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Review

Effect of combining acid modification and heat-moisture treatment (HMT) on resistant starch content: A systematic review

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Abstract: Type 2 diabetes mellitus (DMT2) is a metabolic disease that is increasingly attracting public attention. Diabetes mellitus is expected to reach 439 million in the world in 2030. Resistant starch (RS) is an indigestible starch which has health properties which has health properties that can be used for preventing diabetes mellitus type 2. In order to increase the RS content, a dual modification method consisted of acidification and heat moisture treatment (HMT) can be applied. The Acid-HMT method is affected by various factors, i.e., acid types, acid concentration, water content ratio, HMT temperature and HMT processing time, and different treatments may result in different RS yields. This study aimed to analyze the effective treatment in the Acid-HMT dual modification to enhance RS content by using a systematic review based on the PRISMA method. The studies revealed that there were 11 articles (n = 68 data) which utilized various acid types combined with HMT. The utilization of acid-alcohol, HCl, and organic acid such as citric acid, acetic acid, and lactic acid resulted in different results of RS content in modified starch. In addition to acid types, treatment conditions such as acid concentration, acidification time, acidification temperature, water content ratio, HMT time, and HMT temperature also affected the resulted RS. The treatment with 0.2 M citric acid for 24 hours at 25 °C combined with

HMT with 30% moisture at 110 °C for 8 hours resulted in the highest increase in RS content of modified starch.

Keywords: acid-HMT; dual modification; resistant starch; systematic review

1. Introduction

Carbohydrates are chemical compounds that have the elements carbon, hydrogen and oxygen with various physical and physiological properties and health benefits. The main food carbohydrates can be divided into four general types that is monosaccharides, disaccharides (sugars), oligosaccharides (chains of three to 10 glucose or fructose polymers), and the polysaccharides (with starch and dietary fiber being the main components) [1]. Starch consists of two main components, namely amylose and amylopectin. Amylose is a linear molecule of α-D-glucopyranose connected via α-(1,4) glycosidic bonds. Amylopectin is a molecule of α-D-glucopyranose which has a branched structure, in which there are two types of glycosidic bonds, namely the α-(1,4) glycosidic bond which forms a linear structure in amylopectin and the α-(1,6) glycosidic bond which forms the point branching [2]. Starch is beneficial as the key energy source for humans. Starch are classified as rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) [3]. Starch with high amounts of SDS and RS can increase the health properties of food. SDS can prevent hyperglycemia-related diseases, while RS is beneficial for gut health and protection against colorectal cancer [4].

Resistant starch (RS) is also known as indigestible starch, which refers to the fraction of indigestible starch in the small intestine and fermented in the colon, which results in short-chain fatty acid and other products [5]. The RS is characterized by its smaller molecular structure, with the length of 20–25 glucose residue (a linear polysaccharide that is connected with hydrogen bond). RS has similar characteristics with dietary fiber, which has a prebiotic effect. The RS can also reduce cholesterol and reduce the risks of ulcerative colitis and colon cancer [6], and it may be used as an additional low-calorie food additive that can regulate body weight effectively. The consumption of RS reduces insulin secretion and controls post-prandial blood glucose to prevent diabetes [7] and was registered RS as a dietary fiber for preventing diabetes mellitus type 2 in 1990. The RS also functions as a new food ingredient with low glycemic index. The glycemic index is a number that indicates the potential increase in blood sugar available in a food [8]. Food with a low glycemic index can be used for prevention and treatment strategies for diabetes. Food ingredient with low GI (glycemic index) increases the serum lipid profile, reduce the concentration of C-reactive protein (CRP), helps in body weight regulation, and reduces the risk of cardiovascular disease [9].

The RS content can be increased through modification of starch processing. Several modification methods that are commonly used are physical, chemical, enzymatic, and biochemical modifications. A simple and convenient physical starch modification is conducted by high moisture treatment (HMT). HMT is a physical modification that involves low moisture level, commonly in the range of 10%–30%, and heat treatment at high temperature (90–120 °C), starting from 15 minutes to 16 hours [10]. HMT modification results in the shift of starch crystal structure into its more resistant form against gelatinization, which increases the RS. Based on a meta-analysis, HMT modification of 20% moisture content and 120–130 °C for 0.25–6 hours resulted in optimally increased RS [11]. Acid modification as part of starch modification to produce RS3 is a modification method by suspending starch in an acid solution to hydrolyze starch under gelatinization temperature for various time periods. The acid hydrolysis process results in a lower molecular size of starch and increases the tendency of the paste to form a gel. Acid modified starch has lower viscosity, greater retrogradation tendency, lower granule swelling, and higher increase in stability compared to natural starch [2]. Several studies reported that treating starch with citric acid solution at high temperatures increased the SDS and RS content [12–15].

