Research Article

Conversion of Jerusalem Artichoke Tuber Powder into Fructooligosaccharides, Fructose, and Glucose by a Combination of Microwave Heating and HCl as a Catalyst

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Abstract

The major carbohydrate component of Jerusalem artichoke tuber powder (JATP) is inulin, which is a chain of β-1,2-D-fructose with a glucose terminal. The extracted inulin in the form of oligosaccharides from JATP has been applied as a sugar substitute and in prebiotics. The conventional methods to extract inulin are carried out by enzymatic methods, which are limited by high operational cost, complicated processes, low substrate solubility, narrow range of temperature activity of enzymes, and longer reaction times. This study investigates the feasibility of using a selective chemical method to extract the oligosaccharide from JATP, which could provide a more cost effective and rapid method than the conventional enzymatic extractions. The advantages of microwave radiation (MCR) heating in combination with HCl as a catalyst were explored in this study to determine the suitable conditions to extract fructooligosaccharides, fructose, and glucose from polysaccharides in JATP. Suitable reaction conditions for each saccharide were determined. A low temperature of 130 °C, 0.05 M HCl, radiation time of 15 min, and the ratio of the reaction volume to JATP mass of 10:1 (mL/g), were selective for fructose production with the highest yield of 44.7 %. A small amount of 5-HMF (0.6 %) was found in the hydrolyzed products (HP), and the UV absorbance of the HP at 284 nm was in the average range of 1.1, under these conditions. Glucose and fructose production with the maximal yields of 10.1 % and 24.0 %, respectively, were obtained at 110 °C, 0.4 M HCl, radiation time of 15 min, and the ratio of reaction volume to JATP mass of 10:1 (mL/g). A medium amount of 5-HMF at 5.5 % was generated, and the maximal UV absorbance of the HP was at 2.8 under these reaction conditions. The reaction conditions for a selective fructooligosaccharide production at the highest yield of 12 % was 110 °C, 1.8 M HCl, radiation time of 15 min, and 10:1 (mL/g) ratio of the reaction volume to JATP mass. A low reaction temperature was suitable for selective saccharide production.

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1. Introduction

Jerusalem artichoke (*Helianthus tuberosus* L.) is a species of sunflower which is widely cultivated in different climate zones. It has been conventionally used as food for humans and animals [1]. Jerusalem artichoke tuber (JAT) is considered an excellent potential carbohydrate-rich crop [2] because of its high growth rate, without being affected by pests and plant diseases. It is resistant to poor soil, frost, drought, and requires minimal to no fertilizer [3, 4]. In addition, health products derived from JAT, such as inulin, fructooligosaccharides, fructose, and glucose, have recently been discovered [5].

The main polysaccharide found in JAT is inulin. Inulin is a polysaccharide containing a chain of D-fructose with a glucose terminal (GF_n). D-Fructose connects via β-1,2-glycosidic linkages to form a linear chain structure of inulin, and D-glucose was found at the terminal of inulin with an α-1,2-glycosidic linkage [5].

The advantage of extracted inulin from JAT is its low calories. Thus, it is applied as a fat substitute in low fat fermented sausages [6] and in cheese productions [7]. In some sectors of food production, including orange juice, chocolate and coffee, extracted inulin has been used as a sugar substitute because of its taste [8]. In addition, inulin isolated from JAT has been used as an ingredient in pet food because of its preferred effects on animal digestive systems [9]. Inulin cannot be digested by animal intestinal enzymes and gastric acids because of the glycosidic linkage in its structure. Thus, it is a good source of a calorie free fiber [10] and a carbohydrate source for diabetic patients [8].

Prebiotics are a functional food [11] which have recently drawn much research interest because of their health benefits [12, 13]. However, at this time, natural sources of prebiotics are still limited. Fructooligosaccharides (oligofructose, oligofructan) are common prebiotics [14], and inulin extracted from JAT is a major polysaccharide source to produce fructooligosaccharide prebiotics [15]. Furthermore, fructose and glucose obtained from the hydrolysis of JAT are desirable monosaccharides. For example, fructose has numerous applications in food and beverages as a sweetener, flavor enhancer, humectant, coloring agent, freezing-point depressor, osmotic stabilizer, and pharmaceutical ingredient [16]. Glucose is also widely utilized in food industries as an ingredient in energy drinks and in the health sector [17].

Fructooligosaccharides can be produced by enzymatic methods: by inulinases for hydrolysis reactions of extracted inulin from JAT and other sources [18] and by fructosyl tranferases for the glycosyl transfer reaction of sucrose [19]. These enzymatic methods are limited by high operational cost, complicated processes, low substrate solubility, narrow range of temperature activity of enzymes, and longer reaction times [20, 21]. A chemical hydrolysis of Jerusalem artichoke tuber powder (JATP) would generate fructooligosaccharide in a more cost-effective fashion; however, such a chemical process should be carried out with a selective approach to maximize the productivity. This study integrates microwave radiation (MCR) heating and HCl as a catalyst, to facilitate the hydrolysis of JAT in a selective manner.

The heat generated by MCR has been investigated for its promising applications in various industries [22, 23], including food processing, food drying, polymers, and organic synthesis. When compared to other heating methods, MCR heating has advantages, including non-contact heating, electromagnetic wave energy transfer as a substitute for heat transfer, rapid heating, short reaction time, energy savings because of volumetric heating, homogeneous heating

from the interior of a material, and quick start-up and stopping mechanisms [23, 24]. For an acid catalyst that is also acceptable for food applications, only HCl can be applied in the food industry as a food additive [25]. To the best of our knowledge, the hydrolysis of JATP by a combination of MCR heating and HCl as a catalyst, to extract fructooligosaccharides, fructose, and glucose, has not been reported.

Therefore, we aim to explore the advantages of MCR heating, in combination with HCl as a catalyst, to hydrolyze JATP, in order to circumvent the shortcomings of the enzymatic methods and to determine the optimal conditions to produce both fructooligosaccharides and monosaccharides.

