Functional, thermal, and molecular properties of ozonated starches

K Handarini1,3, J S Hamdani2, Y Cahyana1 and I S Setiasih

1 Laboratory of Food Chemistry, Department of Food Industrial Technology, Universitas Padjadjaran, Jl. Raya Bandung - Sumedang KM 21. Jatinangor, Sumedang, West Java, Indonesia, 40600. Tel/fax: (022) 7798844/(022) 7795780.
2 Laboratory of Horticulture, Department of Agronomy, Universitas Padjadjaran, Jl. Raya Bandung - Sumedang KM 21. Jatinangor, Sumedang, West Java, Indonesia, 40600. Tel/fax: (022) 7798844/(022) 7795780.
3 Laboratory of Food Chemistry, Department of Food Technology, Faculty of Agricultural, Dr. Soetomo University, Jl. Semolowaru no 84 Surabaya 60283 East Java, Indonesia, Tel/fax: (031) 592 5970/(031) 593 8935.

Email: yorasusena28@gmail.com

Abstract. Starch modification by oxidizing agents is often carried out using H2O2 and Sodium Hypochlorite. The use of these chemicals, however, has several drawbacks such as chemical residue left in food, low recovery, high wastewater containing salt, and pollution to the environment. Ozone is a good alternative oxidant having some advantages over the other chemical oxidants in leaving no residues, producing no waste and being a powerful oxidant and generally recognized as safe (GRAS). Starch modification using ozone results in the formation of new carbonyl groups and carboxyl groups. These functional groups are derived from the oxidation of the hydroxyl group present in starch. Therefore the extent of oxidation to the starch is indicated by the amount of carbonyl and carboxyl groups formed, especially in the hydroxyl group in positions C-2, C-3, and C-6. The change in functional group of hydroxyl to carbonyl and carboxyl has an implication to the change of crystallinity, morphological, pasting, functional and thermal properties of native starch granules. Starch modification is also highly dependent on the types of starch. The fact that ozonation of starch gains considerable interest, it is thus very important to elaborate on the different effects of ozone oxidation on starch properties. This information would be useful for the development of new ozone-modified starch materials hence more choices for food industrial applications.

1. Introduction

Starch is one of the renewable resources which utilization is very important in the food and non-food industries. Starch is a biodegradable polymer commonly found in cereals, roots, tubers, nuts [1], and fruits [2, 3]. Starch can be composed of two polysaccharides, namely linear molecules called amylose and branched molecules called amyllopectin [4]. Some industries such as the food, paper, and textile industries use starch as their basic ingredient. But in its utilization, native starch has several undesirable properties. Therefore it is necessary to modify the process to produce starch with properties that are suitable for use by rearranging the structural arrangement of starch granules, resulting in a desired physicochemical increase in a property [5]. The verification process can be carried out physically,
chemically, genetically and enzymatically [3, 4]. One method that is widely used is chemical modification by oxidation.

During the oxidation process, the hydroxyl group of starch is oxidized first into a carbonyl group and then becomes a carboxyl group, which is accompanied by the depolymerization of starch molecules mainly by cleaving the amyllose and amylopectin molecules in α (1–4)-glycosidic linkages [6]. In the food industry, the use of oxidized starch has become increasingly important because it has low viscosity and good binding and good film properties [7]. Researchers have reported that hypochlorite oxidation include starch molecular structure and starch origin [8], sodium hypochlorite concentration [9], and several studies explained that oxidation by hydrogen peroxide decreased the crystallinity from 56.9% in the native to around 52% in the oxidized flour [10], produce starches with high degrees of oxidation [11]; The efficiency of metal ion catalysts to increase the number of functional groups in the modified starch, WO4 [12]. Oxidized starch is also widely used in food products that have a neutral taste, low viscosity is needed starch, e.g lemon curd, salad sauce, and mayonnaise [13]. The commercial production of oxidized starch usually uses sodium hypochlorite as its oxidizing agent, however, oxidation chemicals have several disadvantages. In alkaline slurry produced by the hypochlorite oxidation process, oxidized starch yields low because of the loss of small molecules produced by the starch breakdown [14]. Furthermore, in the process, a large amount of wastewater, containing high concentrations of salt, causes problems of wastewater disposal [15].

The choice of an environmentally friendly oxidation method stimulates research on ozone, where ozone is a strong oxidant with an oxidation potential of 2.07 eV [16, 17]. Ozone has the power to degrade vital components in living cells quickly and to kill microorganisms. Ozone works at a low dose level and does not leave a residue on the product being processed [17]. Ozone can be generated on-site, ozone does not need a container for storage and also does not produce chemical waste problems [16], the guarantee from the United States FDA that states ozone has a generally recognized as safe (GRAS) status as a disinfectant and sanitizer for food when used in accordance with Good Manufacturing Practices (GMP) [18]. Because of these advantages, ozone has been used in water treatment, food processing, grain storage [19] wheat before grinding and steeping corn [20, 21]. Several patents have been filed for a method of oxidizing dry starch and polysaccharides [15], Ozone can be said to successfully modify starch [22]. Several studies have shown this, including modifying starch with ozone carried out on several carbohydrate sources.

The purpose of this article: Knowing the effect of ozone modification on different starch sources on gas and aqueous ozonation concerning functional, thermal and molecular properties. This information would be useful for the development of new ozone-modified starch materials hence more choices for food industrial applications.

2. Advantage of ozone as an oxidation to modify starch

Ozone is a gas produced from dry air and has no color when ozone is produced from pure oxygen. Ozone gas is blue at room temperature and dark blue when the ozone is condensed to a liquid at a temperature of -112 ℃ [23]. Ozone is free radical with an oxidation potential of 2.07V. The ozone boiling point is around -111.9 ± 0.3 ℃; Melting point around -192 ± 0.4 ℃; The critical temperature is -12.1 ℃ and critical pressure at 54.6 atm, ozone has a higher density of around 2.14 g/L compared to air (1.28 g/L) at 0 ℃ [24]. Naturally, ozone is produced through ultraviolet radiation from sunlight. The emission of UV light from sunlight can breakdown oxygen (O₂) in free air which then produces two oxygen atoms, this process is called photolysis. Oxygen atoms from the decomposition results then collide with other oxygen atoms to form ozone (O₃). UV rays at wavelengths of 240–320 nm can be easily absorbed by ozone.