In addition to HMT and acid modification, several studies also performed dual modification to increase the RS content. Several dual modifications combined acidification and HMT method to obtain optimal RS in comparison with one type of modification method. During modification, acid solution was added to hydrolyze the starch and produce a short linear chain. When hydrolysis is performed at under gelatinization temperature, the amorphous region of the 1.6 glycosidic links at the amylopectin branching point will be targeted first by the acid during modification. The starch fraction produced by prolonged hydrolysis at high temperatures results in shorter molecules. The starch was then heated at high temperatures and made starch chains swell from the starch granules. Furthermore, starch undergoes rearrangement that creates a more compact starch structure and more resistance. The HMT treatment with the addition of acid in various starch types resulted in higher RS content compared with the HMT treatment only [12,14,16,17]. In order to determine the effect of dual modification on RS levels, a systematic review was carried out. This study is a systematic review that provides information about the effects of acid and HMT modification (Acid-HMT) on RS content based on the previous study result, and aims to analyze the effects of the combination of acid-HMT modification with different types of acid in the increasing of RS content of modified starch.

2. Methods

Systematic review was employed in this study, using systematic and explicit method, with the objectives to identify, select, evaluate, collect, and analyse data from relevant previous studies [18,19].

2.1. Literature search

The literatures were searched based on PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analysis) statement guidelines [18,19]. The literatures were searched and identified through reputable literature providers, such as Google Scholar, Science Direct, Springer, Cochrane Library, Wiley Online Library, Pubmed, Nature, Microsoft Academic, and ProQuest, which have 30 years of publication. The literature research was conducted with the following keywords; “Heat Moisture Treatment” AND “Acid” OR “dual modification”, “resistant starch”, “digestibility”.

2.2. Literature selection

The identified literatures were then selected and went through filtering and feasibility test, so the chosen literatures were based on the target. The initial selection was based on the title and abstract, then adjusted with exclusion and inclusion criteria. The inclusion criteria consisted of literature research time of the last 30 years (1992–2022), from reputable international journals, which included acid-HMT process (moisture content, time, temperature, types of acid, acid concentration); providing data of starch resistant parameters; as well as primary data studies. The exclusion criteria consisted of review articles, having initial treatment on the samples such as germinated/cooked, as well as irrelevant data.

2.3. Data collection

The articles are collected with Microsoft Excel. The data were identified by the author, year of publication, place, carbohydrate type, resistant starch content in the control and modified starch and acid HMT method, which included water content, acidification and heating time, acid and heating temperature, types of acid, and concentrations of acid.

2.4. Risk of bias assessment

To assess the risk of bias, Cochrane risk of bias was used [20,21]. The criteria observed with the tool were: randomized process, treatment deviation, unavailable result, result measurement, and result selection. Each study was evaluated and assessed with bias risk of “high”, “low”, or “unclear”. A study with a high risk of bias for one (or more) main domains is considered to have a high risk of bias. Study stages, including literature research, data extraction, and risk of bias assessment, were performed independently by one author (Ratu Reni Budiyanti/RRB).

3. Results

3.1. Literature characteristics

The process of literature selection is shown in Figure 1. The process of article seeking were done on 10 databases and resulted in 6818 articles. The articles were then tested for duplication, with the result of 4837 articles. Then, the articles were selected based on the title/abstract, with the result of 59 articles. Finally, 11 articles were used in the systematic review. According to the Cochrane tool, which is shown in Figures 2 and 3, eight studies were assessed as low bias risk, 1 study was assessed as unclear, and three studies were categorized as high bias risk.

Eleven studies, which included 68 data, were published for the last 30 years from 1992 to 2022. The eleven studies performed *in vitro* RS test, where one study conducted RS test with the AOAC method, 1 study conducted RS test with the Englyst et al. (2002) and Sang & Seib (2006) method, while 9 studies used the method by Englyst et al. (1992). PICOS in this study is defined as Population, Intervention, Comparison, Result, and Study Design. The population in this study was resistant starch. The interventions were acid-HMT dual modification method. The comparisons were natural starch and modified starch. The study result was the resistant starch content from types of acid such as HCl, alcohol-acid, citric acid, lactic acid, or acetic acid. The HCl used has a concentration range of 0.3 M to 2 M at a hydrolysis time of 1 to 360 hours. The acid-alcohol used has a concentration range of 0.1 M to 0.2 M with a hydrolysis time of 1 to 78 hours. The citric acid, lactic acid and acetic acid used have a concentration of 0.2 M with a hydrolysis time of 12 to 24 hours. The research design used in this study was completely randomized design.

