



HAL
open science

Prediction of thermal conductivity and specific heat of native maize starch and comparison with HMT treated starch

Leila Aklouche, Jean-Yves Monteau, Sid-Ahmed Rezzoug, Thierry Maugard, Luc Guihard, S. Cohendoz, Zoulikha Maache-Rezzoug

► **To cite this version:**

Leila Aklouche, Jean-Yves Monteau, Sid-Ahmed Rezzoug, Thierry Maugard, Luc Guihard, et al.. Prediction of thermal conductivity and specific heat of native maize starch and comparison with HMT treated starch. *Journal of Renewable Materials*, 2019, 7 (6), pp.535-546. 10.32604/jrm.2019.04361 . hal-02354243

HAL Id: hal-02354243

<https://hal.science/hal-02354243v1>

Submitted on 25 Sep 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Prediction of Thermal Conductivity and Specific Heat of Native Maize Starch and Comparison with HMT Treated Starch

Aklouche Leila¹, Monteau Jean-Yves², Rezzoug Sid-Ahmed¹, Maugard Thierry³, Guihard Luc², Cohendoz Stephane¹ and Maache-Rezzoug Zoulikha^{1,*}

¹LaSIE, UMR CNRS 7356, University of La Rochelle, Avenue Michel Crépeau, 17042 La Rochelle, France.

²GEPEA, UMR CNRS 6144, ONIRIS, Rue de la Géraudière, 44322 Nantes, France.

³LIENSs UMR CNRS 7266, Université de La Rochelle, France.

*Corresponding Author: Maache-Rezzoug Zoulikha. Email: zrezzoug@univ-lr.fr.

Abstract: Specific heat (C_p) and effective thermal conductivity (λ) of native maize starch (NS) were measured by DSC and transient heat transfer method, respectively, at different moisture contents and temperatures. The dependency of temperature (T) and moisture content (W) on the two parameters were investigated. The thermophysical properties of treated starch (TS) by four hydrothermal processes (RP-HMT, IV-HMT, DV-HMT and FV-HMT) were measured and compared to native starch. Hydrothermal treatments were performed at 3 bars (133°C) for 10 min. For C_p and λ measurements, moisture content varied for NS from 5 to 21.5% d.b. and from 8.8 to 25% d.b., respectively, and was fixed at 6% d.b. for TS. Empirical models were developed to specific heat and effective thermal conductivity, using a multiple regression algorithm with subsequent statistical analysis. The proposed models for NS based on T and W predict C_p and λ with a mean absolute error of 3.5% and 1.3%, respectively. Large differences in specific heat were observed between TS and NS. In a temperature range of 40 to 160°C, C_p values varied from 1.964 to 2.699 for NS and 1.380 to 2.085 ($\text{J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$) for TS. In contrast, the conductivity of NS was almost identical to that of treated starch by FV-HMT, followed in an increasing order by those treated by DV-HMT, RP-HMT, and IV-HM processes.

Keywords: Starch; HMT treatment; specific heat; effective thermal conductivity

Nomenclature and abbreviations

T	Temperature (°C)
W	Moisture content (% dry basis)
C_p	Specific heat ($\text{J}/(\text{g}\cdot\text{C})$)
λ	Thermal conductivity ($\text{W}/\text{m}\cdot\text{C}$)
Ea	Activation energy (kJ/mol)
R	Gas constant (kJ/mol. K)
DV-HMT	Direct Vapor-Heat Moisture Treatment.
IV-HMT	Intensification of Vacuum-Heat Moisture Treatment.
RP-HMT	Reduced Pressurized-Heat Moisture Treatment.
FV-HMT	Final Vacuum-Heat Moisture Treatment.
DSC	Differential Scanning Calorimetry.
TS	Treated starch.
NS	Native starch.
SP	Steam pressure.
SMS	Standard maize starch
d.b.	Dry basis (%)

1 Introduction

Starch is a renewable biopolymer and one of the most abundant reserve carbohydrates. This biopolymer is operated in various industries and has many applications in the food processes, where it is used as a thickener, gelling agent, bulking agent and water retention agent. Generally, modification of starch is carried out to enhance the positive characteristics and eliminate the shortcomings of native starches. Starch can be physically transformed by hydrothermal processes involving simultaneous action of heat and moisture as tools of action to give different properties from those present in native state. These processes differ by the water content, temperature and processing time used. The two major hydrothermal processes largely cited by the literature that modify the physicochemical properties of starch, without destroying the granules are annealing [1-3] and Heat-Moisture Treatment (HMT) [4-7]. Annealing process occurs under large excess of water (50 to 60%) and relatively low temperatures, below the gelatinization temperature while HMT process is conducted under restricted moisture content (10-30%) and higher temperatures ($< 140^{\circ}\text{C}$), above its glass transition temperature and below the gelatinization temperature for times of few minutes [8] to hours [7,9-10]. As the HMT treatments lead to more or less significant changes in the structure and the functional properties of starches, many works were focused on the study of physicochemical properties of starch granules after HMT treatment but limited investigations are available on the effect of these treatments on changes in thermophysical properties and taking into account modifications of structural properties. Starch is considered as a reactive porous media, composed of a discontinuous solid phase which plays an important role in internal transports by canalizing flows and developing the thermophysical bonds with the fluid phases [11]. In presence of water and temperatures above 60°C , the physico-chemical properties of starch change due to modifications in its semi-crystalline structure. Bahrani et al. [12] have already shown during the steaming of standard maize starch (SMS) by three HMT processes that the heating of starch granules is the result of transfer of latent heat of steam condensation by direct contact with saturated steam that also contributed to water transfer. Starch temperature rises from room temperature to steam equilibrium temperature. The higher the difference in temperature, the higher the quantity of condensed water, which causes increasing of starch moisture content [13].