The ozone formation process can be done by several methods, including corona discharge, ultraviolet radiation, electrolysis and chemical radiation [25]. According to [26] to produce ozone, each method carried out is influenced by energy to break down and hold bonds. Molecular oxygen atoms can be separated and then re-formed into ozone. One method used is corona discharge, where this process is carried out by giving a high voltage between the air gaps, this aims to break the O₂ molecule into an O
atom by passing air or oxygen between the electrode poles. This process is carried out by passing oxygen
gas in an area that has high pressure between the two electrodes.

Ozone is an oxidant widely used and considered as environmentally friendly, because before and
after reacting with other elements, ozone always produces oxygen (O2). Ozone can be applied in two
phases, namely the gas phase and the liquid phase, but ozone is an unstable component, where the form
and application need to be adjusted. Ozone in the gaseous phase has a longer shelf life than in the liquid
phase, therefore its effectiveness in gaseous phase to oxidise is higher than in liquid phase. The stability
of ozone in the liquid phase is also influenced by the purity of the solution, where low purity solutions
will accelerate the decrease in ozone [23]. Ozone has a higher effectiveness value than other chemical
oxidizers, this is caused by a combination of direct and indirect reactions that occur between ozone and
materials. Indirect reactions occur with the decomposition of materials through a reaction between bonds
that produce hydroxyl (OH) free radicals. The direct reaction is selectively carried out by ozone in the
material when it dissolves in water. The effectiveness of ozone also depends on the composition of
water, especially pH, organic components and alkalinity [23].

The advantage of using Ozone is: (1) Ozone can be used for food plant sanitation and food surface
hygiene as well as [27, 28]; (2) Ozone can be used an effective sanitizer against bacteria, fungi, viruses
and spores [27]; (3) Ozonation is used as an alternative method to thermal treatment as a sanitizer in
foods [29]; (4) Ozone has been used to improve the performance of wastewater treatment units [30] and
to treat drinking water [31]; (5) Ozonation is regarded in the food industry, as an environmentally
friendly technology because it does not leave any residues in foods and it quickly decomposes to oxygen
[32]; (6) Ozone can be used extend shelf life of fresh-cut lettuce [33], fresh-cut celery [34], for improving
shelf life of table grapes [35]; apple juice [36]; (7) Ozone is a more powerful oxidant than common
oxidizing agents, such as hydrogen peroxide and sodium hypochlorite [37]; (8) Ozone is an unstable
substance and its stability is influenced by the purity of a solution [19]; (9) Ozone can be in the form of
a gas phase and a liquid phase; (10) Ozone in the gas phase has longer stability than liquid phase ozone
(liquid) [12], other factors that influence ozone solubility and stability are pH [38], and temperature [39]
and Flow rate [40].

Ozone can react with starch even at ambient temperature without any problem of wastewater disposal
that can be regarded as an alternative to chemical oxidation of starch since it. Besides, high recovery
rates and low purification costs are other advantages of ozone oxidation of starch [4]. Ozone can oxidise
yellow pigment in wheat flour hence increasing whiteness degree of the flour [41]. Products made by
ozone-treated wheat flour include bread [42] and noodles [43]. Effect Ozone on starch polymer
properties and the formation of S-S bonds in dough were observed in study conducted by Sandhu et al
[42].

3. The method of oxidizing starch using liquid phase and ozone phase gas
The method used to modify starch with ozone both gas and liquid phase can be seen in table 1. Several
things are of concern to modify starch with ozone, as follows:

3.1. Source of oxygen and ozone generator
Oxygen or other gases containing oxygen are used as raw materials for ozone makers, in the process
oxygen will be converted first into high energy sources which will then convert the oxygen to ozone. To
be high energy sources, an ozone generator is needed.
3.1.1. **Liquid ozone phase.** Some researchers use oxygen sources from pure oxygen [44–46] while there are some researchers who use oxygen sources from integrated oxygen production units using atmospheric air [47–50].

3.1.2. **Ozone gas phase.** Some researchers use sources of pure oxygen show in table 1, while some other researchers did not specify where the source of oxygen gas came from, only explained using ozone generators as ozone producers [1, 4, 5, 16, 43, 51–54].

3.2. **Flow rate, contact time and concentration**
The ozone flow rate and exposure time between starch and ozone used in the starch modification process are important because they determine the success of ozone in modifying starch. In general, with ozone concentration and increasing time, the effect of changes in the starch modification is usually higher in influencing molecular and functional properties. In the liquid ozone phase and ozone gas, it has been investigated that the flow rate, time and concentration as in table 1. What needs to be underlined is that the regulation of these matters depends on the need of the researchers. The state of the reaction process greatly influences the success of ozone modification of starch, by reacting ozone with starch homogeneously.

3.3. **Liquid ozone phase**
While the liquid ozone phase uses a bubbling system to achieve a homogeneous mixing process of ozone and starch, and is used to also increase the ozone diffusion in the suspension ozone destructor [44–50].

3.3.1. **Ozone gas phase.** In gas-phase ozone the way to react starch with ozone gas there are several methods of mixing starch with gas-phase ozone using the following methods: (1) rotating or stirring treatment [1, 4, 5, 16, 41, 43, 57]; (2) using orbital shakers [53]; (3) using rotated back and forth sideways once every 5 min during [51], d) every 5 min it was vertically rotated [58].

