High quality-cassava flour (HQCF) composites: Their thermal characteristics in retrospect

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Abstract. Researchers and other experts who are involved in food products development using composite flour technology are making noteworthy giant strides worldwide. The escalating global population which is estimated that by 2030 more than eight billion people will be inhabiting the earth, with its associated impacts that will be evidenced in food consumption upsurge, will result in increased penchants for processed foods such as bakery and pastry products. Taking into account the increase in consumption of bread, it should be foreseen that there will be a higher demand for wheat. In consequence, and in the immediate future, global supply of wheat should be expected to decline in. To this end therefore, it is needful to emphasize that other fonts of flour and starch be investigated. The research work on thermal properties of composite flours with reference to its utilization through foodstuffs as bakery and pastry products is, of course, the focus of this review. Blends of flours in which high-quality cassava flour (HQCF) or just cassava flour is one of the compositing flours have been stressed upon vis-à-vis the effect of the cassava flour on the sensory and nutritional qualities besides its overall satisfactoriness. Thermal characteristics of blends of flours from wheat and other sources, have also been reviewed. Integrating cassava flour in baking bread is a step in the direction of value addition to the cassava products chain, as it has been found to be a suitable support for boosting the consumption of a home-grown food stuff above and beyond saving wheat flour importation and enhancing production of HQCF. Gluten-free products development and foods fortification have also seen prospects in recent times. The inclusion of composite flours in bakery and pastry products has also been found to impart desirable characteristics on the final products. Composite flour technology, typically, is gaining acceptance as an innovative technique for taking advantage of the boons in flours that may not be discovered otherwise; this of course, is subject to the proportional presence of individual flours in the amalgam.

1. Introduction

Experts have estimated that given the rate at which the global population is currently increasing, it will reach nine billion people within a short time [1]. The dire consequences of this population increase are the anticipated surge in consumption, with attendant further demand for such foods as biscuit, cake, bread and the like[2]. In consideration of the expected climb in bread consumption, a greater demand for wheat that will result in its global supply as a resource should be expected to diminish also in no distant time. This development gives emphasis to the inevitability of looking up to other sources of starch and flour [1]. [3] posited that cassava flour has an ample prospect as a replacement for wheat flour in bread making in some countries of Africa and, south and Central America. Noorfarahzilah et al., [4] reported that foods development via composite flour has increased and is inviting considerable attention from researchers, particularly in the making of bakery products and pastries. In the tropical regions of the world, namely;
Africa, Asia, and in the Caribbean, the tuber of cassava plant (*Manihot esculenta Crantz*) is a vital food material [5]. The report of IFAD and FAO [6] portrays cassava as being the sixth most essential food crop in the tropics possessing outstanding features such as high starch-yielding potential, drought tolerance and adaptation to tough ecological conditions such as low-fertility acid soils. FAO [7] reported that the production of cassava in 2014 in Brazil, Paraguay and Colombia (in million tons) stood at 23.2, 3.0 and 2.1 respectively.

Cassava is a reliable repository of dietary carbohydrate; namely, starch. It has been shown in the report of [8] that the starch content of cassava roots is about 60%. In consequence of the foregoing, the possibilities for value chain addition of cassava is worth venturing into with hope of good success. The escalating global request for snacks which are generally wheat flour-based in relation to the climatic limitations in wheat cultivation in the tropics calls for an alternative component for baking and confectionery foodstuffs, with a partial substitution of wheat, notwithstanding. A thought-provoking feature, as reported by Abass et al., [9], is that flour is a of product cassava tubers that can be processed with skill that is more economical in water and energy consumption, and is much easier to produce than its other products like starch. Deriving flour from cassava produces lesser amounts of by-products and waste. Besides, cassava contains appreciable amounts of desirable food nutrients. Table 1 shows the components of freshly harvested cassava tubers.

| Component    | Denomination of Measurement | Value |
|--------------|-----------------------------|-------|
| Moisture     | g/100g                      | 59.4  |
| Carbohydrates| g/100g                      | 38.1  |
| Protein      | g/100g                      | 0.7   |
| Fat          | g/100g                      | 0.2   |
| Crude Fibre  | g/100g                      | 0.6   |
| Ash          | g/100g                      | 1.0   |
| Calcium      | mg/100g                     | 50.0  |
| Vitamin C    | mg/100g                     | 25.2  |
| Energy       | kcal/100g                   | 157   |