Direct Vapour (DV-HMT) and Final Vapour (FV-HMT) Heat Moisture Treatments; consisted in heating up starch by saturated steam injected from atmospheric pressure up to processing steam pressure. Both treatments belong to HMT according to the definition of Sair et al. [14]. As regards to Reduced Pressurized (RP-HMT) [15] and Intensification of Vacuum (IV-HMT) of Heat Moisture Treatments, the two processes begin by the setting up of vacuum prior to injection of saturated steam, contributing to intensify its diffusion into the product by reducing the air resistance [11], consequently, the reduction of the time necessary to reach steam equilibrium temperature. IV-HMT and FV-HMT processes are distinguished by the abrupt decompression step out towards the vacuum at the end of the treatment instead of atmospheric pressure as for DV-HMT and RP-HMT. When the pressure drops suddenly, the autovaporization which is an adiabatic transition occurs and the water escapes abruptly accompanied by rapid cooling. The mechanical action and the intense shear of granules contribute to damage the crystalline structure; some mechanical energy is converted into internal energy [16]. Bahrani et al. [11] and Zarguili et al. [17] showed during DV-HMT, RP-HMT and IV-HMT the absence of moisture gradients between the different starch layers, by measuring the moisture content in the thickness direction at different processing times. The presence of initial vacuum in the case of RP-HMT and IV-HMT, contributes to generate a more significant amount of condensed steam than to DV-HMT. For a same SP, an equivalent volume of steam replace the volume of air. The knowledge of the thermophysical properties of starch, are important for monitoring and prediction of mass and heat transport phenomena occurring during hydrothermal treatments [18]. Besides specific heat, thermal conductivity, which measures the ability of a food product to conduct heat, is useful for calculating the energy balance and for the control of the multiple changes during food processes [19]. The need for equations predicting the thermophysical properties as specific heat is recognized since the 19th century. Siebel [20] and later Dickerson [21] proposed empirical equations for the specific heat of food materials. Freeman showed in 1947 that

Siebel's equation which is calculated as the sum of the specific heat of water, air and dry matter in combination of water [22], was not satisfactory for low water contents due to the specific heat of bound water which is higher than that of free water [23]. More recently, many researchers [24-25] have modelled the thermophysical properties of different types of foods, depending on the water content and temperature. Rahman et al. [26] proposed an empirical model for fruits and vegetables expressing the thermal conductivity of as a function of water content, temperature and porosity. Hwang et al. [27] studied the change in specific heat of corn starch. The authors showed that the apparent specific heat of starch mixtures increased with temperature and were higher than values for granular starch when temperatures were $< 70^{\circ}\text{C}$ due to the gelatinization phenomenon.

The objectives of this study were: (1) to develop the specific heat and thermal conductivity prediction models for SMS as function of moisture content and temperature; (2) to estimate the thermal conductivity and specific heat of treated starch by four hydrothermal processes which include a vacuum step either in initial (RP-HMT) or in final phase (FV-HMT), in both phases (IV-HMT) or without vacuum step (DV-HMT) to enhance the heat and mass transfers; (3) to compare the thermophysical properties of native and treated starch in order to quantify the modifications due to the total or partial melting of semi-crystalline structure of starch.

2 Materials and Methods

2.1 Raw Material

Standard maize starch with a moisture content of 13 g H₂O/100 g dry basis (% d.b.), was supplied by Roquette Frères (Lestrem, France).

2.2 Moisture Content Measurement

The moisture water content of starch, whether native or hydrothermally treated were determined using an air oven set at 105°C for 24 hours, according to A.F.N.O.R (NF V03-707, 2000) standard method. Three replicates were performed and the moisture content is expressed by g H₂O/100 g dry basis (% db). Glass desiccators were used to increase the water content of the starch. These desiccators with a grouted and greased seal contain saline water. The choice of salt depends on the targeted water content that increases to reach an equilibrium between product and saline solution. At room temperature, LiCl and CH₃CO₂K were used to reach respectively 12% and 22% relative humidity. For other water content values, sodium bicarbonate was used. An air oven set at 40°C was used to reduce the water content up to 6%.

2.3 Experimental Set-Up

The experimental setup (Fig. 1) consists in a reactor (stainless steel autoclave with a capacity of 12 liters), in which the products are treated at high temperature/high steam pressure. Saturated steam, supplied by a steam generator feeding the reactor, is injected manually via a valve, according to the conditions of hydrothermal treatment process. The steam is directly in contact with the native starch placed in reactor. Decompression to atmospheric pressure or towards vacuum pressure of 50 mbar is carried out inside the tank obtained by a rapid connection between the treatment chamber and the vacuum tank (made of stainless steel with a volume of 1600 liters). A liquid ring pump is used to allow establishing a reduced pressure inside the tank.