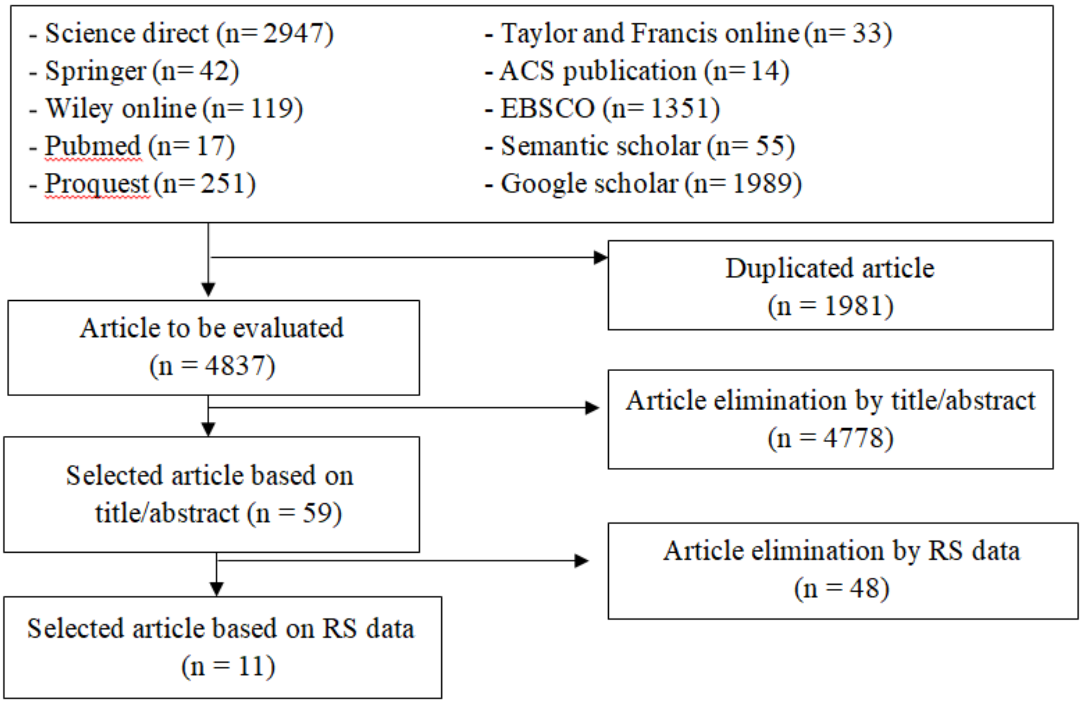

Figure 1. The article selection through PRISMA.

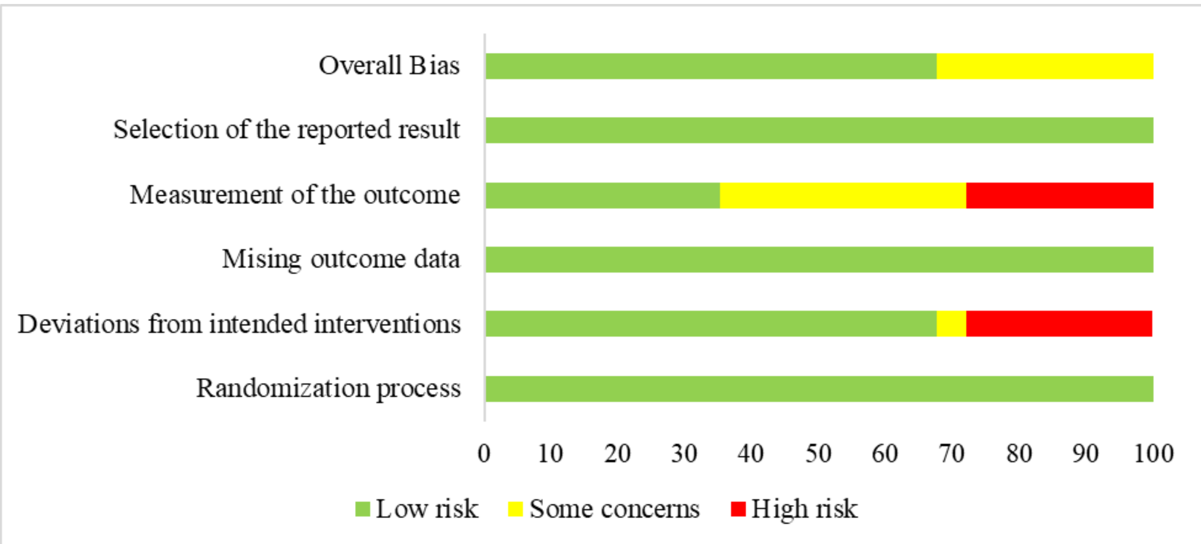

Figure 2. The result of the risk of bias assessment: each risk of bias item is shown as percentages across all included studies.