3.4. **Temperature settings for ozonation**
3.4.1. **Liquid ozone phase.** Temperature regulation in the application of liquid-phase ozonation is an important thing that ensures that the ozonation reaction reaches optimal, but not all describe it clearly. The following is a temperature condition regulated by several researchers. [59] reported that temperature under controlling at 20 °C; [47, 49] reported temperature was kept at 5 °C of the starch-water suspension during ozonation; [37] reported treatment under temperature control and pH conducted at 25 °C and at pH 3.5, 6.5 and 9.5. while some researchers who did not explain the temperature regulation during the liquid phase ozonation were: [49, 50]; no description to control temperature but there is information that the 30-minute ozonation treatment of water was sufficient to give the optimum solubility of the water and the well known that the half-life of ozone in distilled water 20 °C is about 20 to 30 min [44–46, 48, 60].

3.4.2. **Ozone gas phase.** In ozonation using the gas phase, temperature regulation in the ozonation method is not given a special note, as in research by [4, 16, 17, 41–43, 51, 54, 57].

3.5. **Flushing or removal of residual ozone in the reactor**
3.5.1. **Liquid ozone phase.** In the liquid phase ozonation, it is explained about the removal of residual ozone after the oxidation reaction by [47, 49, 55]; reported that undissolved ozone gas was driven to the atmosphere by a discharging tube. [48] reported that need a degasser for removing of undissolved ozone in water and [45] explained that need ozone destructor, which is thermally destroying the residual ozone, releasing oxygen.
Table 1. Methode starch modification with ozone phase gas and liquid.

| Ozone Phase | Source of Starch | Concentration and Flow Rate | Contact Time | Oxygen Source | Author |
|-------------|------------------|-----------------------------|--------------|---------------|--------|
| Aqueous     | Cassava starch   | 36 mg O₃/L (36 ppm), Flow rate 0.5 L/min | 60 min       | Oxygen        | [44]   |
| Aqueous     | Potato starch    | 47 mg O₃/L (47 ppm), Flow rate 0.5 L/minutes | 15, 30, 45 and 60 min | Oxygen by Corona discharge | [46]   |
| Aqueous     | Cassava starch   | 13 mg O₃/L, Under control pH 3.5, 6.5 and 9.5, at 25 °C | 60 min      | Oxygen        | [37]   |
| Aqueous     | Wheat starch     | Concentration: 4.2 mg/L, flow rate of 0.103 L/min | 15, 30 and 60 min, at 5 °C | Oxygen by Corona discharge | [47]   |
| Aqueous     | Rice             | Capacity: 60 g/h, concentration: 4.2 mg/L, Rate of 60 g/h for 1 hour | 60 min      | Oxygen by Corona discharge | [48]   |
| Aqueous     | Wheat, Corn, Potato and Rice Starches | Concentration: 4.2 mg/L | 60 min | Atmospheric air-corona discharge | [55]   |
| Aqueous     | Potato and corn starch | concentration: 4.2 mg/L | 60 min | Atmospheric air-corona discharge | [49]   |
| Aqueous     | Wheat and corn starch | Batch systems (concentration: 4.2 mg/L) | 30 min | Atmospheric air-corona discharge | [50]   |
| Aqueous     | Rice             | Flow rate: 170 mL/minutes, Concentration: 47 mg O₃ L⁻¹, Flow rate: 0.5 L/minutes | 0,15,30 min 15, 30, 45 and 60 min | Pure oxygen ozone generator unit by the Corona discharge | [32]   |
| Gas         | Wheat flour and wheat starch | Exposed to ozone gas 5 mg/L, Flow rate 3.3 L/minutes (1,500 mg/kg, gas flow rate 2.5 L/min) | 0,5, 1, 1.5, 2 hours, Flour: 45 min, Starch: 30 min | Ozone Generator | [51]   |
| Gas         | Starch was isolated from treated flour | Cassava starch | 30,60,90,120 min | Oksigen using an ozone generator atmospheric air | [16]   |
| Gas         | Whole Grain Flour | Pigeon pie, lime bean, and jack bean starches | Tumbler capacity max. 5 g/h, a flow rate of 5 L/min, Rotated at 150 Rpm | Oksigen using an ozone generator ozone generator | [53]   |
| Gas         | Corn, potato, and sago starches | Rotated at 150 rpm | 1, 3, 5, 10 min | Using an ozone generator, ozone generator. | [4]     |
| Gas         | White, red cocoyam and yellow yam | Rotated at 150 rpm | 5, 10 and 15 min | Using an ozone generator, ozone generator. | [5]     |
| Gas         | Corn, sago, and Tapioca | Rotated at 150 rpm | 1, 3, 5, 10 min | Using an ozone generator, ozone generator. | [54]   |
| Gas         | Waxy rice flour and waxy rice starch | Flow rates (2.0 L/minutes) | 0,5, 1, dan 2 hours | Oksigen using an ozone generator | [17]   |
| Gas         | Wheat flour      | Production, 5 g/hours, flow rate 5 L/min | 1, 10, 30 and 60 min | Oksigen using an ozone generator ozone generator | [43]   |
| Gas         | Wheat flour      | Concentration: 120 ppm A flow rate of 5 L/min | 15, 30, 45, and 60 min | Oksigen using an ozone generator ozone generator | [41]   |
| Gas         | Wheat grain      | a flow rate of 33.34 L/min | 15 minutes | Oxygen by the ozone generator | [56]   |
3.5.2. **Ozone gas phase.** In the ozone gas phase, after starch has been modified with ozone, the remaining ozone must be removed from the sample (can be flashed using air ([41, 43, 52]) or destroyed at 350 °C [56], collated with oxygen [1, 4, 5, 57].