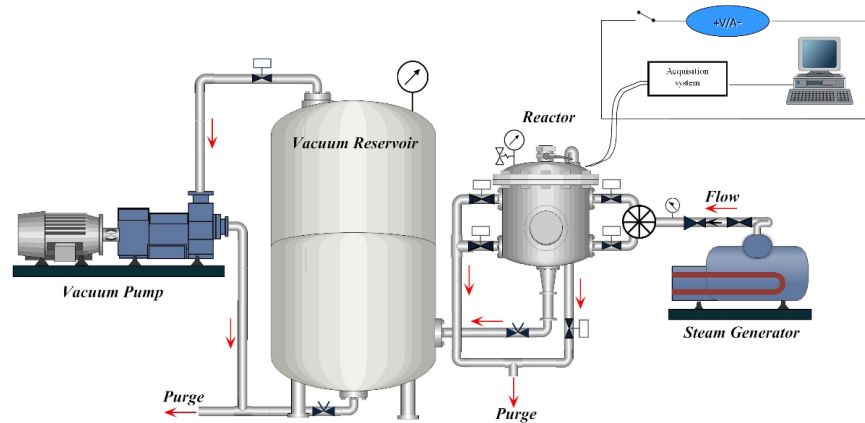


Figure 1: Diagram of the experimental pilot used for starch hydrothermal processes

2.4 Hydrothermal Processes

The hydrothermal treatments were performed by placing a thin layer of 5 mm of NS in a rectangular aluminum container (105 × 80 × 30 mm) at steam pressure (SP) of 3 bars corresponding to saturated steam temperature of 133°C for 10 min. Conversely to the conventional methods (annealing and HMT) starch is introduced into reactor at residual moisture, no hydration step is added [11].

Saturated steam was injected from atmospheric pressure for DV-HMT and FV-HMT while for RP-HMT and IV-HMT processes, reduced pressure of 50 mbar was established in reactor before injection of live steam (Fig. 2). This step is followed by a constant-pressure phase for a fixed processing time, which begins when SP reaches the setting pressure or the equilibrium temperature of saturated steam. After the maintaining phase, the abrupt decompression is performed towards atmospheric pressure for RP-HMT and DV-HMT and to vacuum pressure (50 mbar) for IV-HMT and FV-HMT.

The different phases of hydrothermal treatments are described in Fig. 2 that include common steps to the 4 processes (in bold);

Step 0: Starch was introduced into the reactor at atmospheric pressure. At this phase, the temperature and the moisture content of the sample were ~20°C and 14% d.b., respectively.

Step 1: Reduced pressure of 50 mbar was established in reactor before injection of live steam for only RP-HMT and IV-HMT processes

Step 2: Saturated steam at 3 bar was injected in reactor. In this phase, initial heating of the starch starts from the ambient to the temperature of the saturated steam ($t \leq t_{eq}$).

Step 3: Main isothermal phase of hydrothermal treatments starts when starch granules reached the equilibrium temperature ($T = T_{eq}$) for a fixed processing time of 10 min.

Step 4: Abrupt decompression is performed towards atmospheric pressure for RP-HMT and DV-HMT and to vacuum pressure (50 mbar) for IV-HMT and FV-HMT.

The presence of initial vacuum for both RP-HMT and IV-HMT processes contributes to accelerate the transfer phenomenon associated with simultaneous heat and mass transfer by comparison with DV-HMT and FV-HMT.

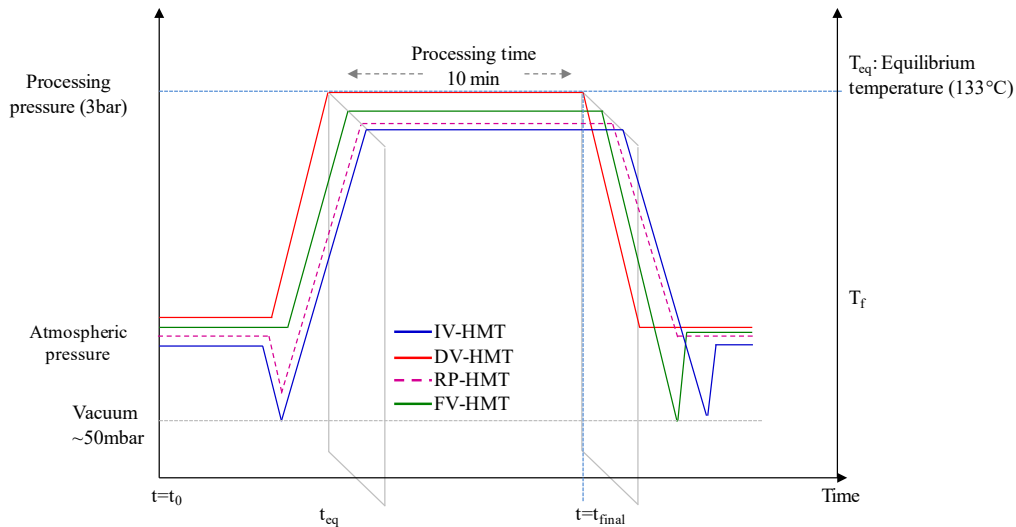


Figure 2: Schematic diagram of typical pressure-time for the four hydrothermal processes investigated

2.5 Specific Heat

The specific heat (C_p) was measured using differential scanning calorimetry DSC Q100 instrument (TA instrument INC). The equipment was calibrated using indium. The method consists of scanning cycle from 20 to 180°C at a heating rate of 10 °C.min⁻¹. The sample size about 35 mg was placed in a stainless steel pan and hermetically sealed to prevent any escape of steam. The specific heat of starch was determined by the heat flow difference between sample and an empty used as a reference. The moisture content of NS ranged from 5 to 21.5% d.b. and was fixed at 6% d.b. for TS. Measurements were made at least in triplicate and analyzed using Universal Analysis 2000 software.