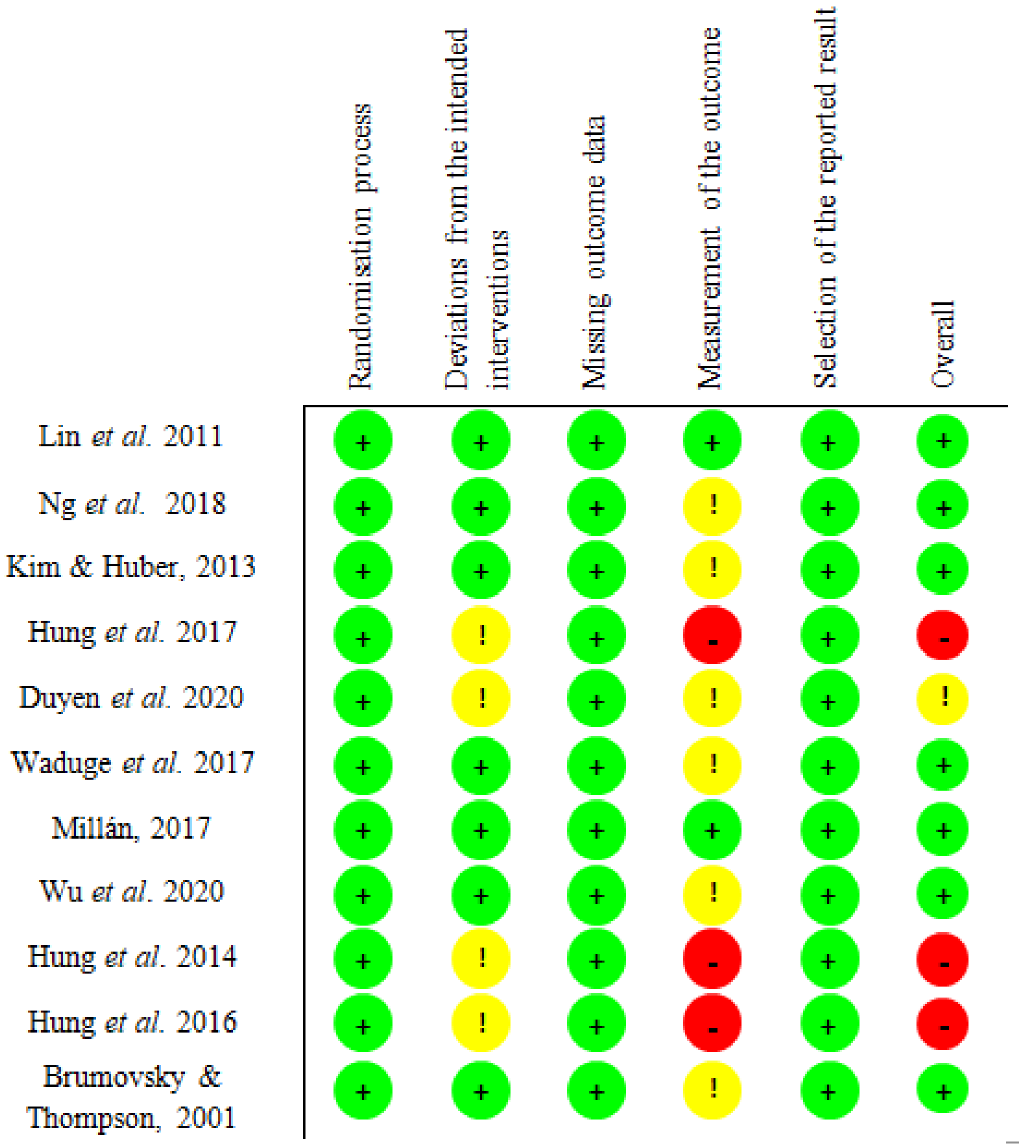

Figure 3. The result of the risk of bias assessment: each risk of bias item for the included studies (green mean low risk of bias, yellow mean unclear risk of bias, red mean high risk of bias).

3.2. Utilization of acid-alcohol in acid-HMT modification

The treatment of acid-alcohol (HCl-ethanol or HCl-methanol) in addition to starch can cause hydrolysis or starch degradation with acid in alcohol suspension. During the treatment, glycosidic bonds in starch, specifically in the amorphous region, were hydrolyzed by acid [22]. Chang et al. (2006) observed that the acid-alcohol treatment showed the capability to control the degradation of starch molecules [23]. Starch with different molecular sizes and polymerization degrees from 10^6 to 10^2 AGU (anhydro glucopyranose unit) can be produced by controlling different acid-alcohol treatment conditions, such as reaction time, temperature, and acid concentrations. Acid-alcohol treatment resulted in the decrease of starch molecule size as well as the increase of RS content during the HMT process [24].

According to Hoover dan Vasanthan (1994), an increase in crystallite compactness or due to the rising interaction between amylose and amylopectin caused increasing the content of RS in HMT treatment [25]. The result shows that the combination of molecular degradation during acidification and rearrangement of crystallites or starch chain during HMT resulted in a positive effect on RS increase. In this systematic review, the concentration of acid-alcohol which were 0.1 M and 0.2 M, with heating temperatures at 35 ℃ and 45 ℃ and acidification time from 1 to 360 hours. The HMT treatment variation consisted of 15%, 20% and 30% moisture content with a heating temperature of 100 ℃ and 110 ℃ for 80 minutes and 12 hours (Table 1). Acid-alcohol of 0.1 M at acidification temperature of 45 ℃ for 360 hours in parallel with 30% HMT at 100 ℃ for 80 minutes resulted in the highest RS increase.

According to Lin et al. (2011), sample type in the dual modification of acid-alcohol HMT has an effect on the increase of RS. In similar acid and HMT conditions, corn starch had higher increase in RS compared to Hylon V and Hylon VII starch. This is caused by the difference in amylose and amylopectin content. Normal corn starch has lower amylose content (27.0%) compared to Hylon V (56.8%) and Hylon VII (71.0%) [26]. During acidification, acid-alcohol will hydrolyze the starch by attacking the amorphous region. Low amylose results in effortless starch hydrolysis [27]. Hydrolysis affects the formation of shorter linear chain, which results in molecular rearrangement that creates more compact starch structure and more resistance against digestive enzymes [28]. RS content also increases along with the increased acidification time in the range of 1 to 360 hours. Acid-alcohol hydrolyzes the starch by slowly attacking the crystalline region [29]. Therefore, the longer acidification process in the acid-alcohol modification results in more starch being hydrolyzed into shorter chains [30].

