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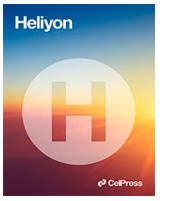

Research article

Optimisation of dry heat treatment conditions for modification of faba bean (*Vicia faba* L.) starch

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ABSTRACT

Faba bean is a protein-rich starchy grain that is underutilised in the UK. The starch of faba bean can be modified using environmentally friendly methods like dry heat treatment (DHT) to enhance functional and its physicochemical properties. This study investigated the impact of dry heat temperature and time on the structure, functional and physicochemical properties of faba bean starch (FBS) using a two-factor central composite rotatable design. Factors (DHT temperature:100–150 °C and DHT time:0.5–5 h) with their respective α mid-point values led to 13 experimental runs. Selected pasting and functional properties were measured as response variables. Corn starch was included as a reference and compared with the FBS modified using the optimized conditions. DHT increased peak (approx. 2205–2267 cP), final (approx. 3525–3642 cP) and setback (approx. 1887–1993 cP) viscosities but decreased the amylose content of FBS. Colour, as measured by lightness value, morphology and crystalline type were not altered but the starches showed a loss of order and an increase in crystallinity after DHT. FBS appeared resilient to DHT but showed higher swelling power and pasting properties compared to the corn starch control. The optimum DHT conditions to produce starch with desirable properties are a temperature of 100 °C for 0.1716 h, with a desirability factor of 66 %.

1. Introduction

Faba bean (*Vicia faba*) is an important grain legume that is rich in protein (approx. 28–39 %) and carbohydrate (51–68 %) [1–3] including starch. Depending on the variety and the source of the grain, the starch content of faba bean may vary between 22 and 45 % on dry weight basis, [4]. Besides the nutritional composition, faba bean also can fix atmospheric nitrogen, in addition to being used as a cover crop within various agroecological systems [5,6]. The main producers of faba bean are China, Ethiopia and the United Kingdom, with the UK producing about 547 800 tons on 136 950 ha of land [7]. Despite the nutritional and agronomic advantages, faba bean remains an underutilised crop in the UK where it is mainly used in animal feed, although there are efforts to enhance its use in beer production through barley supplementation [8]. The underutilisation of crops including pulses has been associated with insufficient research to fully unlock their potential and increase their value [9]. Other reasons for underutilisation and neglect of the crop may be

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due to the presence of antinutrients such as convicine, pyrimidine glycosides, and vicine [10].

The use of traditional food processing technologies such as germination, soaking, cooking, fermentation, and roasting have been used to reduce the level of antinutrients in grains and to enhance their utilisation. Another promising strategy to enhance the use of faba bean is to extract the starch for various industrial uses. For example, it could be used as an emulsifier and a thickening agent in food systems. Globally, the demand for alternative starch sources is increasing [11] and pulses like faba bean can play a significant role in meeting this demand because they are a good source of starch and contain a high level of resistant starch [12]. Previous research efforts showed that faba bean can be used as an industrial starch source [13–17]. However, native starches have very limited use because of their susceptibility to retrogradation, poor freeze-thaw stability and poor resistance to processing conditions such as high shear and temperature. To address this challenge, starches are often modified through physical, genetic, chemical, or enzymatic, methods or sometimes through a combination of these approaches [18]. Physical modifications such as dry heat treatment is considered safe, cheap and environmentally friendly since they do not require chemicals or biological agents [19].

Earlier studies on faba bean starch modification focused on crosslinking [15,20,21], lintnerisation with hydrochloric acid [22], heat moisture treatment (HMT) [23] and gamma irradiation [14]. The study on gamma irradiation of faba bean starch at different irradiation doses of 0, 5, 10 and 15 kGy reportedly increased the water absorption capacity of the starch, but pasting properties and syneresis decreased as the irradiation dose increased [14]. Both gamma irradiation and HMT are physical methods of starch modification that are promising for creating novel starches with unique functionalities in the industry. An early study suggested the use of environmentally friendly alternatives such as annealing, HMT and dry heat treatment (DHT) in starch modification [24]. DHT is a physical modification method that is yet to be explored in the modification of faba bean starch. DHT changes the functional and physicochemical properties of starch without destroying granule structures [25]. According to previous studies, DHT produces starches with similar functionality to that obtained by chemical cross-linking [25,26]. DHT generally involves the heating of starch at a low moisture content (<10 % w/w), varying temperatures (110–150 °C) and times (1–4 h) [27].

Different temperature (110–180 °C) and time (0.5–4h) combinations for DHT of starch from varying botanical origin have been reported in the literature with varied results [25,28–32]. For example, at temperatures below 130 °C, DHT reportedly reduced the swelling power of mung bean starch [31] and sweet potato starch [32], but increased those of high amylose rice starch within the same temperature regime [27]. These results suggest that starches from different sources respond differently to DHT, and thus processing conditions must be optimized for each type of starch. Starch swelling behaviour is unique to the source of the starch and results from dissolution and physical rupture of starch molecules during gelatinization [33]. According to Jia et al. [33] swelling and gelatinization are processes that are frequently encountered and hold significant importance in the food industry.