2.6 Thermal Conductivity

Thermal conductivity (λ) was measured using line heat source probe technique [11], which considers the medium as isotropic and homogeneous. The measures were carried out in temperature range of 25 to 140°C. The probe system consists of a hypodermic needle (45 mm long and 0.80 mm in diameter), equipped with a K-type thermocouple and a heating wire. The needle is placed in the middle of a Pyrex tube (75 mm long and 12 mm in diameter), containing sample. Calibration was performed using glycerin to get the lineic resistance ratio (R/L), which was taken into account in the calculation of the thermal conductivity of the sample, according to the following equation:

$$\lambda = \frac{R}{L} \frac{J^2}{4 \pi s}$$

where: R/L: lineic resistance parameter of heater wire [ohms/m].

J: current in the probe

s: slope of the line

For each temperature, four replications were performed. The results were retrieved using an acquisition system (NIMTECH Front DAQ, France).

2.7 Statistical Analysis

For all measurements, at least triplicate analysis was performed, and the statistical analysis was done using Statgraphics software version 5.1. The impact of temperature and moisture content was examined by analysis of variance (ANOVA) through *p-value* generated by Fisher test (*F-ratio*) to assess whether the different treatments lead to statistically different results. A three dimensional fitting of thermal

conductivity and heat capacity according to temperature and moisture content were also displayed by response surface module of the software for a simple visualization of linear, quadratic and interaction effects of the two studied parameters.

3 Results and Discussion

3.1 Effect of Temperature and Moisture Content on Effective Thermal Conductivity and Specific Heat of NS

Heat and mass transfer phenomena in an inert or reactive porous medium such as food products are strongly dependent on temperature and moisture content. The variation of these parameters can lead to increase or reduce of thermophysical properties such as specific heat and thermal conductivity [28]. In starch-based materials, transfers occurring during hydrothermal processes are not only governed by potential gradients as a driving force, but also by the two phase transitions of the starch semi-crystalline structure which are likely to occur during HMT treatment according to the moisture and temperature [29]: the glass transition that concerns the amorphous phase (mainly the branching regions of the amylopectin and most of amylose chains) and melting of crystallites (formed by adjacent short chains of amylopectin intertwined into double helices). In the literature, the effect of the occurrence of these reactions on the thermophysical properties has received limited attention, although the starch phase transitions are extremely important in the food processing operations. In the calculation of the energy balance the use of predicted thermophysical property values gives more reliable results than the average values calculated from experimental values [30].

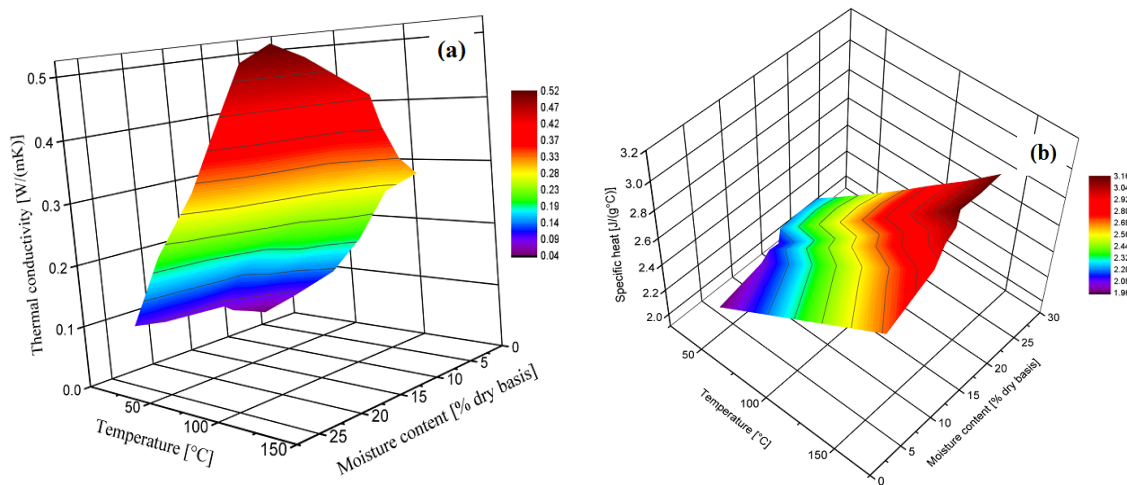


Figure 3: Effective thermal conductivity (a) and specific heat (b) of NS as a function of temperature and moisture content

Fig. 3 shows that the effective thermal conductivity (Fig. 3(a)) and specific heat (Fig. 3(b)) of NS change both as function of temperature and moisture content. The representation by the two-dimensional regression analysis allows visualizing the dependence of C_p and λ on the two parameters. At $T = 100^\circ\text{C}$, the specific heat of NS increased from 2.332 to 2.667 J/g. $^\circ\text{C}$ for moisture contents ranging from 5 to 21.5% d.b, respectively. At the same temperature the thermal conductivity has also increased from 0.195 W/m. $^\circ\text{C}$ for 8.8% d.b. to 0.409 W/m. $^\circ\text{C}$ for 25% d.b. As expected, the dependence of C_p and λ with temperature and moisture content is clearly shown in Fig. 3. Both parameters vary in a non-linear way in the range of experimental data. This tendency was observed by many authors such as Choi et al. [25] or Osborne et al. [31], who suggested 2nd-order polynomial equations as prediction models, function of temperature and moisture content for different food products.