3.6. **Sample preparation to be packaged before analysis**

3.6.1. **Liquid ozone phase.** In liquid ozone modified starch a filtering treatment is required, and drying using an oven with a low temperature of about 35–40 °C, after that it must go through the grinder phase and sieving with a certain size. As explained by [47] Ozonated starch-water suspensions were dewatered by filtration through a Whatman 4 filter paper followed by drying at 35 °C under vacuum for 2 hours. [37] reported that the samples were withdrawn from the reactor and washed with distilled water, after 60 min of reaction, after that the starch must still be dried in the oven at 40 °C until 11% moisture content.

3.6.2. **Ozone gas phase.** In the gas phase ozonation, the drying of starch is not done because the starch which is ozonated is dry, so it is more practical to use than the liquid phase. As explained by the researchers listed in the table. Furthermore, [4] that gas-phase ozonation has the advantage because a dry process using ozone can reduce the purification cost and produce a product with high recovery.

4. **Change of morphology, functional and thermal properties of ozonated starches**

4.1. **Carbonyl and carboxyl**

When starch is modified with ozone as an oxidation agent, two reactions occur including them. The first reaction is the oxidation of the hydroxyl group on starch molecules into carbonyl groups which are mainly on C-2, C-3, and C-6 [61]. The second reaction is that oxidation also causes depolymerization of molle starch by cutting glycosidic alfa 1–4 bonds, the extent of starch oxidation and degree of degradation generally used the carbonyl content, carboxyl content [62, 63].

A large amount of carboxyl group on the starch molecules produce a starch paste which has a low retrogradation, whereas carbonyl groups have a small role in preventing retrogradation. The carbonyl and carboxyl content of starch during oxidation shows how far the starch is oxidized. The abundance of carbonyl and carboxyl in oxidation starch directly influences the Physico-chemical properties of starch which has the potential to cause oxidation starch to be suitable for uses from several industries. Changes in carbonyl and carboxyl content in ozone-modified starches compared to their nature can be seen in table 2.

The amount of carboxyl and carbonyl obtained from modified starches using liquid phase and gas ozone from several researchers in table 2, for carbonyl content ranged from the lowest with a value of 0.04 on potato starch [45] to the highest 0.711% in white cocoyam [5]. While the carboxyl amount ranges from the lowest which is 0.0038% in banana flour [58] and the highest is 0.430 in red cocoyam [5]. The low carboxyl value in banana flour is because there are nonstarch components that prevent the accessibility of ozone to oxidize starch, and when compared to the carboxyl value of banana starch the value immediately rises to 6 times, because it does not contain non-starch components [58].

The measurement of the number of carboxyl and carbonyl groups produced in modified starches can be carried out using FTIR [53], NMR [16] and titration methods to test carbonyl [25] and for carboxyl [64]. The formation of carboxyl and carbonyl groups in ozone oxidation starch is positively correlated with the amount of ozone that reacts [57].

The increase in the amount of carboxyl and carbonyl has a positive correlation with the increased contact time of ozone with starch, this can be seen in table 2, this condition occurs in all the starch sources studied. [45] reported that in addition to increasing contact time of starch and ozone, the modified starch results were also obtained in the presence of reducing sugar levels, decreasing pH and amylose while the reaction conditions suitable as pH 9.5 in cassava starch were studied [37].
Table 2. Carbonyl and carboxyl content of ozone modification starch on aqueous and gas phase.

| Ozone Phase | Source of Starch | Contact Time/pH | Carbonyl Carboxyl (%) | References |
|-------------|------------------|-----------------|-----------------------|------------|
| Aqueous     | Cassava starch   | pH = 9.5        | Carbonyl = 0.11; Carboxyl = 0.028 | [37]       |
| Aqueous     | Potato starch    | 60 minutes      | Carbonyl = ± 0.04 -0.13; Carboxyl = ± 0.03 – 0.10 | [45]       |
| Aqueous     | Cassava starch   |                 | Carbonyl = ± 0.084 Carboxyl = ± 0.09 | [44]       |
| Gas         | Wheat starch     | 45 minutes      | Carbonyl = ± 0.061; Carboxyl = ± 0.063 | [16]       |
| Gas         | Corn, sago, tapioca | 10 minutes   | Carbonyl = ± 0.085; Carboxyl = ± 0.048 | [57]       |
| Gas         | Corn, sago, tapioca (Deproteinized) | 10 minutes | Carbonyl = ± 0.250; Carboxyl = ± 0.058 |          |
| Gas         | White, red cocoyam, white and yellow yam | 15 minutes | Carbonyl = ± 0.11; Carboxyl = ± 0.28; Carbonyl = ± 0.08; Carboxyl = ± 0.22; Carbonyl = ± 0.135; Carboxyl = ± 0.25 | [4]       |
| Gas         | Pigeon pea, lima bean, jack bean starches | 15 minutes | Carbonyl = ± 0.542; Carboxyl = ± 0.227 | [1]       |
| Gas         | Whole grain flour | 45 minutes | FTIR 1384 cm\(^{-1}\) | [53]       |
| Gas         | Waxy Rice Starch | 2 hour          | Carbonyl = 0.113; Carboxyl = 0.145 | [17]       |
| Gas         | Banana Flour and Starch | 60 minutes | Carbonyl Flour = 0.0038; Starch = 0.0235 | [58]       |

4.2. Morphology and crystallinity

4.2.1. Morphology. The microscope is a tool used to visualize the structure of starch granules due to changes in starch modification using high resolution, among others (Scanning Electron Microscopy) SEM, which is used to prove the shape and size of starch granules, Transmission Electro Microscopy (TEM), Polaris Microscopy, Light microscopy, Confocal Scanning Laser Microscopes, and Atomic Force Microscope (AFM) that are useful for characterizing both surface and internal crystalline ultrastructural starch granules [22].

Changes in morphological properties of ozone-modified starch can be demonstrated through changes in surface, shape, and granular size. The modified ozone starch has a different effect depending on the type of starch. In table 3 can be seen that ozone modification studies have an impact on changes in ozone starch, which are distinguished by the phase of liquid ozonation and gas ozonation phase.