Optimization technique is used to obtain design variables and the most effective and efficient set of operating conditions that can save time and cost. Therefore, the novelty of this research stems from the use of optimization technique to model the behaviour of modified starch under controlled conditions of temperature and time. This research aims to determine the structure, functional and physicochemical properties of faba bean starch obtained from optimized conditions of temperature and time during DHT. A reference sample (corn starch) was included in this study and was modified under identical conditions as the faba bean starch. Corn starch was used since it is the most widely used source of starch in the industry.

2. Materials and methods

2.1. Materials

Faba bean seeds were obtained from Elsoms Seeds Ltd, UK. The seeds were stored in the laboratory at ambient temperature (20 ±2 °C). Corn starch obtained from Sigma-Aldrich was included as a reference sample. The solvents and chemicals used for the study were of analytical grade.

2.2. Extraction of starch

Starch was isolated from faba bean seeds following the cowpea starch extraction method by Oyeyinka [11]. Soaking of grains was done for 24 h followed by manual dehulling. Dehulled grains were milled to obtain a slurry using a warring blender. Distilled water was added to the grains during milling in ratio 1:3 of the grains to water, respectively. To obtain the starch, a muslin cloth was used to separate it from the slurry. The resulting starch suspension was then left to settle overnight at 4 °C. The supernatant was decanted and the sedimented starch re-suspended in distilled water. The pH of the slurry was adjusted to pH 10 using 0.05 M NaOH to solubilise the proteins. Sample was centrifuged at 4000×*g* in an Eppendorf Centrifuge (5702R, Hamburg, Germany) for 30 min, the supernatant was decanted, and sample was re-suspended again in water. Subsequently, the sample was neutralized to pH 7 using 2 M HCl, allowed to settle and washed severally with distilled water. Finally, starch sample was left over night to settle at 4 °C. The resulting starch was dried at 50 °C in a hot air oven (Binder GmbH Im Mittleren Tuttlngen/Germany) for 24 h to a moisture content of an average of 8.5 % for two replicate extractions. Dried starch was sieved using a sieve with aperture size of 150 μm and stored in Zip-lock bags until needed for analyses.

2.3. DHT of starch

The DHT experiment was designed using a two-factor central composite rotatable design with 5 centres of rotation ($\alpha = 1.414$) using a Minitab 17.0 software (Minitab Inc. USA). This resulted in 13 experimental runs from two variables, heating temperature

(100–150 °C) and time (1–5 h). These experimental conditions and their corresponding midpoint values are presented in Table 1. The temperature and time ranges used in this study were chosen after reviewing various values reported in the literature [25,28–32]. Dried starch sample (20 g) was weighed into Petri dishes, flattened to have uniform thickness, and heated in the oven at the specified temperature and time. Heated starches were placed in a desiccator to cool down for about 1 h before further analysis. The lightness (L*), functional (water absorption capacity and swelling power) and pasting properties of the native and heat-treated starches were determined and the data obtained were used as response variables to assess the experiment.

2.4. Colour and amylose content

Starch colour for native and heat-treated samples was assessed by measuring the L* values using a colorFlex colorimeter (A60-1014-593, USA). The colorimeter was standardised using a white tile and three snapshots of the starch sample were taken.

The amylose content of the starch samples was determined following the iodine-binding method described by previous authors [34].

2.5. Water absorption capacity (WAC)

The WAC of the native and heat-treated starches was determined as previously described [9]. One gram of starch sample was weighed into a pre-weighed 50 mL plastic centrifuge tube, and 10 mL of distilled water was added. The sample vortexed to dissolve the starch in water and the tube was left in tube holders for 30 min at room temperature (20 ± 2 °C). The tube and its content were subjected to centrifugation at 4000×*g* for 30 min using an Eppendorf Centrifuge (5702R, Hamburg, Germany). The WAC was measured as a gram of water absorbed per gram of starch.

2.6. Swelling power

Swelling power of the native and dry-heated starches was measured using the method described in the literature [9]. Briefly, the starch sample was dispersed in distilled water to a 1 % concentration in a pre-weighed centrifuge tube. The tube was then heated in a shaking water bath at 50, 60, 70, 80 and 90 °C for 30 min each. The heating was followed by centrifugation at 4000×*g* in an Eppendorf Centrifuge (5702R, Hamburg, Germany) for 30 min. The supernatant was removed, and swelling power was determined by weighing the residue post-centrifugation and calculating it relative to the initial dry weight of the starch.

2.7. Pasting properties

The pasting properties of native and dry heated starches were measured using a Perten RVA Tecmaster (PerkinElmer, Bucks, England) according to instrument's standard method. Starch (2.5 g) was weighed into a canister and water was added according to the corrected moisture value provided by the instrument. The starch suspension was mixed with the paddle to disperse the starch properly before starting the test. The temperature program followed a 13-min cycle that included idling at 50 °C, heating from 50 °C to 95 °C, maintaining 95 °C, cooling back to 50 °C, and then holding at 50 °C. The pasting properties were analyzed using Thermocline for Windows RVA software.