The following empirical Eqs. (1) and (2) were obtained through Statgraphics software for predicting the values of the effective thermal conductivity and specific heat, respectively. In the range of temperature and moisture content varying for thermal conductivity from 25 to 140°C and from 8.8 to 25 % d.b, respectively. Whereas, for specific heat temperature and moisture content varied between 40 and 160 °C and from 5 to 21.5 % d.b.

$$\lambda = -9.57 \times 10^{-2} + 1.06 \times 10^{-3} T + 1.23 \times 10^{-2} W + 3.24 \times 10^{-6} T^2 + 8.98 \times 10^{-5} TW - 3 \times 10^{-4} W^2 \quad (1)$$

$$C_p = 1.55 + 5.58 \times 10^{-3} T + 3.18 \times 10^{-2} W + 8.29 \times 10^{-7} T^2 + 1.16 \times 10^{-4} TW + 7.58 \times 10^{-4} W^2 \quad (2)$$

The significance of each regression coefficient was determined using Fisher test (F-ratio) and the probability P (P -value), which displays the variance analysis (ANOVA) for the thermal conductivity and specific heat (Tab. 1). Based on p -values, temperature (T) and moisture content (W) had a strong significant linear effects ($P < 0.00001$) both on λ and C_p . The interaction between T and W were also significant with P -value < 0.00001 and 0.0021 respectively for λ and C_p indicating that the variation of λ and C_p as a function of moisture content depends on the temperature level. As illustrated by the curvatures on Fig. 3 which displays the three-dimensional response surfaces plots, the quadratic effect of moisture content (W^2) was also significant with P -values of 0.021 and 0.002 for λ and C_p , respectively. For both thermophysical properties the non-linear effect of the temperature (T^2) was not significant. The quality of developed models was evaluated based on the coefficient of correlation (R^2) which was close to 98% suggesting that the predicted models reasonably represents observed and therefore experimental values of λ and C_p were sufficiently explained by the two models. R^2 adjusted (R^2_{adj}) to the coefficients of the two models (Eqs. (1) and (2)) were also close to 98%. The mean squares calculated for λ and C_p were largely higher than residues; 0.309 and 2.460 for mean squares compared to 8.2×10^{-4} and 3.2×10^{-4} for residues, respectively. These values allow to obtain the F statistic which is the ratio between mean square and residue and thereafter P -value of the models. The two probabilities were lower than 0.0001 indicating a good accuracy of the two models. Comparison between experimental and predicted data of both parameters revealed that Eqs. (1) and (2) predict the thermal conductivity and specific heat with a mean absolute error of 1.3% and 3.5% , respectively (Tab. 1).

Table 1: Variance analysis for effective thermal conductivity (λ) and specific heat (C_p) of native starch

Source	λ					C_p				
	Sum of square	DF	Mean square	F-ratio	P-value	Sum of square	DF	Mean square	F-ratio	P-value
T	0.513	1	0.513	1660.5	$< 0.00001^*$	3.98	1	3.98	1749.7	$< 0.00001^*$
W	0.113	1	0.113	365.2	$< 0.00001^*$	0.62	1	0.62	271.7	$< 0.00001^*$
T^2	6.5×10^{-4}	1	6.5×10^{-4}	2.1	0.1560	6.3×10^{-4}	1	6.3×10^{-4}	0.03	0.867
TW	0.015	1	0.015	49.7	$< 0.00001^*$	0.024	1	0.024	10.73	0.0021*
W^2	0.002	1	0.002	5.9	0.0212*	0.023	1	0.023	10.3	0.0025*
TE	0.0092	30	3.1×10^{-4}			0.0971	43	0.002		
MAE	0.013					0.035				
R^2	0.985					0.981				
R^2_{adj}	0.983					0.978				

TE: total error; MAE: mean absolute error; R^2_{adj} : adjusted R^2 ; * significant.

Fig. 4 illustrates the quality of predicting models of thermal conductivity and specific heat through the plot of experimental values versus those predicted by the Eqs. (1) and (2). The relationship between

the predicted and experimental values can be described by the two following first order equations: $\lambda_{(\text{observed})} = \lambda_{(\text{predicted})} + 4.10 \cdot 10^{-8}$ and $C_{p(\text{observed})} = 0.998 C_{p(\text{predicted})} + 0.0041$ with a correlation coefficient $R^2 = 0.99$ in the two cases, knowing that an ideal predictive equation would yield a line with one as slope and zero as intercept.