*Source: Eriksson (2013)*

The use of composite flours in bread production is gaining more catholic approval due, possibly, to some motives which are pecuniary, societal, or health. Awoyale et al. [10] has reported that much more studies on the utilization of flour from cassava tubers in dough making are necessary. The proteins contained in flours from other food sources do not have the capability of forming the gluten linkage which is required for retaining the gas released in the course of dough fermentation. To this end, the partial inclusion of such flours in wheat flour pose significant technical hitches. Eriksson [11] correlated that there is potential in High-Quality Cassava Flour (HQCF) to exchange, in part, the wheat flour in bakery foods since consumers have comprehensively endorsed such a swap. There has been effective utilization of HQCF as a partial and/or total replacement for wheat flour in bread, cookies, and other confectionery [12]. HQCF Production, according to [14] is based on the technique advanced by International Institute for Tropical Agriculture (IITA). The IITA’s procedure is appropriate for strict adherence to decent industrial practices so as to get a product with the required potentials. Production of HQCF must be done within 24 hours after harvesting the cassava roots; as vividly described [14].

Virtually all aspects of processing of raw food materials into diverse products involve thermal changes. It could either be a heat absorption or rejection process. Thus a good understanding of the food materials’ thermal characteristics as well as those of the handling systems is sine-qua-non. The knowledge of HQCF’s thermal conductivity and diffusivity, and specific heat capacity, is essential in the design of heat treatment systems for processing of the flour into other products. According to Yang et al. [15], when a food crop is
exposed to heat treatments such as cooling, drying, freezing, frying and smoking, adequate data on its thermal characteristics are required to enhance a comprehensive understanding of the performance of the crop; Zhu et al. [16] reported the usefulness of such knowledge in modelling of heat transfer and temperature distribution during processing. This work aims at taking a retrospective look at the thermal characteristics of composites of HQCF. However, reports of thermal or thermo-physical properties of other types of food materials may also be mentioned.

2. The Review

2.1 Thermal Properties

Thermal properties are those properties which are as a function of the temperature of the material. Food thermal properties can be defined as those properties controlling the transfer of heat in a specified food. The report of Lozano [17] shows that they are usually grouped as thermodynamic properties (such as specific volume, specific heat, enthalpy and entropy). Generally, thermo-physical properties of a foodstuff are controllable when its temperature, heat capacity and heat transport properties; namely, thermal conductivity and thermal diffusivity go above the initial freezing point. The principal thermal properties of food and agricultural products are thermal conductivity and diffusivity, and specific heat capacity [18].

Specific heat is required when estimating the energy quantity necessary to alter a product’s temperature. On their part, and for efficient plant design, thermal conductivity and diffusivity are required in determining the rate of heat transfer. However, thermal properties exhibit some discrepancies at temperatures below the initial freezing point. This, to a large extent, is due to the complex procedures that take place in the course of freezing [19]. In a broad sense, thermo-physical properties of foods include, different types of parameters associated with the heat transfer operations of food processing. Thermal treatments such as pasteurization, concentration, dehydrating, refrigerating, inter alia, are regularly being put in practice when processing, transporting, storing, and cooking foodstuffs [20]. Lots of food materials are thermally treated to prolong their shelf-life and maintain high quality [21].

In the course of processing foods, transferring energy from one interface to another is of critically important. Oftentimes, it involves the stabilization, creation, or manipulation of food structures in such a way that foods which are more appropriate are produced to be disseminated and savoured by the general public [22]. The thermal parameters of a food sample can be measured using thermal analyzer. Measurements using such equipment are on the basis of these two approaches; namely the hot-wire technique used by [23] and [24] and plane source method [25]. The hot wire method is a standard transitory dynamic method based on measuring the temperature increase in a defined distance from a linear heat source (hot wire) implanted in the test material. The plane dynamic source method is based on using an ideal plane sensor which performs a twofold function of a heat source as well as a temperature detector. The plane source method is arranged for a one-dimensional heat flow into a finite sample. The range of the plane and needle probe would be chosen according to the thermo-physical parameters that are known, say from literature. In the course of the measurement, the probe is positioned in the material being measured. In order to guarantee optimum interaction of the probe with the sample being measured, caution must be exercised.