2.8. Numerical optimisation of dry heating conditions

A two-factor central composite rotatable design model (Equation (1)) was used to optimize the dry heating conditions of temperature and time, and to determine the regression coefficients. Optimum conditions were determined by minimizing the pasting temperature, setback viscosity, pasting time, and swelling power (50–90 °C), while maximising the L*, peak viscosity, breakdown viscosity, final viscosity, trough viscosity, and WAC to achieve the highest desirability factor. These parameters were chosen to produce starch that could be used in baking applications.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_{12} AB + \beta_{11} A^2 + \beta_{22} B^2 \quad (1)$$

Where Y is the response, $\beta_1, \beta_2 \ldots \beta_{22}$ are coefficients of regression while A and B are experimental factors.

Table 1
Experimental conditions for dry heated faba bean starch.

Factors	Levels					
	Codes	- α	−1	0	1	α
Temperature (°C)	A	89.64	100	125	150	160.35
Time (h)	B	0.17	0.5	3	5	5.83

2.9. Analyses of faba bean starch and control corn starch under optimized conditions

2.9.1. Functional and pasting properties

The method previously described in sections 2.5-2.7 was used to assess the colour, WAC, swelling power and pasting properties of the optimized sample.

2.9.2. Morphology and particle size

Starch granule morphology was investigated using a scanning electron microscope (FEI Nova NanoSEM 450) at an accelerating voltage of 3 KV. In brief, a thin layer of starch granules was applied to a glass coverslip mounted on top of an aluminium specimen holder. The starch was coated with a gold film of gold approximately 30 nm thick for 2 min [35]. The particle size of faba bean starch granules was determined using a Mastersizer 3000 laser particle size analyser (Malver Instruments, Malvern, UK) as described previously [36].

2.9.3. X-ray diffraction

The powder x-ray diffraction measurements of the starch samples were obtained using a Bruker D8 Discover diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2-theta range of 5°-30° at 40 kV, and an electric current of 40 mA. Briefly, starch was placed onto a zero background silicon wafer and scanned to obtain the diffraction patterns of the samples [9].

2.9.4. Fourier transform infrared spectroscopy (FTIR)

The ordered structure of starch was analyzed using a spectrometer (Model) as reported by Oyeyinka et al. [9]. The spectra were obtained in the transmittance mode with 64 scans from 500 to 4000 cm^{-1}.

2.10. Statistical analysis

Duplicate samples were prepared and these samples were analyzed in triplicates. Data were subjected to one-way analysis of variance (ANOVA) and mean comparisons were done using the Fisher Least Significant Difference test at 5 % level of significance using the Statistical Package for the Social Sciences. Percentages reported in this study are calculated on a dry starch basis.

3. Results and discussion

3.1. Colour, functional and pasting properties of experimental samples

The colour of the starch as measured by the lightness value (L*) and functional properties of faba bean starch under the dry heat treatment conditions of temperature and time are presented in Table S1, while the pasting characteristics are presented in Table S2. The statistical analysis of the data in Table S1 shows that DHT significantly ($p \leq 0.05$) altered the L* value. The L* values of the dry heated faba bean starches (DFS) were generally lower than the native faba bean starch (NFS), although samples heated at 100 °C for 1 h and 100 °C for 5 h showed significantly higher L* values, while the sample heated at 150 °C for 1 h showed similar L* value to the NFS. The variation in the L* values is an indicating that the DHT altered the whiteness of the starch samples. DHT treatment can reduce the whiteness of starch due to the breakdown of the starch molecules, resulting in the formation of brownish compounds through dextrinization and caramelization. Pramodrao and Riar [37] reported a significant decrease in the L* value for taro, potato and sweet potato starches dry heated for 2 and 4 h.

The ability of NFS and DFS to absorb water (WAC) were similar and not significantly ($p > 0.05$) affected by the DHT process (Table S1). Although there were no significant differences among the WAC values, longer heating time seems to favour higher WAC, especially at the same heating temperature. The slightly high but insignificant increase could be due to the minor enlargement in the starch granules after DHT (further details in section 3.3).

Regardless of the experimental conditions of temperature and time, the swelling power of NFS and DFS increased with an increase in test temperature from 50 to 90 °C (Table S1). This increase in swelling power with an increase in temperature is generally associated with the melting of starch crystallites, which suggests starch gelatinization. The impact of DHT on the swelling behaviour of the starch varied with the test temperature (Table S1). Higher test temperatures of 70, 80 and 90 °C did not significantly change the swelling power of the starches. However, the swelling power of the starches showed significant differences at 50 and 60 °C. Within this test temperature (50 and 60 °C), higher dry heat temperatures led to increased swelling power. Similarly, longer dry heating time also displayed higher swelling power. For example, at the same heating time of 5 h, the swelling power of the starch heated at 150 °C (1.17–2.14 g/g) was significantly higher than at 100 °C (1.01–1.78 g/g).

DHT significantly changed the pasting properties of faba bean starch (Table S2). The time to peak for the modified starches were significantly lower than the NFS, indicating that the modification resulted in reducing the time required to form the starch paste. With the exception of the starch modified at 125 °C for 0.17 h and 150 °C for 1 h, the modified starches generally showed lower but not significant pasting temperature than the NFS. Liang et al. [32] also found that both repeated and continuous dry heat treatments did not change the pasting temperature of sweet potato starch. All other pasting properties, i.e., final viscosity, peak viscosity, setback viscosity and trough viscosity of faba bean starch (except for starch heated at 150 °C for 5 h and 125 °C for 5.8 h) increased after DHT (Table S2). Variations have been observed in the impact of DHT on starch pasting properties among different authors. For instance, while certain researchers reported an increase in peak viscosity after DHT [28,29,38], others found the opposite [39,40]. These

variations suggest the need for optimisation which is the focus of this study. In the subsequent section, the optimized sample was compared with the native unmodified counterpart and the corn reference sample.