2. Material and methods

2.1 Material and reagents

2.1.1 Processing of Jerusalem artichoke tuber into JATP

Fresh JAT was purchased from Artichoke View Farm, Singburi province, Thailand. The raw material was cut into small pieces and dried in a hot air oven at 60 °C for 2 days to remove most of the moisture. The dried JAT flakes were ground by a household blender and then sieved to obtain Jerusalem artichoke tuber powder (JATP) with a particle size of less than 250 µm. JATP was kept in an airtight container for further usage.

2.1.2 Reagents

Phenol, sulfuric acid (95 - 97 %), dihydroxyacetone (DHA), Coomassie Brilliant Blue G-250, and albumin were purchased from Merck (Germany). 3,5-Dinitrosalicylic acid, sodium hydroxide, 5-hydroxymethyl-2-furfuraldehyde (5-HMF), methanol, and HCl were purchased from Sigma-Aldrich (USA). Fructose and potassium sodium tartrate were purchased from Ajax FineChem Pty Ltd. (Australia). Xylose was purchased from Senn Chemicals (Switzerland). Galactose and glucose were purchased from Fluka (USA). Standard mannans, which have the same range of retention times on HPLC as the oligosaccharides extracted from the JATP, were synthesized according to the published report [26]. Other reagents for proximate constituent analysis of JATP were of analytical grade.

2.2 Physicochemical hydrolysis of JATP

Prior to hydrolysis, JATP was dried at 60 °C overnight in a hot air oven to remove residual moisture in the raw material. The hydrolysis of the JATP was done in a closed vessel (10 mL), in an MCR reactor (CEM, Discover SP 909155, USA). JATP (0.1 g) was mixed with HCl (aq. 1 mL) at a specified concentration in the MCR vessel. All of the hydrolysis reactions were carried out with the set conditions for MCR: maximal pressure of 290 psi, maximal power of 150 watts, and the ramping time of 2 min.

Afterwards, the vessel was allowed to cool to room temperature. Reverse osmosis (RO) water (8 mL) was added and stirred for 1 h to separate the soluble and insoluble portions. The residual solid was collected by filtering through a Whatman No. 1 filter paper. The supernatant (hydrolyzed product) was continually centrifuged at 14,000 rpm, 4 °C, for 20 min. The combined residual solids, collected from both filtration and centrifugation, were dried at 60 °C overnight in a hot air oven to obtain a constant weight, to determine solid loss. The hydrolyzed products (HP) were kept as an aqueous solution in a refrigerator at 4 °C for further analysis.

2.3 Experimental conditions

2.3.1 The effect of temperature on the hydrolysis of JATP

A reaction temperature of 110 - 200 °C (10 °C increments) was investigated in this study. Based preliminary results, the reaction time, concentration of HCl and the ratio of the reaction volume to JATP mass were set to be 15 min, 0.05 M HCl, and 10:1 (mL/g), respectively.

2.3.2 The effect of HCl concentration on the hydrolysis of JATP

At a temperature higher than 120 °C, Maillard Browning and Caramelization

reactions (MBCR) are accelerated over the reaction time. The caramelization temperature of fructose is 110 °C [27-29]. Thus, the reaction temperature was fixed at 110 °C. The HCl concentration was 0.05 - 2.0 M (0.2 M HCl increments from 0.2 – 2 M). The reaction time was fixed at 15 min. The ratio of the reaction volume to JATP mass was 10:1 (mL/g).

2.4 Methods

2.4.1 Proximate constituent analysis of JATP

The proximate constituents of JATP were analyzed, following a standard method set by the Association of Analytical Communities (AOAC) [30]. Briefly, moisture, total ash, crude protein, and crude fat were measured, respectively, by the hot air oven method at 100 °C for 16 - 18 h, drying ash method at 550 °C for 4 - 6 h, Kjeldahl method with 6.25 as the conversion coefficient, and Soxhlet extraction method.

2.4.2 Solid loss (SL) determination

The SL was calculated by the equation (1) [21, 31],

$$\mathrm{SL} = \frac{\mathrm{IS} - \mathrm{RS}}{\mathrm{IS}} \times 100\ \% \qquad (1)$$

where,

SL: Solid loss (%, based on the dried weight of JATP),

IS: Initial dried solid (g),

RS: Residual dried solid (g).

2.4.3 Total carbohydrate (TC) determination

TC was determined by the phenol-sulfuric acid assay method [32]. The HP (0.2 mL) were diluted to 10 mL using RO water in a volumetric flask. The diluted HP (1 mL) was mixed with 1 mL of aqueous phenol solution (5 %) in a closed test tube, and then 5 mL of sulfuric acid (95 - 97 %) was added to the mixture. The mixture was thoroughly mixed and kept in a water bath at 25 °C for 20 min. The absorbance of the mixture was recorded at 490 nm by using a UV-VIS spectrophotometer (Thermo Fisher Scientific, G10S UV-VIS, USA). A mixture of RO water, aqueous phenol solution (5%) and 95 - 97 % sulfuric acid (1:1:5, v/v) was used as a blank. Fructose aqueous solutions at different concentrations were used to construct a standard curve. TC was reported in % (g of TC in 100 g of the dried weight of JATP).

2.4.4 Reducing sugar (RS) determination

RS in the HP was measured by the dinitrosalicylic acid assay [33]. To prepare dinitrosalicylic acid solution, dinitrosalicylic acid (1 g) and potassium sodium tartrate (300 g) were mixed together in 200 mL of 2 M NaOH. The mixture was then adjusted to 800 mL by RO water. The HP (0.2 mL) and the dinitrosalicylic acid solution (2 mL) were mixed thoroughly in a closed test tube, and then the mixture was immersed in boiling water for 10 min before being rapidly cooled to room temperature by ice water. A UV-VIS spectrophotometer (Thermo Fisher Scientific, G10S UV-VIS, USA) was used to recorded UV absorbance of the mixture at 570 nm. A mixture of RO water and dinitrosalicylic acid solution (0.2:2, v/v) was used as a blank. Fructose aqueous solutions at different concentrations were used to construct a standard curve. RS was reported in % (g of RS in 100 g of the dried weight of JATP).