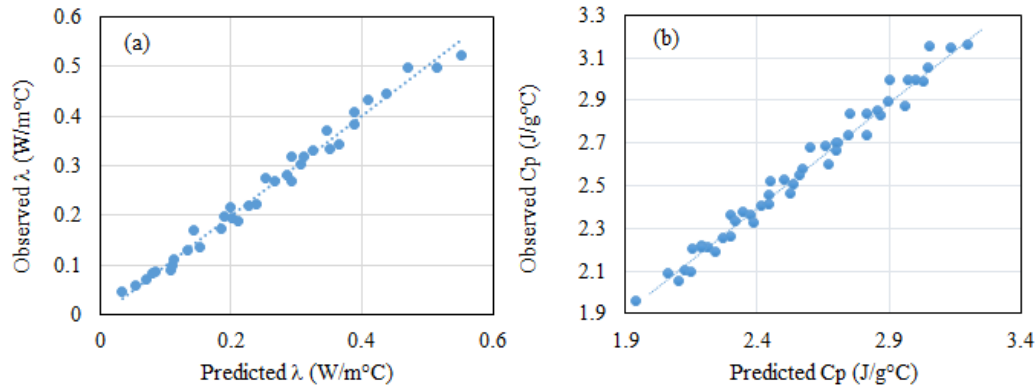


Figure 4: Predicted effective thermal conductivity (a) and specific heat (b) versus experimental values

3.2 Thermophysical Properties of Hydrotreated Starch

Figs. 5 and 6 show the variation of the thermophysical properties as a function of temperature for maize starch treated by RP-HMT, IV-HMT, DV-HMT and FV-HMT processes. The comparison between λ (Fig. 5) and C_p (Fig. 6) values of NS and TS at 133°C during 10 min by different HMT treatments showed significant differences especially for specific heat. The HMT treatments were contributed to increase significantly the effective thermal conductivity of starch compared to the NS and the intensity of changes appears to be related to the process conditions according this order: IV-HMT > RP-HMT > DV-HMT > FV-HMT. It can be observed from evolution of λ as a function of temperature (Fig. 5) that the thermal conductivity of FV-HMT is almost identical to that of NS, whereas the values obtained for starch treated by the two most intense processes (RP-HMT and IV-HMT) are higher. These variations depend not only on the intensity of the loss of crystalline structure of starch granule, as a function of HMT conditions (moisture content and temperature), but also on the physical state of continuous phase structure after treatment.

The thermal conductivity strongly depends on porosity of materials. As thermal conductivity of air in pores is lower than that of the other components, the presence of pores contribute to lowering the effective thermal conductivity. Bahrani [32] observed the decrease in porosity of treated starch after HMT processing. Porosity of NS was of 59.52% and decreased to 57.46 (± 1.29), to 47.02 (± 2.16) and to 51.49 (± 1.76) for TS by DV-HMT, RP-HMT and IV-HMT at 3 bar for 20 min, respectively. The decrease in porosity was attributed to the formation of aggregates confirmed by particle size analysis and by SEM observations at severe processing conditions; SP of 3 bar for DV-HMT and from 2.5 bar for RP-HMT and IV-HMT [17]. *As consequence of the increase of saturated steam pressure*, the partial or total melting of starch granules contributing to the formation of aggregates whose size depends on the number of melted granules. Herrera-Gómez et al. [33] investigated the mechanism of aggregates formation on maize starch granules cooked at reduced moisture content for various temperatures. The authors showed that limited moisture contents have induced formation of aggregates of different sizes maintained together by melted granules showing no cross-polarization.

In contrast to the effective thermal conductivity, large differences in specific heat were observed between TS and NS. In a temperature range of 40 to 160°C, C_p values varied for NS and TS from 1.96 to 2.7 J.g⁻¹.°C⁻¹ and 1.38 to 2.10 J.g⁻¹.°C⁻¹, respectively. In all temperature ranges studied, the specific heat values of treated starch were lower than those of native suggesting that the phase change occurring during

isothermal period of hydrothermal process (temperature of starch granules reached the equilibrium temperature) is responsible for this decreasing. During this period, the exchange is dominated by absorption of the condensed steam by the solid matrix. The potential of transfer according to Fickian diffusion equation is the gradient of moisture content or difference in partial pressure, considering an isotropic and homogeneous material. As starchy materials have a non-inert behavior in the presence of water and heat. The processing time of the isothermal phase was sufficient for irreversible structural changes to occur (partial or total melting, according to conditions) by diffusion of water into the starch granules, and therefore the changes of thermophysical properties. The reduction of enthalpy of gelatinization (ΔH_G) after hydrothermal treatment reflects partial melting of crystalline structure of starch granules [4]. Bahrani et al. [17] observed on SMS treated by DV-HMT, RP-HMT and IV-HMT at steam pressure of 1 and 3 bar, that ΔH_G gradually decreased as SP increased. ΔH_G of 12.2 J/g (native) decreased from 11.9 up to 4.1 J/g, from 11.3 up to 2 J/g and from 10.9 up to 0 J/g for SMS treated by DV-HMT, RP-HMT and IV-HMT at 1 and 3 bar, respectively. The absence of endothermic transition, observed with more intense treatment (IV-HMT at 3 bar/133°C), suggests that the energy released was sufficient to completely melt this structure. The small difference between C_p values of treated starches is mainly due to the difference in absorption of moisture content during direct steaming. But also, to a lesser extent, to the mechanical effect produced during abrupt decompression towards vacuum.