3.2. Numerical optimisation of DHT conditions

The optimisation of heating temperature and time conditions used during the DHT of faba bean starch was done by minimizing the pasting temperature, setback viscosity, pasting time, and swelling power (50–90 °C) and maximising the L*, breakdown viscosity, final viscosity, peak viscosity, trough viscosity, and WAC. The pre-set conditions were specified in Minitab 19.0 software (Minitab Inc., USA). The responses obtained (Tables S1 and S2) were entered into the software and analyzed at the defined maximum and minimum conditions. Table S3 displays the regression coefficients (β_0-β_{12}) for each response along with their corresponding R^2 values as determined by the model. The optimal temperature and time conditions were found to be 100 °C and 0.1716 h, respectively, with a desirability factor (Df) of 66 %. After establishing the optimum conditions, the dry-heated starch under these conditions was produced and compared with the NFS and corn starch. The morphology, amylose content, functional, pasting, particle size distribution, thermal, crystallinity pattern and infrared spectra, of these starches were further characterized.

3.3. Morphology and amylose content

NFS were smooth on the surface and mostly oval-shaped (Fig. 1). The NCS, on the other hand, showed irregular and polygonal-shaped granules (Fig. 1), but were generally smaller in size than the NFS (Table 2). A few corn starch granules had some holes on the surface which is consistent with previous research [41,42]. The morphological characteristics of the starches examined in this study align with earlier studies on faba bean [14,43] and corn starches [41,42,44]. As observed in this study, an earlier research also found larger average particle size for FBS than those of corn starch [43]. Legume starches are generally bigger in size than cereal starches and this variation in size has been asscoiated with differences in botanical origin, soil types, cultural practices and growing conditions.

The DHT did not significantly change the shape and size of faba bean starch, although the granules appeared slightly larger in size after DHT (Fig. 1 & Table 2). The little or no change in granule morphology observed in this study may be attributed to the relatively low temperature (100 °C) and heating time of 0.17 h (approx. 10 min) used to prepare the optimized sample. Although some studies reported that DHT resulted in a cracked appearance in adzuki bean starch [45] and water chestnut starch [46], our finding on native faba bean and corn starches is consistent with the findings of other researchers for mung bean starch [32] and potato starch [47] after DHT. Sun et al. [25] noted that DHT changes the functional and physicochemical properties of starch while preserving the granule structure. These authors reported that dry heated proso millet starch was smooth, but appeared plumper compared with the native one, indicating minimal changes in the granule morphology. SEM images of gelatinized starches, however, showed considerable differences in granule morphology. For example, proso millet starch dry heated at 130 °C for 4 h reportedly had more small holes in the paste than the native starch. In the current study, the morphology of the pasted starch was not measured, hence, it may be difficult to compare the structure of the modified starch when gelatinized. Differences in the impact of DHT on starch granule morphology may be due to DHT

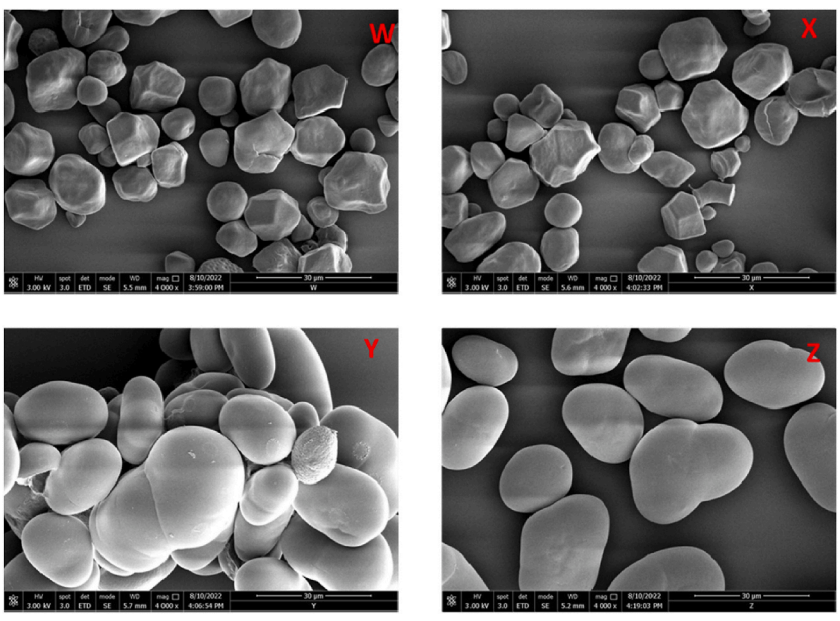

Fig. 1. Scanning electron micrographs of native and modified starches.
Magnification: x4000, W: Native corn starch, X: Dry heated corn starch, Y: native faba bean starch, Z: Dry heated faba bean starch.