The amount of carboxyl and carbonyl shows high levels of starch oxidation which should affect changes in the morphology of starch granules. [37] modified cassava starch with ozone and produced Carbonyl = 0.11% and Carboxyl = 0.028%, this value is relatively small, it can be said that the oxidation rate is relatively small so that the results for morphology are no changes both on the surface, shape, and the size of starch granules, as well as the type of crystallinity remain the same as the native starch and the degree of crystallinity has decreased, which indicates the presence of oxidation reactions in the amorphous region. However, according to [44] reported that the relative crystallinity is increased in ozone-oxidised cassava starches.

Based on table 3, it can be seen that there is a study of starch ozonation which does not change the morphology of starch granules, namely: in cassava starch which is ozonated with the liquid phase [37],


in corn starch and potatoes which are ozonated with liquid phase cannot eliminate Maltese cross [49]; on wheat starch with gas-phase ozonation does not provide a change in both the surface, shape and size of starch granule [16]. Although there are results that do not experience morphological changes due to the ozonation mentioned above, but with modification method changes in liquid phase ozonation treatment with a capacity of 60 g/hours with a treatment for 60 minutes, there are results that show ozone is ably capable of changing starch change of granular surface and shape, become swollen starch in corn and potato starch [55].

With liquid ozonation treatment of potato starch that produced irregular shapes, fissures and pores in the granules surface, roughness and became more heterogeneous after 30 minutes [45]; irregular shapes green ozone is a protein [53]; change in the granule shape and surface in the starch granules; little loss of maltase cross on wheat flour [41]; size reduction became single and small which led to an increase in low-molecular-weight starch granules [51].

4.2.2. Crystallinity. The crystallinity of starch granules can be observed using the X-ray diffraction method. The peak intensity of X-ray diffraction is related to the number of crystalline regions of starch granules using X-ray diffraction to distinguish semi-crystalline regions of starch into type A (cereals) Type B (tubers) Type C (Combined between Type A and B, usually found in grains), Type V (Amylose complex with other compounds). The non-crystalline portion of starch granules is called the amorphous region, which is often indicated by the branching area of amylpectin and amylose molecule. The degree of crystallinity varies depending on the source of starch and the method of calculation. Changes in starch with ozone modification with its degree of crystallinity can be seen in table 3.

Based on table 3. the crystallinity type in ozone modified starch tends to be unchanged or the same as its native starch both liquid and gas phase ozonation, however, ozonation starch phase gas in white and red cocoyam, white and yellow yam resulted that the-CB-type crystalline in native starches change to CA-types [5].

The value of relative crystallinity varies depending on the source of starch used. there is relative crystallinity in the ozonated starch which has no change compared to the control in potato starch with liquid ozone [45], in wheat starch with ozonation phase gas [16]. There was an increase in relative crystallinity in cassava starch [44] however, there was also a decrease in relative crystallinity in cassava starch [37], in pigeon pea, jack bean, and lima bean [1]; in banana flour and starch [58].

According to [44] on starch cassava with liquid phase has the same type of crystallinity with natural starch, namely Type A. The relative increase in crystallinity occurred in this study due to a decrease in the total area of X-Ray analysis which can be said with low detection amorphous region. In this study ozone cannot reach the depth of the interior of the starch granule, it can only oxidize some hydroxyl groups into carbonyl and carboxyl groups and hydrolyze the most suitable molecules for oxidation. [58] reported that in the flour and oxidized banana starches using gas-phase ozone did not show changes in crystallinity type, namely fixed type B. Reduced Relative crystallinity slightly by 1.8% in both flu and starch forms.

4.3. Functional and pasting properties

Modification of starch oxidation with ozone both the liquid phase and the gas phase can affect the functional properties of the modified starch, which can be shown in table 4. The functional properties that are mostly examined in oxidation using ozone are swelling power, solubility, water absorption index, and gel strength. Swelling power is the ability of starch to hydrate under specific conditions. Solubility is the percentage of molecules leached from starch granules after swelling at specific conditions [22]. The water absorption index is related to the composition of the granule and the physical properties of starch after being added to a certain amount of water. Starch granules can be wet and spontaneously dispersed in water. The absorbed water is caused by the absorption of granules that are physically and intramolecularly related to the amorphous part [65].
| Ozone phase | Source of starch | Morphology | Crystallinity | Reference |
|-------------|----------------|------------|--------------|-----------|
| Aqueous     | Cassava starch  | Surface: no changes Shape: no changes Size: no changes | Type crystallinity: no difference with control Relative crystallinity: decrease | [37] |
| Aqueous     | Cassava starch  | No observation | Type crystallinity: no change (still type A crystallin) Relative crystallinity: increase | [44] |
| Aqueous     | Potato, Corn, wheat, rice Starches | Wheat and rice starch no change in surface, shape and size, but in corn and potato starch change of surface and shape granular, become swollen starch | No observation | [55] |
| Aqueous     | Corn and potato starches | Ozone is not able to eliminate Maltese crosses in starches and the shapes: were changed, surface: became rough and fibrous size: no changes | No observation | [49] |
| Aqueous     | Potato starch   | surface: roughness and became more heterogeneous and after 30 minutes the shapes: irregular shapes surface: fissures and pores in the granules | Type crystallinity: no change (still type B crystallin) Relative crystallinity: no difference with control | [45] |
| Gas         | Pigeon pea, lima bean and jack bean starches | No observation | Type crystallinity: no change (still type Cn crystallin) Relative crystallinity: decrease CB-type crystalline in native starches change to CA-type | [1] |
| Gas         | White, red cocoyam, and white and yellow yam | | | [5] |
| Gas         | Whole grain flour | irregular shapes, some physical damage to particles and a loss of protein zones in the starch granules | No observation | [53] |
| Gas         | Wheat starch    | did not reveal any visible differences in granule morphology | Type crystallinity: no change (still type A crystallin) Relative crystallinity: no difference | [16] |
| Gas         | Banana flour and starch | No observation | Type crystallinity: no change (still type B crystallin) Relative crystallinity: decrease | [58] |
| Gas         | Wheat flour     | little loss of maltase cross on wheat flour weaken the starch granule structure and increase the starch damage | No observation | [41] |
| Gas         | Wheat starch    | Size reduction became single and small which led to an increase in low-molecular-weight starch granules | No observation | [51] |