2.4.5 Protein determination

Protein in the HP was quantified by the Bradford method [34, 35]. Coomassie Brilliant Blue G-250 (0.2 g) and 100 mL of ethanol (95 %) were mixed together, and then 200 mL of 85 % phosphoric acid was added to the Bradford reagent. The mixture was thoroughly mixed and diluted to 2 L in a volumetric flask. Before using, the Bradford reagent was filtered through a Whatman No. 1 filter paper. HP (0.1 mL) was diluted to 1 mL by RO water, and then 5 mL of the Bradford reagent was added. The mixture was incubated at room temperature for 5 min. The absorbance of the mixture at 595 nm was recorded by using a UV-VIS spectrophotometer (Thermo Fisher Scientific,

G10S UV-VIS, USA). A mixture of RO water and Bradford reagent with a ratio of 1:5 (v/v) was used as a blank. Albumin aqueous solutions with different concentrations were used to construct a standard curve. Protein content was reported in % (g of protein in 100 g of the dried weight of JATP).

2.4.6 UV absorbance level for determination of intermediate degradation products of MBCR

The UV absorbance levels of the HP at 50-fold dilutions were recorded by using a UV-VIS spectrophotometer (Thermo Fisher Scientific, G10S UV-VIS, USA) at 284 nm [36, 37]. RO water was used as a blank.

2.4.7 5-hydroxymethyl-2-furfuraldehyde (5-HMF) determination

An HPLC (Agilent 1260 Infinity, G1329B, Germany), equipped with C18 (Agilent, ZORBAX Eclipse Plus C18, 959961-902, USA), was used to quantify 5-HMF in the HP [21]. The diluted HP was neutralized and filtered through a 0.2 µm membrane, and 20 µL of the sample was injected into the HPLC. A mixture of deionized water (DI) to methanol (90:10, v/v), filtered through a 0.2 µm membrane, was used as a mobile phase with a flow rate of 1 mL/min [21]. A UV detector on the HPLC was used to record the absorbance of 5-HMF at 284 nm [36, 37]. 5-HMF aqueous solutions with different concentrations were used to construct a standard curve. DHA was used as an internal standard for all HP and a standard curve. The amount of 5-HMF was reported in % (g of 5-HMF in 100 g of dried JATP).

2.4.8 Analysis of the saccharide compositions of HP

The saccharide compositions of the HP were analyzed by an HPLC (Agilent 1260 Infinity, G1329B, Germany), equipped with a carbohydrate column (Transgenomic CARBOSEP CHO682, LEAD column, CHO-99-9854, USA) and a guard column (Transgenomic CARBOSEP CHO 682, Guar Kit, CHO-99-2354, USA). The diluted HP was neutralized and filtered through a 0.2 µm membrane, and then 20 µL of the sample was injected into the HPLC. DI water, filtered through a 0.2 µm membrane, was used as the mobile phase, with a flow rate of 0.4 mL/min. During the analysis process, the column's temperature was maintained at 80 °C. A refractive index detector on the HPLC was used to monitor monosaccharides and fructooligosaccharides in the HP. Fructose, glucose, galactose, xylose, arabinose, and mannan oligosaccharide aqueous solutions with different concentrations were used to construct the standard curves. DHA, as an internal standard, was applied to all HP and the standard curves. Saccharide compositions were reported in % (g of each saccharide in 100 g of dried JATP)

2.4.9 Statistical analysis of data

Following the analysis procedures done in the previous studies [21, 31, 38], the experiments were repeated three times. All of the data were expressed as mean ± standard deviation (n = 3).

3. Results and discussion

3.1 Analysis of proximate constituents of JATP

JATP is rich in carbohydrates, especially fructose and glucose [5, 8, 39-41]. The TC in the dried weight of JATP was 83.1 ± 0.1 %, which makes up the majority of the JATP weight (Table 1).

Table 1. Proximate constituents of JATP (%)

Moisture	3.39 ± 0.18
Total ash	3.66 ± 0.01
Crude protein	8.91 ± 0.18
Crude fat	0.91 ± 0.03
Total carbohydrate	83.13 ± 0.07

With the advantages of the combination of the MCR heating and HCl as a catalyst, we aim to extract most of the TC in JATP and preserve the quality of extracted

fructooligosaccharides and monosaccharides in the HP.

3.2 Oligosaccharides and types of monosaccharides analyses by HPLC with carbohydrate column

The percentage of oligosaccharides, types, and proportions of monosaccharides in the HP of JATP were directly quantified by HPLC without the need of chemical derivatizations. Glucose, xylose, galactose, arabinose, and fructose were the common monosaccharides with retention times on HPLC chromatograms at 20.6, 22.4, 24.5, 27.0, and 29.3 min, respectively. The retention times of the standard mannan oligosaccharides and the extracted fructooligosaccharides in the HP were distinctively shorter, at around 9 to 16 min. A carbohydrate column (Transgenomic CARBOSEP CHO682, LEAD column, CHO-99-9854, USA), with a simple and inexpensive eluent (DI water), allows the HPLC assay to directly profile the saccharides in the HP of JATP and avoid significant errors from incomplete chemical derivatizations that often occur in typical analysis methods [21, 42].

3.3 The effect of reaction temperatures on the hydrolysis of JATP

In general, the reaction temperature has a small positive effect on the overall hydrolysis process of JATP within 110 - 160 °C. The levels of SL (Eq. (1)) and TC increased with increasing reaction temperature, within this range. Reaction temperatures higher than 160 °C negatively affected the SL, TC, and RS (Figure 1A).

The SL level gradually increased and reached a maximal value of 80.8 ± 0.6 % at 170 °C, and it subsequently decreased with increasing reaction temperature because some carbohydrates and proteins were burned, generating a black residual solid at high temperature. This observation corresponds to a decrease in TC, RS, and protein levels at high temperature. TC slowly increased and reached a maximal value of 72.1 ± 1.0 % at 140 °C. The extracted TC was high, considering that the available carbohydrate in JATP is 83.1 ± 0.1 % (Table 1). The TC level remained constant from 140 - 160 °C before drastically decreasing at higher temperatures. The RS level, which refers to monosaccharide and low molecular weight of oligosaccharides, remained constant, around 51.8 ± 1.5 %, for 110 °C to 180 °C. Beyond this range, it dramatically decreased to a minimal value of 37.2 ± 1.2 % at 200 °C. Some carbohydrates and proteins were degraded to form the degradation intermediates of MBCR [27-29], which were in agreement with the decrease of TC and RS, and a significant increase in 5-HMF, as well as the UV absorbance level of HP (Figure 1B).