According to ASHRAE [19], a good knowledge of foods’ thermal properties is necessary in execution of the task of computing the heat transfer parameters in the design of equipment for preservation; and also in appraising the process times in low- and high-temperature systems. According to Drouzas et al., [26], these properties of foods are essential in the design, modelling and appraisal of various food-processing procedures and are also expedient in studies of packaging and storage stability of different foodstuffs. Despite the fact that there is an enormous volume of collected works on thermal properties of foods, the statistics lean towards being in disarray; and the arrangement and origin (species, strain), treatment situations, in addition to the structure of the foods, on many occasions, remain poorly recorded thus subverting the import of the information [27]. A number of approaches to measure thermal properties were studied by Valentas et al., [28]. Those considered most dependable and most universally used are calorimetry (employed in the measurement of enthalpy and apparent specific heat capacity) and guarded
hot-plate and line-source probes (employed in measuring thermal conductivity). The reports of some researchers [29] and [30] indicated that the probe technique designed for concurrently measuring thermal conductivity as well as thermal diffusivity has been among the most extensively used because it can be operated without much difficulty, and commercially produced.

Differential Scanning Calorimeter (DSC) has been developed as an innovative contrivance for quantifying the gelatinization and thermal characteristics of foodstuffs [31] (Sharma and Kothari, 2016). The DSC generates a curve known as thermogram, which is a curve of heat flux against temperature or time.[32] studied the thermal properties of rice flour by choosing two thermo-mechanical treatments according to the viscosity exhibited by the flour while it was being processed using a Perkin–Elmer DSC-7. As reported by Beninca et al., [33], by means of a DSC-60 (Shimadzu, Japan), they logged DSC graphs at 100ml/minute air flow-rate, and 5°C/minute rate of heating. In the work of [33], water and starch were blended in the ratio of 4:1 (w/w) and allowed to stay for two (2) hours so as to balance the moisture content. Tests were performed with the aim of studying the gelatinization by taking 100 ml of each suspension into a sealed aluminum crucible. For ease of obtaining the DSC curves, the apparatus was calibrated with indium (which is 99.99% purity, melting point of 156.6°C and specific enthalpy, h = 28.71J/g, and a vacant aluminum crucible used as reference. The DSC curves made it possible to determine the gelatinization enthalpy, which increased according to the temperature the authors employed and the acid concentration. [34] applied DSC to gather data on gelatinization temperature and heat of gelatinization of rice starch at a constant heating rate; even as Ho and Noor Aziah [35] determined the thermal properties of composite flour mixtures supplemented with hydrocolloids using DSC (Q200, TA Instruments, Waters, LLC, New Castle, DE) that was previously calibrated with pure indium as a standard. Lacerda et al., [36] carried out thermal characterization of partially hydrolyzed cassava starch granules and concluded that a thermal degradation commenced at lower degradation temperatures after enzymatic action and a DSC analysis indicated virtually an equivalent range of gelatinization temperatures. They however noted that the enthalpies of gelatinization were moderately increased for the partially hydrolyzed starch granules. Jankovic [37] did a thermal characterization on cassava starch taking record of thermo-gravimetric (TG) and derivative thermo-gravimetric (DTG) graph by means of a synchronized TGA-DTA SDT 2960 apparatus (TA Instruments, 159 Lukens Drive, New Castle, DE 19720), at 100ml/min air flow-rate; and at the varying heating rates ranging between 10 and 40°C/min, but at 10°C/min increments. In a similar manner, Kaewtatip [38] determined the thermal properties of cassava starch grafted with different content of polystyrene. The report recognized a fact that the process of disintegration ensues through three key phases. Firstly, the discharge of H2O molecules plus other minor molecular species. Secondly, a chain of competitive reactions, which includes depolymerization as well as consequent disintegration of amyllopectin and amylase-breakdown products; with one extra sub-phase appended to the second degeneration phase. The last reaction phase comprises heavy carbonization reactions that leads to the formation of amorphous carbon structures. Onwulata and Helsinger [39] studied the thermal properties of syrupy composites of saccharides and milk-fat using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-7 (Perkin-Elmer Corp., Norwak, CT), flushed with liquid nitrogen at 20 psi.

In determining the thermal properties of foods, the parameters which are measured include; specific heat capacity (c), thermal conductivity (κ), thermal diffusivity (α) and sometimes enthalpy (H). Thermal properties also include, emissivity, absorptivity, surface conductance and transmissivity.