Table 2
Amylose content, functional and physicochemical properties of native and modified corn and faba bean starches.

Parameters	NCS	DCS	NFS	DFS
Peak viscosity (cP)	$1340.00^{d} \pm 18.52$	$1539.33^{c} \pm 13.79$	$2205.00^{b} \pm 19.93$	$2267.00^{a} \pm 11.00$
Trough viscosity (cP)	$835.00^{a} \pm 24.06$	$945.67^{b} \pm 10.02$	$1637.33^{a} \pm 46.09$	$1649.33^{a} \pm 29.95$
Breakdown viscosity (cP)	$505.00^{c} \pm 10.15$	$660.33^{a} \pm 45.35$	$567.67^{b} \pm 29.26$	$617.67^{b} \pm 16.26$
Final viscosity (cP)	$1225.00^{d} \pm 14.79$	$1423.33^{c} \pm 17.93$	$3524.67^{b} \pm 17.56$	$3642.00^{a} \pm 42.58$
Setback viscosity (cP)	$390.00^{d} \pm 38.30$	$459.67^{c} \pm 32.62$	$1887.33^{b} \pm 28.54$	$1992.67^{a} \pm 43.66$
Peak Time (min)	$5.33^{a} \pm 0.07$	$5.31^{a} \pm 0.03$	$4.73^{b} \pm 0.07$	$4.71^{b} \pm 0.07$
Pasting Temperature (^{o}C)	$86.47^{a} \pm 0.06$	$83.68^{b} \pm 0.46$	$72.63^{c} \pm 0.06$	$72.62^{c} \pm 0.03$
Amylose content (%)	$27.04^{b} \pm 0.30$	$21.95^{c} \pm 0.86$	$31.58^{a} \pm 0.01$	$27.29^{b} \pm 0.33$
Ratio of 1045/1022 cm^{-1}	$1.36^{a} \pm 0.04$	$1.34^{a} \pm 0.07$	$1.31^{a} \pm 0.12$	$1.24^{a} \pm 0.18$
Ratio of 1022/955 cm^{-1}	$0.54^{c} \pm 0.01$	$0.58^{bc} \pm 0.01$	$0.62^{b} \pm 0.04$	$0.72^{a} \pm 0.03$
L*	$99.65^{a} \pm 0.46$	$99.93^{a} \pm 0.16$	$97.63^{b} \pm 0.15$	$97.53^{b} \pm 0.04$
a*	$3.15^{b} \pm 0.04$	$3.15^{b} \pm 0.04$	$3.48^{a} \pm 0.02$	$3.46^{a} \pm 0.03$
b*	$5.16^{a} \pm 0.07$	$5.08^{a} \pm 0.06$	$4.34^{b} \pm 0.16$	$4.38^{b} \pm 0.04$
Dv (10) μm	$7.58^{b} \pm 0.04$	$7.71^{b} \pm 0.03$	$16.17^{a} \pm 0.42$	$16.17^{a} \pm 0.12$
Dv (50) μm	$15.99^{b} \pm 0.12$	$16.17^{b} \pm 0.13$	$26.23^{a} \pm 0.74$	$26.25^{a} \pm 0.22$
Dv (90) μm	$27.86^{b} \pm 0.51$	$28.07^{b} \pm 0.46$	$38.66^{a} \pm 1.10$	$38.73^{a} \pm 0.36$
WAC (g starch/g water)	$1.53^{a} \pm 0.09$	$1.75^{a} \pm 0.27$	$1.68^{a} \pm 0.08$	$1.70^{a} \pm 0.20$

Values expressed are mean ± standard deviation. Mean with the same superscripts in a row shows no significant difference ($p > 0.05$); WAC: Water absorption capacity; SP: Swelling power; L*: Lightness; 0 is black, 100 is white, a* (red-green) axis-positive values are red; negative values are green and b* (yellow-blue) axis-positive values are yellow; negative values are blue; PV: peak viscosity; TV: trough viscosity; BV: breakdown viscosity; final viscosity, SV: setback viscosity; PT: pasting temperature and Pt: peak time. NCS: Native corn starch; DCS: Dry heated corn starch; NFS: Native faba bean starch; DFS: Dry heated faba bean starch; Dv (10) represent the diameter of starch granules when the cumulative distribution of particles diameter is 10 %; Dv (50) represent the diameter of starch granules when the cumulative distribution of particles diameter is 50 %; Dv (90) represent the diameter of starch granules when the cumulative distribution of particles diameter is 90 %.

conditions, starch source composition as earlier reported [47].

The amylose content for NFS (31.58 %) was significantly higher than that of corn starch (27.04 %). The amylose content recorded in this study is within the range (29–40 %) reported for legume starches [48,49]. Legumes are generally characterized by higher amylose content than cereal starches, except for high amylose maize starch. DHT reduced the amylose content of both starches to 27.29 % and 21.95 %, respectively. Reduction in amylose content after DHT is suggested to result from the partial destruction of amylose molecules [27,32]. According to Li et al. [50], amylose is easily cracked under high temperature and the degree of destruction may vary with the heating temperature and time, resulting in a modification of the amylose chains [30]. The impact of DHT seems to vary among different researchers. For example, DHT reportedly reduced the amylose content of starches from adzuki bean [45], cassava [51] and chestnut [46]. Ge et al. [45] found a correlation between reduction in amylose content and reduction in the molecular weight of amylose, further suggesting possible depolymerisation during DHT. Nevertheless, some authors found an increase in amylose content of potato starch subjected to DHT [47]. The longer heating time of up to 9 h reported by Zhang et al. [47] may explain the difference.