The effect of moisture content in acid-alcohol HMT modification causes differences in resulted in RS. According to Ng et al. (2018), in identical conditions, lower moisture content (between 15% and 20%) resulted in the increase of higher resistant starch. Lower moisture content will restrict the starch chain mobility, which reduces the vulnerability of starch molecules to enzyme hydrolysis. On the contrary, high moisture content results in a more flexible molecule chain, which facilitates the enzymatic attack in increasing the starch digestibility [31].

3.3. Utilization of HCl in acid-HMT modification

The HMT modification treatment was initialized by adding hydrochloride acid (HCl) shown in Table 2. The HCl-HMT modification resulted in different effects of RS change. The utilization of HCl in acid-HMT modification was carried out by 3 researchers with different treatment conditions. Brumovsky and Thompson (2001) with Kim and Huber (2013), stated that the HCl addition at concentration range of 0.3–1 M at 25 ℃ for 1 hour and 15%–30% moisture content at 100–140 ℃ for 3 and 8 hours resulted in decreased RS [32,33]. The decrease in RS content is possibly caused by starch hydrolysis, which results in damaged amylopectin structure due to short linear chains that cause the molecule mobility. Hydrolysis with HCl causes the formation of hydrolysates with the polymer of fewer than 10 units of glucose. This is caused by the formation of optimal RS, where the polymers < 10 units of glucose can inhibit retrogradation and significantly affects the RS content. According to Schmiedl et al. (2000), the optimal chain length form type 3 RS is α-(1-4)-D-glucan with polymerization degree range of 10–40 [34].

Table 1. The results of acid alcohol-HMT modification.

No	Author	Type of Carbohydrate	Sample	Acid			HMT			RSc	RSe (%)	Result (%)	Findings
				Time	Conc	Temp	Moisture	Temp	Time	(%)			
1	Lin *et*	Cereals	Corn	1 h	0.1 M	45 °C	30%	100 °C	80 min	23.30	27.20	Increase 16.74	Acid-alcohol treatment in acid-HMT modification
2	*al.* 2011			6 h						23.30	35.60	Increase 52.79	increased the RS content. The highest RS increase
3				24 h						23.30	41.90	Increase 79.83	was found on 0.1 M alcohol acid for 360 hours
4				72 h						23.30	45.80	Increase 96.57	treatment using corn starch. The acidification
5				120 h						23.30	47.00	Increase 101.72	temperature was 45 °C, with 30% moisture content
6				168 h						23.30	47.60	Increase 104.29	at HMT temperature of 100 °C for 80 minutes.
7				360 h						23.30	47.70	Increase 104.72	
8			Hylon V	1 h						71.00	72.40	Increase 1.97	
9				6 h						71.00	73.40	Increase 3.38	
10				24 h						71.00	82.10	Increase 15.63	
11				72 h						71.00	82.40	Increase 16.06	
12				120 h						71.00	82.20	Increase 15.77	
13				168 h						71.00	83.00	Increase 16.90	
14				360 h						71.00	83.80	Increase 18.03	
15			Hylon	1 h						74.00	75.20	Increase 1.62	
16			VII	6 h						74.00	81.20	Increase 9.73	
17				24 h						74.00	81.60	Increase 10.27	
18				72 h						74.00	83.60	Increase 12.97	
19				120 h						74.00	84.20	Increase 13.78	
20				168 h						74.00	84.90	Increase 14.73	
21				360 h						74.00	85.50	Increase 15.54	
22	Ng *et*	Stem	Sago	24 h	0.1 M	35 °C	15%	110	12 h	61.90	64.80	Increase 4.68	The acid-alcohol treatment affected RS content. The
23	*al.* 2018				0.2M			°C		61.90	62.40	Increase 0.81	highest RS content was found through alcohol acid
24					0.1M		20%			61.90	59.80	Decrease 3.39	on 0.1 M concentration for 24 hours at 35 °C with
25					0.2M					61.90	57.10	Decrease 7.75	15% moisture content at 110 °C HMT for 12 hours.

Note: Conc = concentration; Temp = temperature; RSc = Resistant Starch Control; RSe = Resistant Starch Experiment.

Table 2. The results of HCl-HMT modification.