Based on table 4, it can be shown that the swelling power and solubility values in ozonation starch provide varied results. There is an increase in swelling power and solubility values in the study, as follows: potato starch [46]; wheat starch [16]; whole grain flour [53]; banana flour and starch [58]; wheat flour [41]: corn starch: increase swelling power and sago: increase of solubility [57]; lima bean starch...
and jack bean starch: increase of swelling power, pigeon pea, and lima bean starches was increased of solubility [1]. However, there are also results of research that show a decrease in swelling power that is sago and tapioca: decrease of the swelling power and sago starch was decreased of the solubility [57]; white cocoyam and red cocoyam [5]; waxy rice starch: the first Increase but decrease when increasing expose ozone until 2 hours [17].

Table 4. Functional properties of starch modification with ozone liquid phase and gas.

| Ozone Phase | Source of starch | Swelling power | Solubility | Gel strength | References |
|-------------|------------------|----------------|------------|--------------|------------|
| Aqueous     | Potato starch    | Increase       | Solubility: increase Water absorption index: increase | the 15-min sample reached a gel strength that was similar to the native, the 30-min ozonated sample, its increase gel strength ozonated samples (45 and 60-min) did not form consistent gels. | [46] |
| Gas         | Wheat starch     | Increase       | No observation | No observation | No observation | [16] |
| Gas         | Whole grain flour| Increase       | Increase    | No observation | No observation | [53] |
| Gas         | Waxy Rice Starch | Increase until 0.5 hours, and then decrease when 1 hour and more decrease until 2 hours expose | No observation | No observation | No observation | [17] |
| Gas         | Banana Flour and Starch | Increase | Water absorption index and water-soluble index increase | | [58] |
| Gas         | Wheat flour      | Increase       | Increase    | No observation | No observation | [41] |
| Gas         | Corn, sago, tapioca starch | Corn starch: increase Sago and tapioca: decrease | Sago: increase Tapioca: decrease | No observation | No observation | [57] |
| Gas         | Corn, sago, tapioca starch | No observation | No observation | Corn and sago: Increase firmness Tapioca: no difference | No observation | [54] |
| Gas         | Pigeon pea, lima bean and jack bean starches | Pigeon pea: lima bean: increase jack bean: increase | All of starches increase except jack bean | | No observation | [1] |
| Gas         | White, red cocoyam and white, yellow yam | White cocoyam: decrease Red cocoyam: decrease White Yam: increase Yellow Yam: increase | Increase all of starches | No observation | No observation | [5] |
| Gas         | Waxy Rice Starch | Increase But decrease when increasing expose ozone until 2 hours | No observation | No observation | No observation | [17] |

4.4. Pasting properties
Brabender Viscoamylograph or a Rapid Visco-Analyzer are measurements generally using determine the changes that occur in starch granules during gelatinization and retrogradation [62, 66]. Based on table 4, it can be shown the changes in the pasting properties of some modified starches with ozone,
both liquid and gas phases. Pasting properties consist of: peak viscosity, final viscosity, setback, and breakdown.

4.4.1. Pasting temperature. There are researchers who report that there is an increase in pasting temperature due to modification of ozone to starch, including [49] (corn and potato starch). This can be attributed to the formation of smaller starch molecules after ozonation, requiring a higher gelatinization temperature [67]. However, [58] reported that the pasting temperature remained unchanged when starch and banana flour were ozonated.

[45] reported that there was an increase in pasting temperature in ozonated potato starch. This increase is due to depolymerization during oxidation which requires higher temperatures for the gelatinization process when compared to polymers which have longer polymers. Conversely, other researchers showed a decrease in pasting temperature from the sample, such as by [57] in sago starch ozonation; [8] potato starch, rice, corn which is oxidized with hypochlorite; [5] on white and red cocoyam starch with ozone and [47] on ozone oxidized wheat starch. This shows that botanical sources and process conditions significantly influence the nature of modified starch.

4.4.2. Peak viscosity. Some studies have demonstrated increased peak viscosity when ozonation starch [1, 17] (hot and cold viscosity); [58]; [41]. [43] stated that peak viscosity, though, final viscosity had a significant increase during 60 minutes of ozonation. These results obtained that there were conformational re-ordering and re-arrangement of affected wheat starch by ozone. [41] report the peak viscosity, final viscosity, breakdown, though and setback viscosity increase in value with increasing ozone time. The increase in peak and final viscosity is caused by the change in the hydroxyl group to carboxyl which is easier to absorb water during the gelatinization process so that the granule has increased swelling due to a large amount of ion charge in the carboxyl group that refuses, which also increases the swelling volume. [1] results from oxidation show an increase in peak viscosity, cold, hold pasting viscosity with a slight deviation in starch five beans. The occurrence of cross-linking during oxidation is responsible for increasing viscosity. [16] reported no significant difference peak viscosity compare with control, however, some researcher have reported decreased peak viscosity [4, 49, 51, 53]. [53] report that ozone treatment results in a decrease peak viscosity, which is caused by the partial cutting of glycosidic bonds which results in a decrease in molecular weight of starch and protein, which results in lower share force resistant molecules, and consequently decreases swelling capacity [28]. This reduction in viscosity is in line with the research of [51].