The formation of 5-HMF and the degradation intermediates of MBCR require the consumption of protons (H^+) [27-29]. Thus, the final pH of HP increased to the highest value of 2.5 ± 0.0, at 160 °C. At higher temperatures, the pH decreased because some carbohydrates also converted into organic acids: acetic, formic, glycolic, and lactic acids, via various reaction pathways, especially by decomposition reactions [21, 43-45]. In addition, at high temperature, 5-HMF in the HP also degraded to form organic acids, such as formic acid and levulinic acid [21, 46, 47], which also led to a decrease of the final pH of HP, at high temperature. The released proteins reached a maximal value of 2.3 ± 0.1 % at 120 °C, and then it decreased with increasing temperature because proteins were degraded at high temperatures.

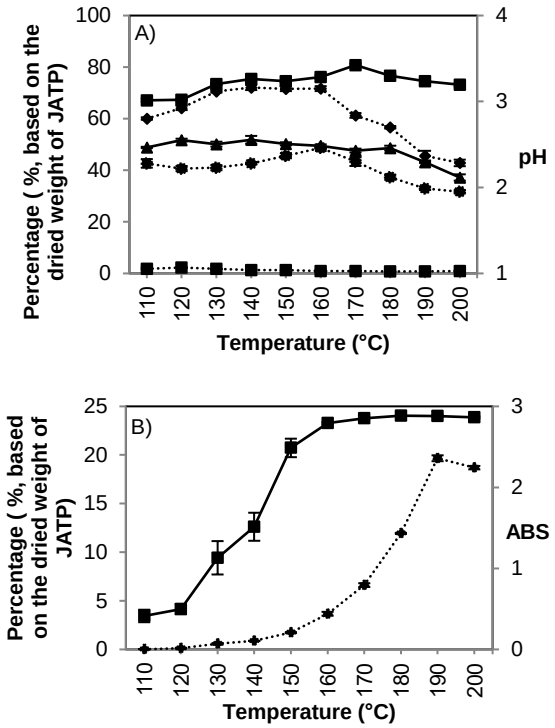

Figure 1. The effect of temperature on the hydrolysis of Jerusalem artichoke tuber powder: A) solid loss (■, solid line), total carbohydrate (♦, dotted line), reducing sugar (▲, solid line), final pH of the hydrolyzed products (●, dotted line), and protein (■, dotted line) and B) 5-HMF (♦, dotted line) and UV absorbance level of the hydrolyzed products (■, solid line) of the hydrolyzed products (15 min, 0.05 M HCl, 10:1 (mL/g) ratio of reaction volume to Jerusalem artichoke tuber powder mass).

A combination of the heat generated by MCR and 0.05 M HCl as a catalyst accelerates the hydrolysis of polysaccharides in JATP to produce fructooligosaccharides, which were continually degraded to form monosaccharides. Generally, the obtained monosaccharides, total monosaccharides (TM), and oligosaccharides decreased with increasing reaction temperature (Table 2).

The major monosaccharides found in JATP were fructose and glucose, which is in agreement with the literature [5, 8, 39-41]. The maximal values of fructose and TM found in HP were 44.7 ± 0.5 % and 57.4 ± 0.3 %, respectively, at 130 °C, and then they decreased to the lowest value of 3.7 ± 0.7 % and 17 ± 1.8 %, respectively, at 200 °C. MBCR accelerate with high temperature [27-29]. Thus, fructose and TM significantly decreased with increasing reaction temperature. For the second major monosaccharide in JATP, the obtained glucose increased and reached the highest value of 9.7 ± 0.5 %, at 190 °C.

The percentage of glucose and minor monosaccharides (xylose, galactose, and arabinose) in the HP slowly increased, while the proportion of fructose decreased when a higher reaction temperature was applied because of the caramelization reaction temperature of fructose at 110 °C, which is lower than those of other monosaccharides. For example, both glucose and galactose have the caramelization reaction temperature at 160 °C [27-29]. The oligosaccharides yield had a maximal value of 1.9 ± 0.1 % at 110 °C, and then decreased with increasing temperature because the oligosaccharides were degraded to form monosaccharides (glucose, xylose, galactose, arabinose, and fructose), and/or produce other intermediate degradation products (methylglyoxal, α-dicarbonyl compounds) of MBCR at high temperature [27, 48-50]. Low reaction temperatures tend to produce more oligosaccharides from the hydrolysis process of JATP.

Table 2. The effect of reaction temperatures on the saccharide compositions of HP (15 min, 0.05 M HCl, 10:1 (mL/g) ratio of reaction volume to Jerusalem artichoke tuber powder mass).

Temperature (°C)	Saccharide compositions (%, based on the dried weight of JATP)						TM
	Oligosaccharides	Glucose	Xylose	Galactose	Arabinose	Fructose	
110	1.87±0.08	4.98±0.16	1.59±0.26	0.52±0.34	0.89±0.44	44.13±0.71	53.36±0.90
120	1.37±0.04	5.80±0.18	2.62±0.11	0.67±0.22	0.98±0.16	41.81±0.44	52.80±0.41
130	1.32±0.01	7.92±0.34	2.79±0.16	0.82±0.29	0.35±0.04	44.67±0.52	57.43±0.28
140	1.38±0.10	5.86±0.61	2.77±0.21	0.65±0.35	0.56±0.29	34.30±0.45	45.05±1.51
150	1.28±0.10	6.46±0.31	2.58±0.33	0.62±0.11	0.94±0.30	36.37±0.64	47.86±1.30
160	1.55±0.08	5.05±0.78	2.83±0.11	1.15±0.58	1.45±0.45	34.10±0.71	45.60±1.16
170	1.20±0.06	7.99±0.63	2.86±0.08	1.16±0.27	1.49±0.25	30.41±0.51	44.69±1.50
180	0.96±0.06	7.02±0.39	2.85±0.18	1.67±0.55	1.15±0.34	19.15±0.73	32.48±1.67
190	0.94±0.05	9.66±0.46	2.78±0.20	1.64±0.09	0.97±0.16	10.02±0.64	25.68±1.28
200	1.12±0.40	7.05±0.59	2.33±0.08	2.22±0.90	0.85±0.47	3.67±0.65	16.96±1.82