No	Author	Type of Carbohydrate	Sample	Acid			HMT			RSc (%)	RSe (%)	Result (%)	Findings
				Time	Conc	Temp	Moisture	Temp	Time				
1	Kim *et al.* 2013	Tubers	Potato	1 h	1 M pH 6	25 °C	15%	120 °C	3 h	93.08	85.53	Decrease 8.11	Modification of HCl-HMT results in a reduction in RS formed. The highest elevation was performed using 0.1 M HCl at pH 5 and a temperature of 25 °C for 1 hour with 15% humidity at HMT temperature of 120 °C for 3 hours.
2					1 M pH 5					93.08	85.83	Decrease 7.79	
3					1 M pH 6		20%			93.08	75.34	Decrease 19.06	
4					1 M pH 5					93.08	72.16	Decrease 22.48	
5					1 M pH 6		25%			93.08	45.33	Decrease 51.30	
6					1 M pH 5					93.08	47.79	Decrease 48.66	
7	Mill´an, 2017	Cereals	Rice	4 h	2 M	25 °C	30%	120 °C	12 h	3.26	6.43	Increase 97.24	Modification of HCl-HMT with 2 M HCl concentration led to an increase in RS formed. The highest increase in RS was obtained by using potato samples at an acidification temperature of 25 °C for 4 hours with 30% humidity and HMT temperature of 120 °C achieved for 12 hours.
8		Cereals	Maize							4.36	11.29	Increase 158.94	
9		Tubers	Potato							2.65	14.54	Increase 448.68	
10	Brumovsky and Thompson, 2001	Cereals	High Amylose Maize	6 h	0.3 M	25 °C	30%	100 °C	8 h	78.70	70.30	Decrease 10.67	Modification of HCl-HMT with a concentration of 0.3 M HCl resulted in a decrease of RS formed. The highest increase in RS was achieved by using HCl for 78 hours with an HMT temperature of 100 °C at an acid temperature of 25 °C and 30% humidity and HMT time of 8 hours.
11								120 °C		78.70	59.20	Decrease 24.78	
12								140 °C		78.70	44.10	Decrease 43.96	
13				30 h				100 °C		78.70	73.70	Decrease 6.35	
14								120 °C		78.70	66.00	Decrease 16.14	
15								140 °C		78.70	48.70	Decrease 38.12	
16				78 h				100 °C		78.70	78.10	Decrease 0.76	
17								120 °C		78.70	60.60	Decrease 23.00	
18								140 °C		78.70	48.20	Decrease 38.75	

Note: Conc = concentration; Temp = temperature; RSc = Resistant Starch Control; RSe = Resistant Starch Experiment.

Table 3. The results of citric acid-HMT modification.

No	Author	Type of Carbohydrate	Sample	Acid		HMT				RSc (%)	RSe (%)	Result (%)	Findings
				Time	Conc	Temp	Moisture	Temp	Time				
1	Hung *et al.* 2017	Tubers	Cassava	24 h	0.2 M	25 °C	30%	110 °C	8 h	20.30	40.20	Increase 98.03	At the same HMT acidity conditions, the highest increase in RS was obtained by using citric acid in cassava samples.
2		Tubers	Potato							22.50	39.00	Increase 73.33	
3	Duyen *et al.* 2020	Peas	Mung Bean Low Amylose	24 h	0.2 M	25 °C	30%	110 °C	8 h	10.10	25.90	Increase 156.44	At the same HMT acidic conditions, the highest increase in RS was obtained by using citric acid in the sample species, perhaps low amylose beans.
4		Peas	Mung Bean Medium Amylose							13.40	32.20	Increase 140.30	
5		Peas	Mung Bean High Amylose							15.60	35.60	Increase 128.21	
6	Waduge *et al.* 2016	Peas	Pea	12 h	0.2 M	25 °C	26%	95 °C	8 h	27.95	36.09	Increase 29.12	The 29.12% increase in RS was accomplished by using 0.2 M citric acid for 12 hours at 25 °C with 26% humidity and HMT treatment at 95 °C for 8 hours.
7	Wu *et al.* 2020	Fruits	Banana	24	0.2 M	25 °C	30%	90 °C	16 h	59.31	48.00	Decrease 19.07	The highest increase in RS was achieved with the use of citric acid at an HMT temperature of 90 °C.
8								110 °C		59.31	38.35	Decrease 35.34	
9	Hung *et al.* 2014	Tubers	Sweet Potato	24 h	0.2 M	25 °C	30%	110 °C	8 h	14.70	42.10	Increase 186.39	At the same HMT acidity conditions, the highest increase in RS was performed by using citric acid in sweet potato samples.
10		Tubers	Yam							21.60	46.40	Increase 114.81	
11	Hung *et al.* 2016	Cereals	High Amylose Rice	24 h	0.2 M	25 °C	30%	110 °C	8 h	6.30	39.00	Increase 519.05	Under the same HMT acid conditions, the highest increase in RS was obtained by using citric acid in high amylose rice samples.
12		Cereals	Normal Rice							6.50	36.60	Increase 463.08	
13		Cereals	Waxy Rice							10.20	35.30	Increase 246.08	

Note: Conc = concentration; Temp = temperature; RSc = Resistant Starch Control; RSe = Resistant Starch Experiment.

Table 4. The results of lactid acid-HMT modification.