4.4.3. Breakdown viscosity. Some researcher has demonstrated increased breakdown viscosity when ozonation starch [16]; [17]; white and red cocoyam cultivars [5]; Banana flour [58]. However some studies have reported decreased breakdown viscosity [49]; [51]; [57]; [4]; white and yellow yam cultivars [5]; Banana starch [58]. [57] reported that breakdown viscosity for oxidized sago starch increased, however, all oxidized corn and tapioca starches decreased considerably. Oxidized sago starch with ozone had increased breakdown viscosity, which could be attributed to the weakened structure of the granules, which facilitated disruption of the granular structure. Similar to the result in banana flour [58]; [32] have reported that ozonation has increased the breakdown viscosity of rice starch. Oxidized corn and tapioca starches with ozone had a reduction in breakdown viscosity, which resulted from the introduction of new substituent groups into the oxidized starches [13].

[57] report that some samples showed a positive correlation between carboxyl and breakdown viscosity but other samples showed a negative correlation, this shows no direct correlation between carboxyl amount and breakdown viscosity. The main factors that affect damage viscosity, not carboxyl, but are caused due to the effect of ozone on the degradation of amorphous regions of starch granules.

4.4.4. Setback. The setback viscosity indicates the degree of retrogradation of starch, mainly amylose [68]; a high setback value indicates a high tendency of starch to retrograde. Some studies have reported
increased setback viscosity when ozonation starch [17]. However there was some researcher have resulted in decreased setback viscosity when ozonation starch: [4, 49, 51, 57, 58].

**Table 5.** Pasting properties of starch modification with ozone liquid phase and gas.

| Ozone Phase | Source of starch | Pasting properties | References |
|-------------|------------------|--------------------|------------|
| Aqueous     | Potato starch    | No increase in the apparent viscosity was observed at 55 and 60 °C for all the samples. Presented a higher apparent viscosity and a higher gel strength when gelatinized at 65 and 70 °C, compared to the native sample. | [46] |
| Aqueous     | Corn and Potato starch | The pasting temperature of samples increased considerably after ozonation. Peak viscosity of the ozonated samples decreased. Breakdown viscosities of ozonated starches were considerably lower than the viscosities obtained for the control. All starch samples showed a decrease in final viscosity after ozonation | [49] |
| Gas         | Wheat starch     | Peak Viscosities no significant difference. Increase of breakdown on starch ozonation | [16] |
| Gas         | Wheat flour      | Peak viscosity: decrease All of the parameters are decrease | [51] |
| Gas         | Whole grain flour | Peak viscosity: decrease | [53] |
| Gas         | Waxy Rice Starch and Waxy Rice Flour | Increased the pasting viscosity of waxy rice flour. The peak viscosities of waxy rice flour of ozone treatments were increased. For waxy rice starch, pasting viscosity was increased after 0.5 h of treatment, but decreased as treatment time extended. The ozone treatment decreased the gelatinization temperature of waxy rice starch. | [17] |
| Gas         | Banana Flour and Starch | Peak, hold and final viscosity of flour was also higher than those of starch. In the flour form, the increase in the breakdown and final viscosity was observed while setback did not change following the ozonation. The Lower breakdown value Ozonation tended to increase peak, hold and final viscosity of both. | [58] |
| Gas         | Wheat flour      | Peak, Final, and Breakdown were a significant increase. The setback was decreased with increase OGT Pasting Temperature of Pigeon pea significant different on ozonation time for 5 minutes, but not significantly different after 10 and 15 minutes. Lima bean starch was increased pasting temperature after ozonation 10 and 15 minutes | [41] |
| Gas         | Corn, sago, tapioca starch | Peak viscosity: decrease | [57] |
| Gas         | Corn, sago, tapioca starch (Deproteinized) | Pasting Viscosity of all ozonation starch was decrease after the OGT increase. | [4] |
| Gas         | Pigeon pea, lima bean and jack bean starches | Peak, cold and hold viscosities were increased. | [1] |
| Gas         | White, red cocoyam and white, yellow yam | Peak viscosity of ozone-oxidized white and yellow yam starches decreases. White cocoyam was decreased in peak viscosity, hot paste viscosity and cold paste viscosity white and red cocoyam cultivars: increase in breakdown viscosity white and yellow yam cultivars: decrease in breakdown viscosity | [5] |
4.5. Thermal properties

Differential Scanning Calorimetry (DSC) thermograms possibly give transition enthalpies occurring during the melting of the starch. Therefore, DSC was used to analyze the gelatinization of starch in control and ozonated samples in the presence of excess water to see if there is an effect of ozonation on the gelatinization characteristics of the sample or not. Starch gelatinization characteristics including onset temperature (temperature at which the gelatinization begins to progress), peak temperature (temperature at maximum rate of gelatinization), conclusion temperature (temperature at which the gelatinization is completed) and enthalpy (the energy that has to be supplied to obtain complete starch gelatinization) of control and ozonated samples.

Table 6. Thermal properties of starch modification using ozone.

| Ozone Phase | Source of starch | Thermal properties | Reference |
|-------------|------------------|--------------------|-----------|
| Aqueous     | Corn and Wheat   | T onset, T peak and enthalpy of gelatinization wheat and corn samples ozonated semi-continuously increased significantly. But not change for the batch system. | [50] |
| Aqueous     | Corn and Potato  | T onset, T peak and conclusion, enthalpy of gelatinization for ozonated samples increased significantly | [49] |
| Aqueous     | Rice             | There is a significant difference between both the onset temperature and peak temperature of control before 1 hr, However after 1 hr ozonated rice starch, there was not a significant difference. T onset of rice starch was significantly reduced, while, T peak was increased after 1 hr ozonation process. While ΔH did not change. | [48] |
| Aqueous     | Cassava          | No significant difference in T onset, T peak and conclusion between ozonated cassava starch and control, however, ΔH was significantly different. | [44] |
| Gas         | Pigeon pea, lima bean and jack bean | Among all the starch samples, only lima bean starch exhibit a slight difference in Tc. Significant differences are observed in ΔH gel for lima bean and jack bean starches upon oxidation while slight differences are observed for pigeon pea starch types. | [1] |
| Gas         | white cocoyam, red cocoyam, white yam dan yellow yam | The, T0, Tp and Tc and (ΔHgel) of the ozone-oxidized starches were insignificantly different from those of the native starches. | [5] |
| Gas         | Waxy rice flour  | The temperature of pasting and enthalpies from ozonated waxy rice flour is not significantly different. However, the peak and enthalphy temperatures decreased significantly. | [17] |
| Gas         | -SF (starch isolated from control flour) | Thermal properties were not affected by Ozone. Similarly, gelatinization change (ΔH) were not significantly different among SOF, OS and SF starch isolates. | [16] |
| Gas         | -S-OF (starch isolated from ozonated flour) | | |
| Gas         | -OS (starch that was ozonated after isolation from control flour) | | |
| Gas         | Corn, sago and tapioca | The gelatinization properties of corn starch, sago and tapioca did not change significantly | [54] |