5-HMF is a key degradation intermediate of MBCR, and the degree of MBCR depend on the reaction temperature, time, pH and water activity [27-29]. 5-HMF is produced from monosaccharides, which were hydrolyzed from the polysaccharide of JATP and protein via MBCR [27, 29]. The UV absorbance level of the HP at 284 nm represents the magnitude of the degradation products of MBCR [36, 37]. The intermediate degradation products of MBCR are undesirable products generated during the hydrolysis reaction of JATP. Thus, the amount of 5-HMF in the HP was monitored, and the UV absorbance level of the HP was recorded to determine the effect of reaction temperature and HCl concentration on the formation of MBCR intermediates. This information will facilitate the optimization conditions for the hydrolysis reaction of JATP, to selectively produce fructooligosaccharides and monosaccharides.

The 5-HMF and UV absorbance levels of the HP increased with increasing reaction temperature (Figure 1B). The UV absorbance level of the HP exponentially increased and reached the highest value of 2.8 at 180 °C. Then, it remained constant at the higher reaction temperatures. 5-HMF in the HP dramatically increased with the reaction temperature from 110 - 190 °C and reached the maximal value of 19.7 ± 0.3 % at 190 °C. With a temperature higher than 190 °C, 5-HMF decreased because it was degraded to form organic acids such as formic acid, and levulinic acid [21, 46, 47]. This observation also corresponds to the decrease of final pH of the HP at high temperature (Figure 1A). The extents of the MBCR are proportional to the reaction temperature [27-29]. Thus, the percentage of 5-HMF and UV absorbance level of the HP increased at high reaction temperatures. This is in agreement with the decrease of oligosaccharides, TM, monosaccharides, and protein. In addition, it should be noted that low reaction temperatures tend to generate more oligosaccharides and significantly limit MBCR.

In summary, a reaction temperature within the range of 110 – 160 °C has a small positive effect on the hydrolysis process of JATP. The SL, TC, RS, and glucose slightly increased with increasing temperature. However, the amounts of fructose and TM significantly decreased at higher reaction temperatures. At the same time, the extracted oligosaccharides were low and the intermediate degradation products of MBCR were very high.

3.4 The effect of HCl concentrations on the hydrolysis of JATP

Reaction conditions with a low temperature of 110 °C, and with a low range of HCl concentrations, have a positive effect on the hydrolysis process of JATP. SL (Eq. (1)), TC, and RS dramatically increased when increasing the HCl concentration from 0.05 to 0.4 M (Figure 2A) and reached a maximal value of 86.4 ± 0.4 %, 78.9 ± 0.6 %, and 65.3 ± 0.4 % at 0.4 M HCl, respectively. The TC level in the HP at 0.4 M HCl was 78.9 ± 0.6 %, which accounted for most of the available TC in JATP (83.1 ± 0.1 %, Table 1).

With an increase of HCl concentration to 2 M, SL slightly decreased while TC and RS significantly decreased to the minimal values of 36.4 ± 0.6 % and 33.4 ± 0.4 % at 2 M, respectively. At high HCl concentrations, the extracted carbohydrates were degraded to form MBCR intermediate products [27-29], which led to a decrease of TC and RS. This observation corresponds to the significant increase of UV absorbance level of HP and 5-HMF at high HCl concentrations (Figure 2B). A decrease of RS at the HCl concentrations higher than 0.4 M also corresponds to a decrease of monosaccharide and TM (Table 3). Protein is sensitive to low pH. Thus, the released proteins from JATP were slightly decreased from the maximal value of 1.8 ± 0.3 % at 0.05 M, to 0.9 ± 0.2 % at 2 M HCl (Figure 2 A). MBCR were accelerated at high HCl concentrations [27-29]. Thus, TC, RS and proteins decreased.

At a low temperature of 110 °C, the HCl concentration is a major reaction parameter that positively affects the hydrolysis of JATP to produce fructooligosaccharides. The amounts of fructose dramatically decreased when the HCl concentration increased (Table 3). The extracted fructooligosaccharides significantly increased with increasing HCl concentrations. The maximal yield of oligosaccharide was 12.0 ± 0.3 % at 1.8 M HCl. TM, and fructose, drastically decreased from the highest yield of 53.4 ± 0.9 % and 44.1 ± 0.7 % at 0.05 M HCl, to 4.1 ± 1.0 % and 0.8 ± 0.5 %, at 2 M HCl, respectively. The higher HCl concentrations accelerated the degradation of TM and fructose into the intermediates of MBCR [27-29]. This is in agreement with the increase of UV absorbance level of HP and 5-HMF at higher HCl concentrations. The yield of glucose increased and reached a maximal value of 10.1 ± 0.4 % at 0.4 M HCl, and then it decreased. The levels of the minor monosaccharides, which are xylose, galactose, and arabinose, were the highest at 0.4, 1.4, and 1.8 M HCl, respectively.

The 5-HMF levels dramatically increased when the concentration of HCl increased from 0.05 M to 0.6 M. The 5-HMF level reached the highest value of 10.4 ± 0.1 % at 1.2 M HCl, and then it decreased. 5-HMF can be converted into other non-harmful compounds, such as levulinic and formic acids in the presence of high concentrations of HCl [51, 52] (Figure 2B). Therefore, it would also be advantageous to use higher concentrations of HCl in the hydrolysis in order to accelerate the degradation of 5-HMF and to produce more fructooligosaccharides (Table 3). MBCR were limited by a low temperature of 110 °C [27-29]. Thus, the maximal value of 5-HMF found in the HP was 10.4 ± 0.1 % at 1.2 M HCl, which was significantly lower than at 190 °C and 0.05 M HCl. The UV absorbance of the HP suddenly increased from 0.4 ± 0.1, at 0.05 M HCl, to 2.7 ± 0.1 at 0.2 M HCl, and then it remained constant when higher HCl concentrations were applied.