No	Author	Type of Carbohydrate	Sample	Acid			HMT			RSc (%)	RSe (%)	Result (%)	Findings
				Time	Conc	Temp	Moisture	Temp	Time				
1	Hung *et al.* 2017	Tubers	Cassava	24 h	0.2 M	25 °C	30%	110 °C	8 h	20.30	31.20	Increase 53.69	At the same HMT acid conditions, the highest increase in RS was performed by using 0.2 M lactic acid in cassava samples.
2		Tubers	Potato							22.50	29.70	Increase 32.00	
3	Hung *et al.* 2014	Tubers	Sweet Potato	24 h	0.2 M	25 °C	30%	110 °C	8 h	14.70	40.10	Increase 172.79	At the same acid-HMT conditions, the highest increase in RS was obtained by using 0.2 M lactic acid in sweet potato samples.
4		Tubers	Yam							21.60	41.00	Increase 89.81	
5	Hung *et al.* 2016	Cereals	High Amylose Rice	24 h	0.2 M	25 °C	30%	110 °C	8 h	6.30	35.10	Increase 457.14	Under the same HMT acid conditions, the highest increase in RS was obtained by using 0.2 M lactic acid in high amylose rice samples.
6		Cereals	Normal Rice							6.50	32.40	Increase 398.46	
7		Cereals	Waxy Rice							10.20	33.50	Increase 228.43	

Note: Conc = concentration; Temp = temperature; RSc = Resistant Starch Control; RSe = Resistant Starch Experiment.

Table 5. The results of acetic acid-HMT modification.

No	Author	Type of Carbohydrate	Sample	Acid			HMT			RSc (%)	RSe (%)	Result (%)	Findings
				Time	Conc	Temp	Moisture	Temp	Time				
1	Hung *et al.* 2014	Tubers	Sweet Potato	24 h	0.2 M	25 °C	30%	110 °C	8 h	14.70	37.50	Increase 155.10	At the same acid-HMT conditions, the highest increase in RS was obtained by using 0.2 M acetic acid in sweet potato samples.
2		Tubers	Yam							21.60	39.00	Increase 80.56	
3	Hung *et al.* 2016	Cereals	Waxy Rice	24 h	0.2 M	25 °C	30%	110 °C	8 h	10.20	30.70	Increase 200.98	Under the same HMT acid conditions, the highest increase in RS was obtained by using 0.2 M lactic acid in high amylose rice samples.
4		Cereals	High Amylose Rice							6.30	33.00	Increase 423.81	
5		Cereals	Normal Rice							6.50	30.40	Increase 367.69	

Note: Conc = concentration; Temp = temperature; RSc = Resistant Starch Control; RSe = Resistant Starch Experiment.

However, a study by Kim dan Huber (2013) showed the difference in RS content on different 1 M HCl conditions (pH 5 and pH 6). Starch with pH 6 condition had a higher decline in RS compared to starch at pH 5 condition. The stronger the acidic condition (pH 6 and 5), the more glycosidic bonds are broken down, which causes more short linear chains experience retrogradation, which makes them resistant to digestive enzymes. Kim dan Huber (2013) also stated the difference in moisture on dual HCl-HMT modification causes the change in RS. At 15% to 25% moisture content, lower moisture content works effectively in increasing the RS content. This is due to the lack of mobility of starch molecules and less susceptibility to being hydrolyzed [31].

Brumovsky dan Thompson (2001) showed that the increase of RS is directly proportional to the acidification time, ranging from 6 to 78 hours with 0.3 HCl at 25 °C and the same HMT conditions [32]. Longer acidification time results in increased starch hydrolysis. Besides, HMT temperature in HCl-HMT causes the difference in RS change. In a similar condition, HMT treatment at 100 °C to 140 °C showed a decline in RS at higher HMT temperatures. This is possibly caused by the structure formed from HCl-HMT modification. The increase in temperature during acidification causes a change in amylose. In addition to amylose, amylopectin bonds also weaken and gradually break with increasing temperature. HMT temperature at 100 °C results in a more stable structure. HMT temperature that is too high will damage the starch molecules, so it cannot form resistant starch structures against enzymatic hydrolysis [32].

Millán (2017) showed the difference in carbohydrate type in HCl-HMT dual modification [35]. Tuber samples have less amylose compared with cereals. Amylose content in potatoes (20.9%) less than in corn (22.7%) and rice (46.4%) [36]. During the hydrolysis process with HCl, it will attack the amorphous region precisely and attack slowly on the crystalline region nearby amylopectin fraction [30], which it results in a more compact starch structure after the heating treatment and causes the starch to be more resistant to hydrolysis. The structure that is responsible for type III RS is predicted to be based on the formation of double helix, especially in the amorphous region of amylose fraction [37].

3.4. Utilization of organic acid in acid-HMT modification

The addition of organic acid in acid-HMT dual modification can be done using citric acid, lactic acid, and acetic acid. Citric acid is an organic acid that is commonly used as an acidifying agent in pharmacy and food industries due to its low toxicity [38–40]. The increase in RS content from acid-HMT treatment is due to the hydrolysates with low molecular weight (both branched and linear structures of amylose and amylopectin) from the acid hydrolysis [41]. The formation of double helix from amylose-amylose, amylopectin-amylopectin, and amylose-amylopectin chains during HMT is considered to be resistant to enzymatic hydrolysis [11].