Thermal properties of starch depend on size, microstructure and degree of crystallinity, as well as the proportion of amylose and amylopectin [69]. Enthalpy gelatinization is the amount of thermal energy including the gelatinization process, the higher the gelatinization enthalpy value can be connected with a stronger crystalline structure [70] then gelatinization enthalpy in cassava starch increases after ozonation due to the occurrence of macromolecular breakdown (especially amylopectin, such as which is proven in GPC), with the possibility of double helix reshaping, this is what makes it difficult to experience breakdown during gelatinization.
Based on table 6, it can be shown that the thermal properties in ozonation starch give varying results. The results of ozone modification with starch as follows: in white cocoyam, red cocoyam, white yam and yellow yam [5]; Waxy rice flour [17]; [16]; corn, sago and tapioca starch [54] provide results that are not significantly different. However, there is also a thermal property which increases gelatinization properties in the study, as follows: Corn and Wheat [50]; Corn and Potato [49]. The gelatinization properties using DSC had no significant in Cassava starch however ΔH was significantly different [44]. Mei et al. (2015) [50] states that the increase in gelatinization temperature and gelatinization enthalpy in wheat starch and semi-continuous corn when compared to batch systems is caused by the efficiency of the contact system design in semi-continuous systems, ozone application doses, gas transfer to liquid, in container operation and the number of ozone molecules that will expose starch granules. The ozone treatment causes oxidative cutting in starch molecules to produce molecules with lower molecular weight [4]. It is known that small starch intact molecules have a higher gelatinization temperature [67] which causes a possible re-association of small molecules during heating. This is what causes the need for higher temperatures to break down starch which forms the structure above. [49], gelatinization temperature (onset, peak, conclusion, and gelatinization enthalpy) for ozonation samples increased significantly. Ozone treatment may cause oxidative cutting in corn and potato starch molecules to produce molecules with lower molecular weight [4], however, gelatinization enthalpy from ozonation starch has decreased when compared to control. Although it requires a higher gelatinization temperature, the overall gelatinization process takes place in a shorter time and gives a smaller enthalpy value. This can be caused by the lack of crystallinity of the granules due to the cutting of starch molecules. This gelatinization characteristic can be advantageous in this case where the stability of starch to higher heat is required with less energy for thermal treatment.

The gelatinization properties depend on crystallinity, granule size, amylose amyllopectin ratio, increase in gelatinization temperature and decreased enthalpy gelatinization obtained from our study, caused by the application of liquid-phase ozonation, rather than exposure to dry starch powder exposed to ozone gas. It can be stated that the efficiency of the application of ozone in liquid media is higher than the application in the form of gas [71]. Then ozonation with the liquid phase can produce decryption in the crystalline region.

[48] stated that there were significant differences in the temperature of onset and peak, from control and 1-hour ozonation starch, whereas there was no significant difference in conclusion temperature and gelatinization enthalpy from control and 1-hour ozonation rice starch. [44] stated that the gelatinization properties using DSC had no significant difference in the onset, peak and conclusion temperatures between ozonated cassava starch and control, however, the gelatinization enthalpy or ΔH was significantly different.

The thermal properties of starch depend on the size, microstructure and degree of crystallinity, and also the proportion of amylose and amyllopectin [69]. Enthalpy gelatinization is the amount of thermal energy including the gelatinization process, the higher the gelatinization enthalpy value can be connected with a stronger crystalline structure [71] then gelatinization enthalpy in cassava starch increases after ozonation due to the occurrence of macromolecular breakdown (especially amyllopectin, such as which is proven in GPC), with the possibility of double helix reshaping, this is what makes it difficult to experience breakdown during gelatinization.

5. Conclusions
Based on the results of the review it was shown that ozone can be used as an alternative substitute for starch oxidizing chemicals, because it does not leave a residue on the material, is very environmentally friendly, and has high recovery from the modified starch process. Ozone has the advantage of answering the shortcomings of starch oxidizing chemicals such as hypochlorite, hydrogen peroxide. Gas-phase ozonation is considered more practical to develop because, the reaction process does not require a bubbling system, regulation of temperature and pH, and modified starch can be stored or utilized without having to go through a drying process such as liquid phase ozonation. Ozone converts the hydroxyl groups from carbohydrates and converts them to carbonyl groups which are continued to carboxyl,
which can affect the functional, thermal and molecular properties of starch. The number of carbonyl groups and carboxyl groups is used to see how far the starch can be modified with ozone. The ability of starch to be oxidized depends on the type of starch, botanical sources, and the structure of native starch granules, as well as the ozonation method used, which is described through the results of changes in starch properties such as morphology, crystallinity, functional, pasting and thermal obtained. Ozone modified starch can be utilized in the application of making healthy and attractive food products. In the future, research is needed on an exploration of gas-phase ozone modified starch in other starches, as well as the application of ozonation starch to food products, the shelf life of ozone-modified starches, and industry-scale research to scale up.

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