3.4. WAC and swelling power of optimized samples

DHT insignificantly ($p \geq 0.05$) increased the WAC of NFS and NCS (Table 2). The same trend of insignificant increase in the swelling ability of the starches was also observed after DHT, except for the swelling power at 50 and 60 °C test temperatures (Fig. S1). Native and modified FBS generally displayed higher swelling ability than the corn starches which may be linked with the differences in granule size (Fig. 1). Jia et al. [33] noted that granule morphology and surface changes in starch granules can influence starch swelling properties. The slight increase in swelling power may be attributed to variation in the amylose content of the starches (Table 2) and possibly suggest little or no starch damage after DHT [52,53]. Previous studies showed that the swelling capacity of starch positively correlated ($r = 0.992$, $p < 0.01$) with the damaged starch content [52]. The increased swelling is however accompanied by a progressive fragmentation of amylopectin and increased solubilization which can gradually reduce swelling potential [53,54]. When starch is heated in the presence of water, water molecules penetrate the amorphous region of the starch granule forming new bonds with starch molecules [33]. This is accompanied by starch granule swelling, amylose leaching and increase in viscosity. Further heating may result in starch granule damage (cracking) which may enhance further swelling of starch. Previous studies, though found significant changes in functional properties of starches after DHT [27,28,31,47], the temperature (>100 °C) and time (1–9 h) combination used as well as the source of the starch may explain the differences observed. Furthermore, the different impact of DHT on the crystallinity of different starches may also explain the variation in the results reported for DHT on starch swelling power [33].

3.5. Pasting properties of optimized samples

Regardless of modification, the pasting profiles of faba bean starches are similar (Fig. 2), though their properties differ (Table 2). Under optimized conditions of temperature and time, the DHT increased all the pasting properties of faba bean starch except the time to peak and pasting temperature, which were very similar and showed a slight but insignificant decrease. Peak viscosity which

represents the swelling peak of faba bean starch increased from 2205 cP to 2267 cP, which is about a 3 % increase. Corn starch control also showed an increase in peak viscosity after DHT but with a much higher increase (approx. 15 %). Starch peak viscosity is affected by various factors including amylose content, the amount of damaged starch, and the distribution of amylopectin chain length in starch [55–57]. Previous studies reported that starch with high amylose tends to exhibit limited swelling during pasting [58]. Thus, the higher peak viscosity of faba bean starch compared to the corn starch control may be due to differences in amylose content (Table 2). Furthermore, variation in peak viscosity after modification could also be due to the loosening of the starch structure which enhances the ingression of water into the granule interior and swelling during pasting [11]. Another plausible reason is the presence of minor non-starch components, such as lipids, in cereal starches. These components may form inclusion complexes, which could further restrict the swelling of starch granules [11].

Setback viscosity is an important pasting parameter that dictates the retrogradation tendencies of starch. DHT generally increased the setback viscosity of both faba bean and corn starches, though the latter had a much higher value than the former. The observed increase in setback viscosity suggests that DHT would produce faba bean starch with a greater tendency for retrogradation and hence, may find applications in the production of breakfast cereals [59]. Furthermore, starches with a high rate of retrogradation could also be used to develop foods for the diabetic due to their slower rate of digestion and controlled release of glucose into the bloodstream [60, 61].

The final viscosity of faba bean starch and corn starch which corresponds to the viscosity after the paste is cooled to 50 °C also increased significantly after DHT. Faba bean starch displayed a greater final viscosity compared to the corn starch control, presumably due to its relatively higher amylose content (Table 2). The increased final viscosity suggests that modified faba bean starch can increase the viscosity of foods better than unmodified faba bean starch at the same concentration, especially after DHT.

An increase in starch pasting properties after DHT has also been reported for rice starch [27,29] and quinoa starch [62]. However, a significant reduction in pasting properties was also reported by other researchers [28,31,47]. It is possible that starch source may influence the behaviour of starches to DHT. This seems plausible since most of the studies that reported reduced pasting properties are potato starch which are tuber starches [28,31,47]. Other possible sources of variation are amylose to amylopectin ratio and the molecular structure of these starch components. The chain length distribution of amylopectin and amylose molecular size is well-known to significantly influence starch pasting properties [55]. For example, Huang et al. [63], found positive correlation between higher pasting peak viscosity and greater proportion of long chain amylopectin in cowpea starch. Thus, it is also possible that the DHT has changed the molecular architecture of amylopectin during the treatment. According to Cai et al. [64], the extent of damaged starch can also influence the pasting properties of starches. More recently, the molecular size of DHT starches was positively correlated with pasting parameters such as final viscosity, peak viscosity, setback viscosity and trough viscosity [30], indicating that changes in the molecular structures of the faba bean and corn starches may have influenced the observed changes in the functional and physicochemical properties. Future studies should therefore evaluate the changes in the chain length of starches subjected to DHT.