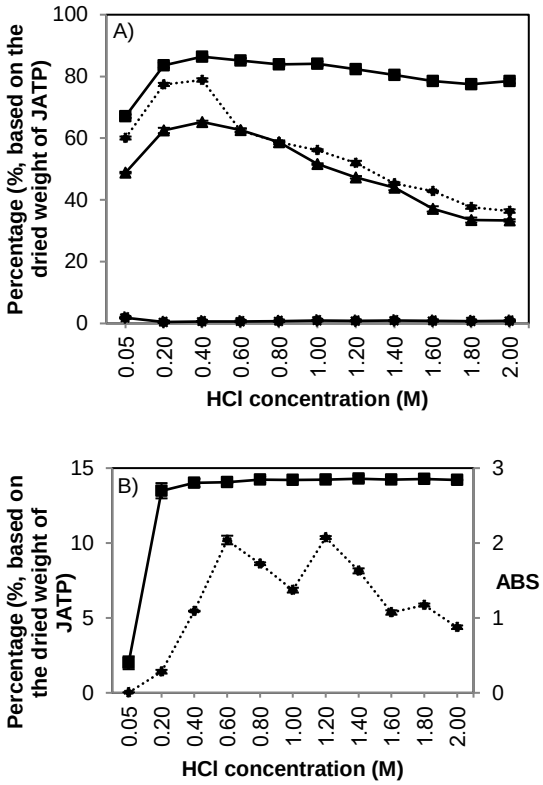

Figure 2. The effect of HCl concentrations on the hydrolysis of Jerusalem artichoke tuber powder: A) solid loss (■, solid line), total carbohydrates (♦, dotted line), reducing sugars (▲, solid line), and protein (●, solid line) and B) 5-HMF (♦, dotted line) and UV absorbance level of the hydrolyzed products (■, solid line) (110 °C, 15 min, 10:1 (mL/g) ratio of reaction volume to Jerusalem artichoke tuber powder mass).

Table 3. The effect of HCl concentrations on the saccharide composition of HP (110 °C, 15 min, 10:1 (mL/g) ratio of reaction volume to Jerusalem artichoke tuber powder mass).

HCl concentration (M)	Saccharide compositions (%, based on the dried weight of JATP)						TM
	Oligosaccharides	Glucose	Xylose	Galactose	Arabinose	Fructose	
0.05	1.87±0.08	4.98±0.16	1.59±0.26	0.52±0.34	0.89±0.44	44.13±0.71	53.36±0.90
0.20	1.32±0.02	2.39±0.40	1.29±0.08	1.02±0.06	0.82±0.40	16.69±0.68	22.20±1.40
0.40	3.31±0.29	10.14±0.41	2.22±0.11	1.59±0.42	1.14±0.25	24.01±0.67	39.11±1.13
0.60	2.74±0.27	5.09±0.63	1.56±0.02	1.31±0.34	0.84±0.23	9.57±0.84	18.37±1.83
0.80	5.67±0.16	1.00±0.28	1.83±0.04	2.20±0.85	1.40±0.83	6.82±0.45	13.26±2.35
1.00	3.96±0.15	0.42±0.23	1.17±0.04	1.17±0.17	0.76±0.22	1.42±0.63	4.94±1.04
1.20	5.61±0.35	0.94±0.28	1.49±0.03	1.26±0.66	0.61±0.12	0.96±0.65	5.27±1.08
1.40	10.05±0.16	5.33±0.54	1.84±0.06	2.26±0.06	1.09±0.53	1.04±0.42	11.57±1.42
1.60	7.84±0.22	1.47±0.19	1.38±0.03	1.52±0.56	1.01±0.65	0.72±0.24	6.11±1.09
1.80	12.04±0.26	1.56±0.19	0.53±0.06	1.51±0.69	1.88±1.74	1.25±0.60	6.72±2.72
2.00	11.19±0.20	1.17±0.21	0.99±0.03	0.81±0.40	0.28±0.05	0.80±0.53	4.05±1.04

In summary, the concentration of HCl significantly affected the hydrolysis reaction of JATP. At 110 °C, the levels of SL, TC, and RS dramatically increased with HCl concentrations from 0.05 M to 0.4 M HCl. The amounts of fructose and TM decreased with high HCl concentrations, while fructooligosaccharides increased when high HCl concentrations were applied. Furthermore, the formation of degradation intermediates from MBCR, which were indicated by the 5-HMF percentage and the UV absorbance level of HP, were limited by a low reaction temperature of 110 °C. In comparison with the subcritical water treatment [21], the introduction of the HCl catalyst, in this study, obviously facilitates the hydrolysis of polysaccharides. The effective hydrolysis can take place at lower temperatures (130 °C versus 250 °C), thus preventing the decompositions of the obtained saccharides. In addition the equipment required in this developed method is less sophisticated than the subcritical water method.

4. Conclusion

In this study, we successfully develop a rapid method to selectively produce fructose, glucose, and fructooligosaccharides, and profile the saccharides obtained from the hydrolysis, using an HPLC assay. The temperature and HCl concentration have considerable effects on the hydrolysis reaction of Jerusalem artichoke tuber powder, although the reaction temperatures from 100° C to 170 °C only have small positive effects on the hydrolysis. To produce fructose, the selective conditions were 130 °C, and 0.05 M HCl. Suitable conditions for both glucose and fructose production were 110 °C and 0.4 M HCl. At 1.8 M HCl, and 110 °C, the highest yield of fructooligosaccharides was obtained, but only a medium amount of 5-HMF was generated. A low reaction temperature of 110 °C is the best option for the production of both monosaccharides and oligosaccharide with various HCl concentrations. The developed method, utilizing a combination of MCR heating and HCl as a catalyst, is able to extract most of the carbohydrate content in Jerusalem artichoke tuber powder and selectively convert it into fructooligosaccharides and monosaccharides in a relatively short reaction time with a low reaction temperature.

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6. References

[1] Ma, X.Y., Zhang, L.H., Shao, H.B., Xu, G., Zhang, F., Ni, F.T. and Brestic, M., Jerusalem Artichoke (*Helianthus tuberosus*), a Medicinal Salt Resistant Plant Has High Adaptability and Multiple Use Values, Medicinal Plants Research, Vol. 5, pp.1272-1279, 2011.