The addition of citric acid in starch hydrolysis is conveniently performed at high temperatures, since amylopectin is more vulnerable compared to amylose during citric acid-HMT modification [17]. Based on Table 3, the increase of RS was influenced by the amylose content of the sample. In the same acid and HMT condition, tubers with lower amylose content result in higher RS compared to tubers with higher amylose content [12,17,42]. Hung et al. (2014) showed the comparison of RS increase in sweet potato and yam [43]. Sweet potato had higher RS increasing compared to yam. Sweet potato had amylose content of 18.7%, while yam had amylose content of 22.3%. This is in accordance with Duyen et al. (2020) study that showed there is less increase in RS along with the increase of amylose content in pea samples [42,44].

Hung et al. (2017) showed that cassava starch had higher RS content compared to potato starch. During the acid-HMT treatment process, the potato starch crystal structure shifted from type B to type C, while cassava starch retained its type A crystal structure. Type B crystal structure has lesser density compared to type A crystal structure. This is caused by cassava starch which possesses type A crystal structure which more resistant to digestive enzymes. The change of starch crystal is affected by the intermolecular structure rearrangement and double helix in the granules during HMT process [17].

High amylose rice sample with amylose content of 30.6% showed a higher RS increase compared with normal rice (24.3%) and waxy rice (4.7%) with 0.2 M citric acid treatment at 24 °C for 24 hours and proceeded by HMT with 30% moisture content for 8 hours at 110 °C on Hung et al. (2016) study. Higher RS content in cereals with higher amylose content on acid-HMT treatment was possibly caused by the hydrolysates from acid hydrolysis, which results in starch fraction that are resistant to enzymes. Hydrolyzed starch will experience the formation of double helix from amylose-amylose, amylopectin-amylopectin, and amylose-amylopectin chains during HMT process [45].

Although overall, the combination of citric acid-HMT treatment results in the increase of resistant starch, citric acid-HMT dual modification on banana sample showed a noticeable decline during the increase of HMT temperature [46]. This was possibly caused by the higher temperature (110 °C) on banana sample, which made it easier to open the double helix chain and resulted in weaker and more susceptible starch granule structure to digestive enzymes [45].

Lactic acid and acetic acid as organic acids are also commonly used in dual modification of HMT process [17]. The addition of lactic acid and acetic acid shows increase in RS [12,47]. Both acids contribute to starch hydrolysis, which produces hydrolysates, which it will form double helix during HMT process, which results in enzyme-resistant starch [12,47]. In Tables 4 and 5, on the same acid-HMT condition, tuber types samples had lower RS increasing compared to cereal types samples. Cereals have a more open structure which makes it more vulnerable to acid hydrolysis and results in more starch that are hydrolyzed. In addition, the utilization of cassava also showed higher RS compared to potatoes [17]. Sweet potato sample also showed a higher increase in RS compared to yam [12].

The highest RS increasing on 0.2 M lactic acid treatment was shown on high-amylose rice at 24 °C for 24 hours, followed by HMT with 30% moisture for 8 hours at 110 °C. The highest RS increasing was also found on high amylose rice with 0.2 M acetic acid treatment for 24 hours and proceeded by HMT with 30% moisture for 8 hours at 110 °C. The addition of organic acids such as citric acid, lactic acid, and acetic acid on the samples and similar acid-HMT dual modification showed differences in the RS increasing. Citric acid resulted in a better RS increasing compared to lactic acid and acetic acid. Hung et al. (2016) stated that higher RS from citric acid-treated starch was possibly caused by high variation of short chains, which increases the molecule mobility and enables a more efficient rearrangement in starch during HMT process [17].

Differences in the type of acid from acid-HMT modification produce differences in the resulting RS. The organic acids showed the highest increasing compared to acid-alcohol and HCl. Organic acids (citric acid, lactic acid and acetic acid) are weak acids that can be partially ionized in water. HCl is a strong acid that completely ionizes in water. The number of H^+ ions are produced by the use of high-concentration acids and long acidification times during modification results in a linear chain that is too short, making the retrograde process as long as HMT is inefficient.

4. Conclusions

Starch modification through acid-HMT method gives different effects on each treatment. Various acid types like acid-alcohol, HCl, and organic acid (citric acid, lactic acid, and acetic acid) were used and combined with HMT to increase the resistant starch content. In addition to types of acid, other conditions in acid-HMT dual modification also need to be observed. Acid concentration, acidification time and temperature, moisture content, HMT temperature and time during the modification gave different results on RS content. Cereal sample, which was treated with 0.1 M alcohol acid treatment (HCl-ethanol) with an acidification temperature of 45 ℃ for 360 hours and HMT at 30% moisture content and 100 ℃ for 80 minutes, had the highest RS content. HCl 2 M on tuber sample with an acidification temperature of 25 ℃ for 4 hours, followed by HMT with 30% moisture content at 120 ℃ for 12 hours had the highest RS content. The highest RS increase was carried out using organic acid, which was 0.2 M citric acid for 24 hours at 25 ℃, then followed by HMT with 30% moisture content at 110 ℃ for 8 hours. The best conditions of this modification can be used to increase the RS content in starch according to the type of acid used.

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Conflict of interest

The authors state that they have no conflicts of interest in this review paper.

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