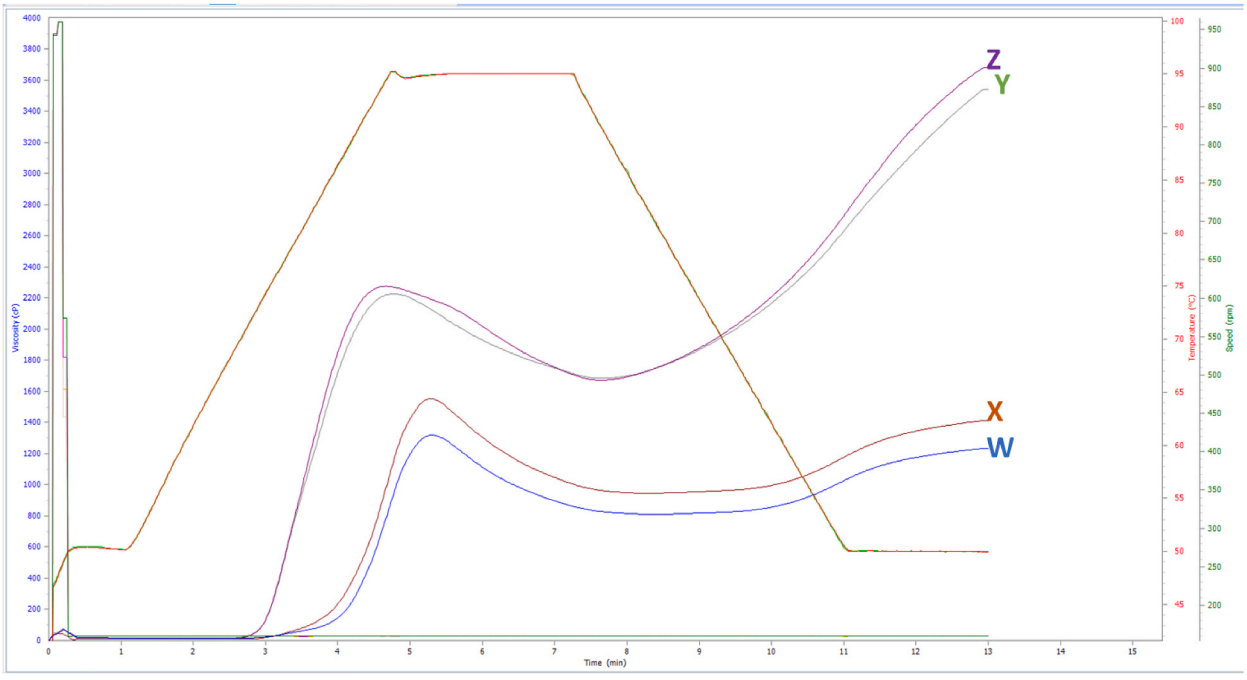

Fig. 2. Pasting curves of native and modified starches.
W: Native corn starch, X: Dry heated corn starch, Y: native faba bean starch, Z: Dry heated faba bean starch.

3.6. FTIR and XRD of optimized samples

Native and modified starches showed very identical FTIR spectra, typical characteristics of starch (Fig. 3). The starches showed peaks in the broadband region of 3000–3650 cm^{-1}, which corresponds to the stretching of hydroxyl groups [65]. All the starches also displayed an absorption peak at about 2930 cm^{-1} which could be attributed to the stretching of the C–H bonds [66]. A sharp peak which has been previously assigned to the stretching of C–O was found in the starches at around 1000 cm^{-1}. This peak falls within the fingerprint region and indicates the vibrations of the glucose bond within the starch structure [67,68]. The impact of DHT on the starch structure was assessed by determining the ratio of the peaks at 1045 and 1022 cm^{-1} and the ratio of the peaks at 1022 and 955 cm^{-1}. These peaks are important as their ratios are used to evaluate the degree of order within starch granules [69]. The peaks at 1022 and 1045 cm^{-1} correspond to the amorphous and crystalline regions of starch, respectively. An increase in the intensity of the peak at 1022 cm^{-1} was associated with the loss of starch-ordered structures in a previous study [70]. This peak also showed an increase in intensity in this study, suggesting a possible loss of ordered structures. Furthermore, the ratio of the peaks at 1045 and 1022 cm^{-1} was reduced for both faba bean and corn starches after DHT (Table 2). On the other hand, the ratio of the peaks at 1022 and 955 cm^{-1} increased after DHT. This result indicates that the amorphous region of faba bean and corn starches was more affected by the DHT than the crystalline region which may explain the reduction in amylose content of the starches as well as an increase in peak viscosity after DHT (Table 2). It is worth noting amylopectin plays a significant role in swelling of starch and the crystalline structure in starch granules predominantly contains amylopectin. Therefore, an increase in swelling peak after DHT is an indication that the crystalline content increased.