The specific heat of foodstuffs depend highly on their composition. For high-moisture food materials, the specific heat is largely dominated by water content [34]. In the case of our material, treated at low moisture content ($W < 30\%$ d.b.), the decrease in C_p values may be due to the decrease in water availability which is mobilized in the phase change. For limited moisture content none of reported studies have investigated combined influences of moisture-temperature and the phase transitions occurring during melting, or developed a model to predict changes in specific heat of starch, as a function of degree of phase transitions.

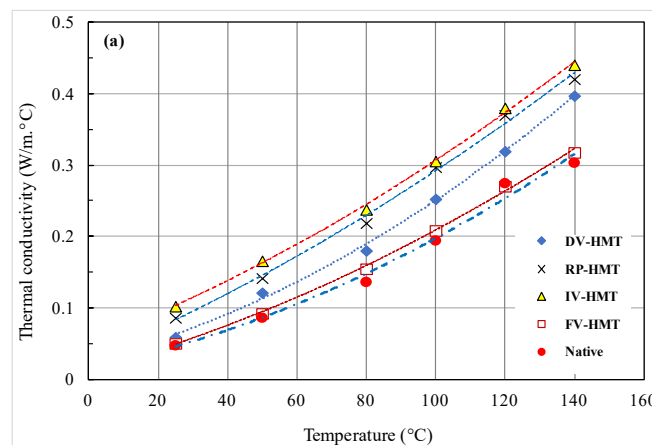


Figure 5: Experimental effective thermal conductivity as a function of temperature for TS by four processes

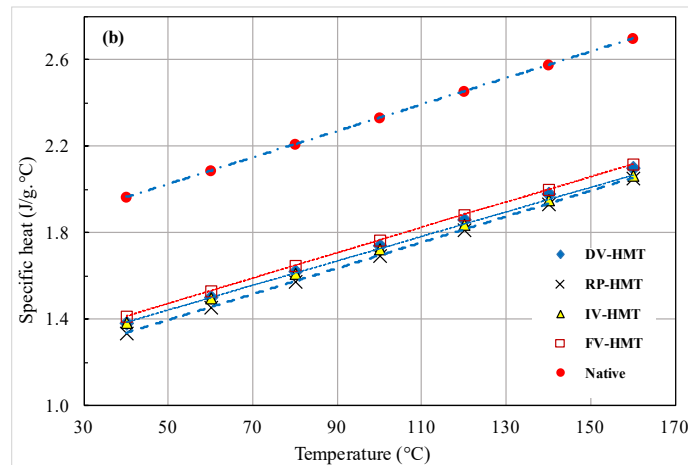


Figure 6: Experimental specific heat as a function of temperature for TS by four processes

4 Conclusion

In the present work, some literature assumptions were confirmed concerning the change in thermophysical property values as a function of temperature and moisture content which is important for establishing the energy balance and for choosing the hydrothermal treatment process. Empirical equations were developed to predict the values of λ and C_p as a function of temperature and moisture content for native starch. The results showed that the predictive values are very close to those measured with a correlation coefficient $R^2 = 0.98$ and with a mean absolute error of 1.3% and 3.5% for thermal conductivity and specific heat, respectively. The comparison between native and hydrothermally treated starches indicated that the change of structure during the treatment modifies the intrinsic properties of the material and hence its thermophysical properties. The evaluation of four hydrothermal treatments (RP-HMT, IV-HMT, DV-HMT and FV-HMT) showed that the application of the initial vacuum has a greater impact than the final vacuum on the variation of thermophysical properties.

References

1. Tester, R. F., Morrison W. R. (1990). Swelling and gelatinisation of cereal starches. Effects of amylopectin, amylose and lipids. *Cereal Chemistry*, 67, 551-557.
2. Stute, H. (1992). Hydrothermal modification of starches: the difference between annealing and heat-moisture treatment. *Starch/Stärke*, 44, 205-214.
3. Tester, R. F., Debon, S. J. J., Sommerville, M. D. (2000). Annealing of maize starch. *Carbohydrate Polymers*, 42, 287-299.
4. Arns, B., Bartz, J., Radunz, M., Evangelho, J. A. D., Pinto, V. Z. et al. (2015). Impact of heat-moisture treatment on rice starch, applied directly in grain paddy rice or in isolated starch. *LWT-Food Science and Technology*, 60, 708-713.
5. Zen, F., Ma, F., Kong, F., Gao, Q., Yu, S. (2015). Physicochemical properties and digestibility of hydrothermally treated waxy rice starch. *Food Chemistry*, 172, 92-98.
6. Sui, Z., Yao, T., Zhao, Y., Ye, X., Kong, X. et al. (2015). Effects of heat-moisture treatment reaction conditions on the physicochemical and structural properties of maize starch: Moisture and length of heating. *Food chemistry*, 173, 1125-1132.
7. Kong, X., Sun, X., Xu, F., Umemoto, T., Chen, H. et al. (2014). Morphological and physicochemical properties of two starch mutants induced from a high amylose indica rice by gamma irradiation. *Starch-Stärke*, 66, 157-165.
8. Lim, S. T., Chang, E. H., Chung, H. J. (2001). Thermal transition characteristics of heat-moisture treated corn and potato starches. *Carbohydrate Polymers*, 46, 107-115.

