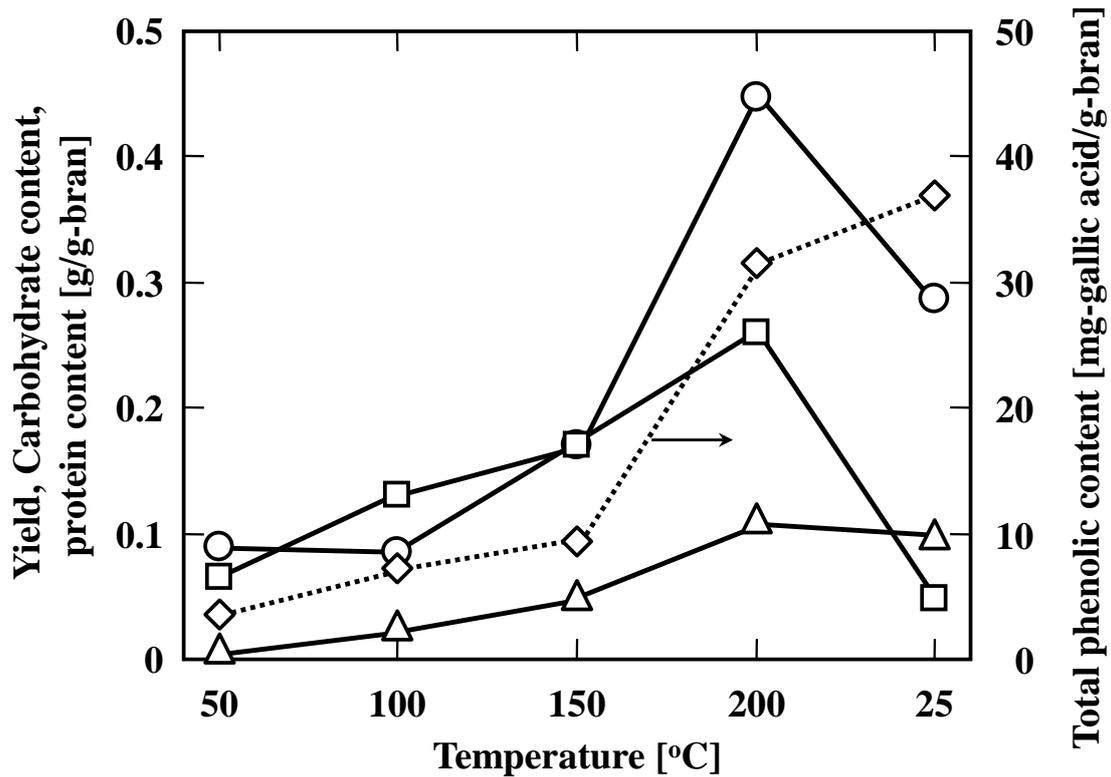


Fig. 10. Yield (○) and carbohydrate (□), protein (△), and total phenolic (◇) content of defatted rice bran extracts treated with water or subcritical water at various temperatures.

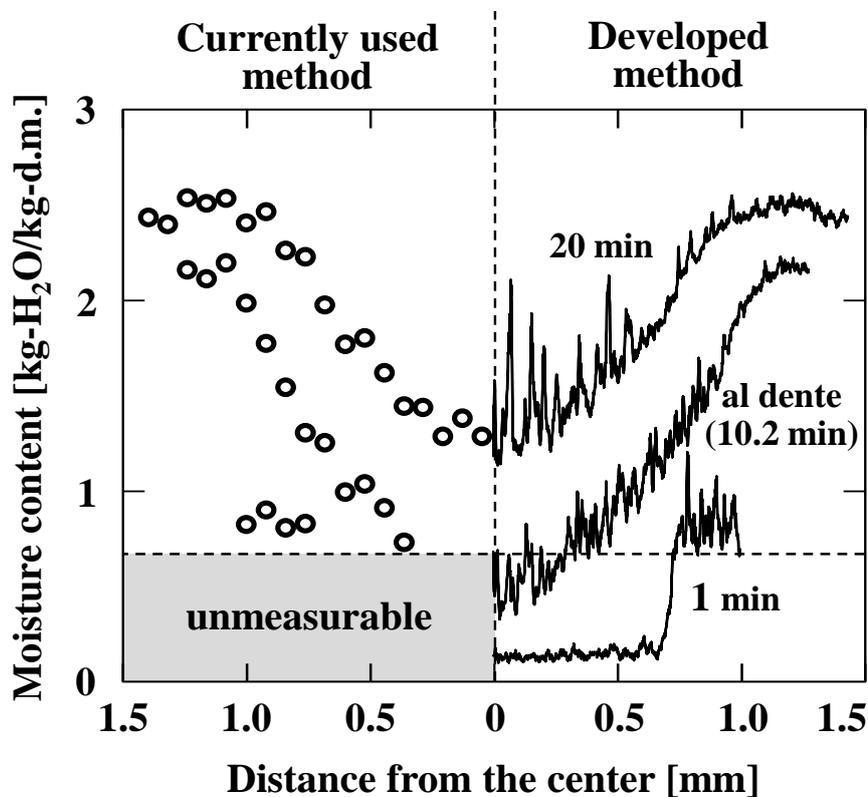


Fig. 11. Right: Moisture profiles of spaghetti rehydrated for 1, 10.2, and 20 min that were measured by the developed image processing method. Left: Imaginary profiles that can be measured using the current method.