NFS showed a slightly different XRD result from the corn starch control (Fig. 4). Corn starch showed the typical A-type crystallinity pattern with a significantly connected doublet at 17° and 18° (2θ) and a single peak at 23° (2θ), while the native faba bean starch showed similar peaks except for the absence of the doublet. Legume starches including faba bean starch are generally known to exhibit the C-type crystalline pattern, while cereal starches such as corn starch show the A-type crystallinity. Legume starches can be further categorized into C_A-type, which more closely resembles the A-type polymorphs and C_B-type, which is more similar to B-type polymorphs [64,71]. The crystalline type observed for the faba bean starch can thus be considered the C_A-type crystallinity, as it closely resembles the A-type polymorph. Previous researchers also found the C-type crystalline pattern in faba bean starch [2,13,49]. DHT did not alter the crystal structure of either faba bean or corn starches (Fig. 4) but significantly enhanced their relative crystallinity. This may explain the increase in the ratio of the peaks at 1022 and 955 cm^{-1} after DHT, confirming the possible selective damage of the amorphous region compared to the crystalline region. This result is also consistent with the reduction in amylose content and a corresponding increase in peak viscosity after DHT (Table 2).

4. Conclusion

The result of this study indicates that the optimum dry heat temperature and time to produce starch with desirable characteristics were 100 °C and 0.17 h, respectively with a desirability factor (Df) of 66 %. The model described above offers a rapid way to produce faba bean starch with desirable functionality for various applications. DHT under the optimized conditions produce starch with reduced amylose content, increased peak, setback, and final viscosities compared with the native faba bean starch, presumably due to the damage in the amorphous region. The modified starch shows an insignificant change in granule morphology, a loss of order and an increase in crystallinity as evident in the SEM, FTIR and XRD data, respectively. DHT is a unique method that has the potential to significantly change starch pasting properties without substantial changes to granule morphology. Future research should explore the application of the modified starch in food systems, including noodles and breakfast cereals. Indeed, the optimum conditions corresponds to the lowest time of the experimental plan, though the temperature was not the lowest, hence, further investigations are

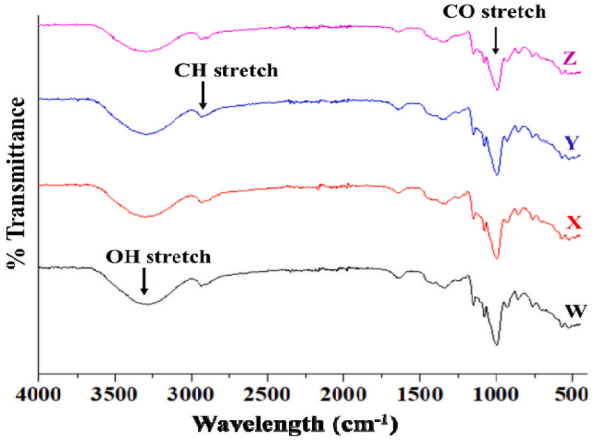

Fig. 3. FTIR Spectra of native and modified starches.
W: Native corn starch, X: Dry heated corn starch, Y: native faba bean starch, Z: Dry heated faba bean starch.

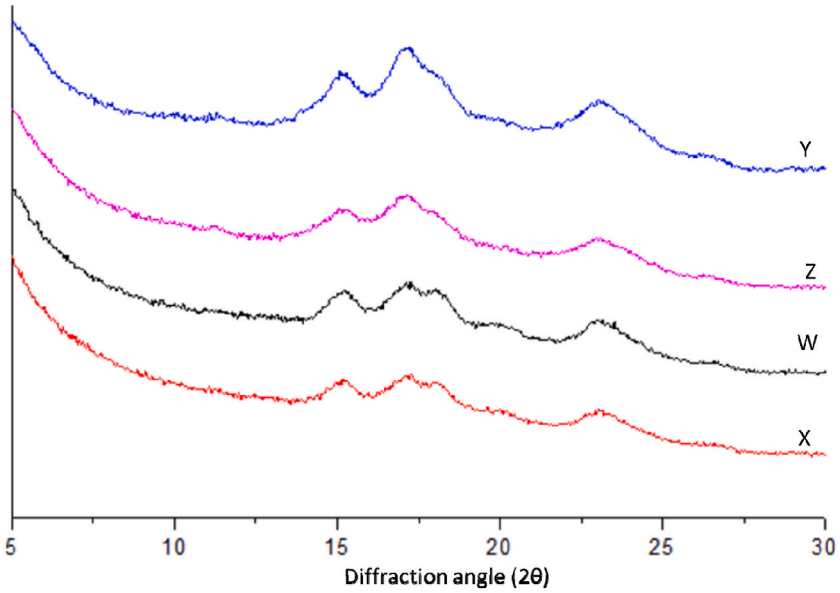

Fig. 4. X-ray diffraction patterns of native and modified starches.
W: Native corn starch, X: Dry heated corn starch, Y: native faba bean starch, Z: Dry heated faba bean starch.

needed using much lower temperature range and shorter treatment times.

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Oluwatosin B. Fasakin: Methodology, Investigation, Data curation. **Ogonnaya F. Uchenna:** Methodology, Investigation, Data curation. **Oluseyi M. Ajayi:** Writing – original draft, Validation, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation. **Bukola A. Onarinde:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Formal analysis. **Sumit Konar:** Writing – original draft, Validation, Resources, Project administration, Methodology, Formal analysis. **David Seung:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation. **Samson A. Oyeyinka:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e35817.

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