[2] Stauffer, M.D., Chubey, B.B. and Dorrell, D.G., Growth, Yield and Compositional Characteristics of Jerusalem Artichoke as It Relates to Biomass Production, Am. Chem. Soc., Div. Fuel Chem., Prepr (United States), Vol. 25, 1980.

[3] Duke, J.A., Handbook of Energy Crops, NewCROPS Publiscation, Purdue University, Center for New Crops and Plants Products, 1983.

[4] Slimestad, R., Seljaasen, R., Meijer, K. and Skar, S.L., Norwegian-Grown Jerusalem Artichoke (*Helianthus tuberosus* L.)-Morphology and Content of Sugars and Fructo-Oligosaccharides in Stems and Tubers, Journal of the Science of Food and Agriculture, Vol. 90, pp.956-964, 2010.

[5] Yang, L., He, Q.S., Corscadden, K. and Udenigwe, C.C., The Prospects of

Jerusalem Artichoke in Functional Food Ingredients and Bioenergy Production, Biotechnology Reports, Vol. 5, pp.77-88, 2015.

[6] Mendoza, E., Garcıa, M.L., Casas, C. and Selgas, M.D., Inulin as Fat Substitute in Low Fat, Dry Fermented Sausages, Meat Science, Vol. 57, pp.387-393, 2001.

[7] Hennelly, P.J., Dunne, P., O'sullivan, M. and O'riordan, E.D., Textural, Rheological and Microstructural Properties of Imitation Cheese Containing Inulin, Journal of Food Engineering, Vol. 75, pp.388-395, 2006.

[8] Gaafar, A.M., Boudy, E.A. and El-Gazar, H.H., Extraction Conditions of Inulin from Jerusalem Artichoke Tubers and Its Effects on Blood Glucose and Lipid Profile in Diabetic Rats, Journal of American Science, Vol. 6, pp.36-43, 2010.

[9] Flickinger, E.A. and Fahey, G.C., Pet Food and Feed Applications of Inulin, Oligofructose and Other Oligosaccharides, British Journal of Nutrition, Vol. 87, pp.S297-S300, 2002.

[10] Flores, A.C., Morlett, J.A. and Rodríguez, R., Inulin Potential for Enzymatic Obtaining of Prebiotic Oligosaccharides, Critical Reviews in Food Science and Nutrition, Vol. (Just accepted), 2015.

[11] Al-Sheraji, S.H., Ismail, A., Manap, M.Y., Mustafa, S., Yusof, R.M. and Hassan, F.A., Prebiotics as Functional Foods - A Review, Journal of Functional Foods, Vol. 5, pp.1542-1553, 2013.

[12] Roberfroid, M., Prebiotics - the Concept Revisited, The Journal of Nutrition, Vol. 137, pp.830S-837S, 2007.

[13] Rolim, P.M., Development of Prebiotic Food Products and Health Benefits, Food Science and Technology (Campinas), Vol. 35, 3-10, 2015.

[14] Gibson, G.R., Probert, H.M., Loo, J.V., Rastall, R.A. and Roberfroid, M.B., Dietary Modulation of the Human Colonic Microbiota - Updating the Concept of Prebiotics, Nutrition Research Reviews, Vol. 17, pp.259-275, 2004.

[15] Singh, R.S. and Singh, R.P., Production of Fructooligosaccharides from Inulin by Endoinulinases and Their Prebiotic Potential, Food Technology and Biotechnology, Vol. 48, pp.435, 2010.

[16] Hanover, L.M. and White, J.S., Manufacturing, Composition, and Applications of Fructose, The American Journal of Clinical Nutrition, Vol. 58, pp.724S-732S, 1993.

[17] Rayner, C.K., Park, H.S., Wishart, J.M., Kong, M.F., Doran, S.M. and Horowitz, M., Effects of Intraduodenal Glucose and Fructose on Antropyloric Motility and Appetite in Healthy Humans, American Journal of Physiology - Regulatory, Integrative and Comparative Physiology, Vol. 278, pp. R360-R366, 2000.

[18] Fernandes, V.S., Rosa, M. and Jiang, B., Fungal Inulinases as Potential Enzymes for Application in the Food Industry, Food Science and Technology, Vol. 5, pp.1031-1042, 2013.

[19] Yun, J.W., Fructooligosaccharides - Occurrence, Preparation, and Application, Enzyme and Microbial Technology, Vol. 19, pp.107-117, 1996.

[20] Sen, S. and Puskas, J.E., Green Polymer Chemistry - Enzyme Catalysis for Polymer Functionalization, Molecules, Vol. 20, pp.9358-9379, 2015.

[21] Khuwijitjaru, P., Pokpong, A., Klinchongkon, K. and Shuji, A., Production of Oligosaccharides from Coconut Meal by Subcritical Water

Treatment, International Journal of Food Science and Technology, Vol. 49, pp.1946-1952, 2014.

[22] Hoz, A.d.l., Microwave Heating as a Tool for Sustainable Chemistry, CRC Press Publication, Boca Raton, 2010.

[23] Thostenson, E. and Chou, T.W., Microwave Processing-Fundamentals and Applications, Composites Part A - Applied Science and Manufacturing, Vol. 30, pp.1055-1071, 1999.

[24] Haque, K.E., Microwave Energy for Mineral Treatment Processes - A brief Review, International Journal of Mineral Processing, Vol. 57, pp.1-24, 1999.

[25] F.A.O. and W.H.O., Codex Alimentarius - General Standard for Food Additives, Food and Agriculture Organization of the United Nations and World Heald Organization, Viale delle Terme di Caracalla, 00153 Rome, Italy, 2015.

[26] Yongyat, C., Ruchirawat, S. and Boonyarattanakalin, S., Polymerization of Mannosyl Tricyclic Orthoesters for the Synthesis of α(1–6) Mannopyranan-the Backbone of Lipomannan, Bioorganic and Medicinal Chemistry, Vol. 18, pp.3726-3734, 2010.