9. Wang, H., Zhang, B., Chen, L., Li, X. (2016): Understanding the structure and digestibility of heat-moisture treated starch. *International Journal of Biological Macromolecules*, 88, 1-8.
10. Ji, N., Li, X., Qiu, C., Li, G., Sun, Q. et al. (2015). Effects of heat moisture treatment on the physicochemical properties of starch nanoparticles. *Carbohydrate Polymers*, 117, 605-609.
11. Bahrani, S. A., Monteau, J. Y., Rezzoug, S. A., Loisel, C., Maache-Rezzoug, Z. (2014). Physics-based modeling of simultaneous heat and mass transfer intensification during vacuum steaming processes of starchy material. *Chemical Engineering and Processing*, 85, 216-226.
12. Bahrani, S. A., Loisel, C., Doublier, J. L., Rezzoug, S. A., Maache-Rezzoug, Z. (2012). Role of vacuum steps added before and after steaming treatment of maize starch. Impact on pasting, morphological and rheological properties. *Carbohydrate Polymers*, 89, 810-820.
13. Zarguili, I., Maache-Rezzoug, Z., Loisel, C., Doublier, J. L. (2006). Influence of DIC hydrothermal process conditions on the gelatinization properties of standard maize starch. *Journal of Food Engineering*, 77, 454-461.
14. Sair, L., Fetzer, W. R. (1944). Water sorption by starches, water sorption corn starch and commercial modifications of starches. *Industrial and Engineering Chemistry*, 36, 205-208.
15. Maruta, I., Kurahashi, Y., Takayano, R., Hayashi, K., Yoshino, Z. et al. (1994). Reduced-pressurized heat-moisture treatment: A new method for heat-moisture treatment of starch. *Starch/Stärke*, 46, 177-181.
16. Huang, Z. Q., Lu, J. P., Li, X. H., Tong, Z. F. (2007). Effect of mechanical activation on physico-chemical properties and structure of cassava starch. *Carbohydrate Polymers*, 68, 128-135.
17. Zarguili, I., Maache-Rezzoug, Z., Loisel, C., Doublier, J. L. (2009). A mathematical model to describe the change of moisture distribution in maize starch during DIC Hydrothermal treatment. *International Journal of Food Science and Technology*, 44, 10-17.
18. Bahrani, S. A., Loisel, C., Rezzoug, S. A., Cohendoz, S., Buléon, A. et al. (2017). Physicochemical and crystalline properties of standard maize starch hydrothermally treated by direct steaming. *Carbohydrate Polymers*, 157, 380-390.
19. Donsi, G., Ferrari, G., Nigro, R. (1996). Experimental determination of thermal conductivity of apple and potato at different moisture contents. *Journal of Food Engineering*, 30, 263-268.
20. Siebel, E. (1892). Specific heats of various products. *ICE and Refrigeration*, 2, 256-257.
21. Dickerson, R. W., Read Jr, B. R. (1968). Calculation and measurement of heat transfer in foods. *Food Technology*, 12, 37-48
22. Kaletunç, G. (2007). Prediction of specific heat of cereal flours: a quantitative empirical correlation. *Journal of Food Engineering*, 82, 589-594.
23. Freeman, M. E. (1943). Heat capacity and bound water in starch suspension. *Archives of Biochemistry*, 1, 27-39.
24. Gupta, T. R. (1990). Specific heat of Indian unleavened flat bread (Chapat) at various stages of cooking. *Journal of Food Process Engineering*, 13, 217-227.
25. Choi, Y., Okos, M. R. (1986). Effects of temperature and composition on thermal properties of foods. *Food Engineering and Process Applications*, 1, 93-101.
26. Rahman, M. S., Chen, X. D., Perera, C. O. (1997). An improved thermal conductivity prediction model for fruits and vegetables as a function of temperature, water content and porosity. *Journal of Food Engineering*, 31, 163-170.
27. Hwang, C. H., Heldman, D. R., Chao, R. R., Taylor, T. A. (1999). Changes in specific heat of corn starch due to gelatinization. *Journal of food science*, 64, 141-144.
28. Gonul, K. (2007). Prediction of specific heat of cereal flours: a quantitative empirical correlation. *Journal of Food Engineering*, 82, 589-594.
29. Maache-Rezzoug, Z., Zarguili, I., Loisel, C., Queveau, D., Buléon, A. (2008). Structural modifications and thermal transitions of standard maize starch after D.I.C. hydrothermal treatment. *Carbohydrate Polymers*, 74, 802-812.
30. Azadbakht, M., Khoshtaghaza, M. H., Ghobadian, B., Minaei, S. (2013). Thermal properties of soybean pod as a function of moisture content and temperature. *American Journal of Food Science and Technology*, 1, 9-13.
31. Osborne, N. S., Stimson, H. F., Ginnings, D. C. (1939). Chemie, Mikrobiologie. *Technologie Lebensmittel*, 23, 197.

32. Bahrani, S. A. (2012). *Modification des propriétés physico-chimiques de l'amidon par procédés hydrothermiques: contribution à l'étude des transferts couplés chaleur-masse (Ph.D. Thesis)*. University of La Rochelle, France.
33. Herrera-Gómez, A., Canónico-Franco, M., Ramos, G. (2005). Aggregate formation and segregation of maize starch granules cooked at reduced moisture conditions. *Starch/Stärke*, 57, 301-309.
34. Singh, R. P. (1995). Thermal properties of frozen foods. In: M. A. Rao and S. S. H. Rizvi (Eds.), *Engineering properties of foods*, 2nd ed, pp. 139-167. New-York, Marcel Dekker.