[27] Simpson, B.K., Nollet, L.M.L., Toldrá, F., Benjakul, S., Paliyath, G. and Hui, Y.H, Food Biochemistry and Food Processing, A John Wiley and Sons Ltd. Publications, Iowa (USA), 2006.

[28] Kroh, L.W., Caramelisation in Food and Beverages, Food Chemistry, Vol. 51, pp.373-379, 1994.

[29] Campbell-Platt, G., Food Science and Technology, A John Wiley and Sons Publiscations, Oxford (UK), 2009.

[30] A.O.A.C., Official Methods of Analysis of AOAC International, AOAC International, Maryland, 2000.

[31] Khuwijitjaru, P., Watsanit, K. and Adachi, S., Carbohydrate Content and Composition of Product from Subcritical Water Treatment of Coconut Meal, Journal of Industrial and Engineering Chemistry, Vol. 18, pp.225-229, 2012.

[32] Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A. and Smith, F., Colorimetric Method for Determination of Sugars and Related Substances, Analytical Chemistry, Vol. 28, pp.350-356, 1956.

[33] Chaplin, M.F. and Kennedy, J.F., Carbohydrate Analysis - A Practical Approach, IRL Press Ltd. Publiscation, Oxford; Washington, DC, 1994.

[34] Bradford, M.M., A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein Dye Binding, Analytical Biochemistry, Vol. 72, pp.248-254, 1976.

[35] Noble, J.E. and Bailey, M.J.A., Quantitation of Protein, Methods in Enzymology, Vol. 463, pp.73-95, 2009.

[36] Jiang, B., Liu, Y., Bhandari, B. and Zhou, W., Impact of Caramelization on the Glass Transition Temperature of Several Caramelized Sugars. Part I - Chemical Analyses, Journal of Agricultural and Food Chemistry, Vol. 56, pp.5138-5147, 2008.

[37] Haghparast, S., Shabanpour, B., Kashiri, H., Alipour, G. and Sudagar, M., A Comparative Study on Antioxidative Properties of Carameled Reducing Sugars; Inhibitory Effect on Lipid Oxidative and Sensory Improvement of Glucose Carameled Products in Shrimp Flesh, Journal of Agricultural Science and Technology, Vol. 15, pp.87-99, 2012.

[38] Passos, C.P. and Coimbra, M.A., Microwave Superheated Water Extraction of Polysaccharides from Spent Coffee Grounds, Carbohydrate Polymers, Vol. 94, pp.626-633, 2013.

[39] Li, H., Zhu, H., Qiao, J., Du, J. and Zhang, H., Optimization of the Main Liming Process for Inulin Crude Extract from Jerusalem Artichoke

Tubers, Frontiers of Chemical Science and Engineering, Vol. 6, pp.348-355, 2012.

[40] Roberfroid, M.B., Nutritional and Health Benefits of Inulin and Oligofructose, Nutrition, Vol. 129, pp.13955-15025, 1999.

[41] Sarchami, T. and Rehmann, L., Optimizing Acid Hydrolysis of Jerusalem Artichoke - Derived Inulin for Fermentative Butanol Production, BioEnergy Research, Vol. 8, 1148-1157, 2015.

[42] Gomis, D.B., Tamayo, D.M. and Alonso, J.M., Determination of Monosaccharides in Cider by Reversed Phase Liquid Chromatography, Analytica Chimica Acta, Vol. 436, pp.173-180, 2001.

[43] Kabyemela, B.M., Adschiri, T., Malaluan, R.M. and Arai, K., Glucose and Fructose Decomposition in Subcritical and Supercritical Water - Detailed Reaction Pathway, Mechanisms, and Kinetics, Industrial and Engineering Chemistry Research, Vol. 38, pp.2888-2895, 1999.

[44] Calvo, L. and Vallejo, D., Formation of Organic Acids during the Hydrolysis and Oxidation of Several Wastes in Sub- and Supercritical Water, Industrial and Engineering Chemistry Research, Vol. 41, pp.6503-6509, 2002.

[45] Sasaki, M., Fang, Z., Fukushima, Y., Adschiri, T. and Arai, K., Dissolution and Hydrolysis of Cellulose in Subcritical and Supercritical Water, Industrial and Engineering Chemistry Research, Vol. 39, pp.2883-2890, 2000.

[46] Kruse, A. and Gawlik, A., Biomass Conversion in Water at 330-410 °C and 30-50 MPa. Identification of Key Compounds for Indicating Different Chemical Reaction Pathways, Industrial and Engineering Chemistry Research, Vol. 42, pp.267-279, 2003.

[47] Gomes, F.N.D.C., Pereira, L.R., Ribeiro, N.F.P. and Souza, M.M.V.M., Production of 5-Hydroxylmethylfurfural (HMF) via Fructose Dehydration - Effect of Solvent and Salting out, Brazilian Journal of Chemical Engineering, Vol. 32, pp.119-126, 2015.

[48] Kroh, L.W., Jalyschko, W. and Häseler, J., Non-Volatile Reaction Products by Heat - Induced Degradation of α-Glucans. Part I - Analysis of Oligomeric Maltodextrins and Anhydrosugars, Starch-Stärke, Vol. 48, pp.426-433, 1996.

[49] Farkas, P.H., Örsi, F. and Kroh, L.W., Methylglyoxal Determination from Different Carbohydrates during Heat Processing, Food Chemistry, Vol. 59, pp.157-163, 1997.

[50] Hollnagel, A. and Kroh, L.W., Degradation of Oligosaccharides in Non-Enzymatic Browning by Formation of α-Dicarbonyl Compounds via a "Peeling off" Mechanism, Journal of Agricultural and Food Chemistry, Vol. 48, pp.6219-6226, 2000.

[51] Kuster, B.F. and Temmink, H.M.G., The Influence of pH and Weak Acid Anions on the Dehydration of D-Fructose, Carbohydrate Research, Vol. 54, pp.185-191, 1977.

[52] Asghari, F.S. and Yoshida, H., Acid Catalyzed Production of 5-Hydroxymethyl Furfural from D-Fructose in Subcritical Water, Industrial and Engineering Chemistry Research, Vol. 45, pp.2163-2173, 2006.