2.1.1 Specific Heat Capacity (c). In studying the thermal characteristics of food handling systems or the apparatuses for heat-treatment of foods, specific heat is an indispensable quantity. It is defined as the measure of thermal energy received or rejected by a unit mass of matter to bring about a unit increase or decrease in temperature, without a phase-change in matter. It measures of the capability of a substance to store heat. In actual fact, specific heats are used to estimate the heating and cooling processes of food products as well as founding the design considerations for food processing equipment [40]. Specific heat is the capacity of a food material to accumulate thermal energy comparative to its capacity to conduct, reject or accept it. This property is firmly involved in the quantity of energy required, and not on the degree it takes to raise the temperature. From the standpoint foodstuffs, specific heat is influenced by the constituents
that make up a food, temperature, moisture content, and pressure. This thermal property food increases with rising moisture content of the product. Oladunmoye et al., [41] established the specific heat of bread dough from wheat-maize and wheat-cassava composite flours by the mixture technique. In this method, the dough of pre-determined mass and temperature was dropped into glycerin of known mass and temperature enclosed in a calorimeter (model 6300EA; Preiser Scientific, Louisville, KY, USA). For the bread dough from wheat-cassava flour blends, for dry basis (db) moisture content between 44.02 ± 2.04 and 51.31 ± 2.99%, specific heat capacity ranged from 2.51 ± 0.61 to 3.01 ± 0.42 kJ/kgK; whereas the wheat-maize blend presented values of moisture content ranging between 44.14 ± 1.94 and 45.09 ± 1.26% (db), and specific heat capacity was between 1.77 ± 0.17 and 2.61 ± 0.63 kJ/kgK. Aviara et al., [42] reported that specific heat increased linearly with moisture content. This also agrees with the report of Arku et al., [43], Aviara and (2001)[44].

2.1.2 Thermal Diffusivity (α). Thermal Diffusivity, denoted by α, is the ratio of thermal conductivity to specific heat. In analyzing heat transfer procedures, thermal diffusivity is customarily computed through dividing thermal conductivity by density and specific heat capacity at constant pressure – and would be denoted by αp. It measures the rate of transmission of heat of a material from the hot side to the cold side. It is a measure of the capacity of a material to transfer a thermal disturbance. Thermal diffusivity determines the rate at which thermal energy disseminates or disperses over and within a substance. Estimation of the time required in such processes as canning, heating, refrigerating, freezing, frying or cooking is carried out using thermal diffusivity. The report of Fontana et al., [45] indicates that the structure, temperature, moisture content and porosity of a food material influence thermal diffusivity. Gordon and Thorne [46] identified two leading procedures designed for the determination of thermal diffusivity of foods namely; the slope and the lag methods. In the slope method, the food sample to be tested is heated or cooled in a temperature-regulated medium, with the temperature change with time being logged. At this juncture, thermal diffusivity is derived from the gradient of the graph of the logarithm of dimensionless temperature-time. The basis of this technique is on the solution of the transient heat conduction differential equation for solids, and has been applied to food products. In the lag method, iterative numerical techniques is used in simulating an experimental heating or cooling data. A result of the solution of the appropriate differential equation is applied in forecast of temperatures for different periods at an arbitrarily designated thermal diffusivity value, which, as a matter of fact is diverse pending when the discrepancy between the values of the temperature - predicted and experimental - becomes reasonably negligible. Poulsen [47] identified a technique of measuring thermal diffusivity by means of inexpensive and easy equipment existing in many laboratories. In that work, the food material to be tested was packed into a tube, then placed in a water bath whose temperature was regulated by a thermostat, followed by plotting a thermo-gram. The diffusivity was subsequently computed from the thermo-gram. Oliveira et al., [48] determined thermal diffusivity by means of the infinity tube technique with the temperature at the tube wall being increased at consistent intervals, and calculated it using the equation below;

\[ \alpha = \frac{AR^2}{4(T_w - T_c)} \]  

(1)

Where \( R \) - radius of the tube. If \( T_c \) begins to increase at a regular interval after time (t), then Equation (1) is valid. By carrying out the linear regressions of \( T_w \) and \( T_c \) for the period of time t, and the mean values of the mean values of gradients calculated, value of A in Equation (1) was computed. The temperature variance \( T_w - T_c \) is the mean of all variances after time, t. Specific heat capacity has been reported to increase with moisture content (Usman et al., 2018),49] and varies significantly with cultivar [50]. In the report of Mari et al., [51] thermal diffusivity was established for cassava and wheat flours by using a set-up that comprised a glowing bulb (110 volts), a binary thermocouples linked to a processor and an aluminum vessel. The values they got for the cassava and wheat flours were 7.4838 \times 10^{-8} \text{ and } 7.3997 \times 10^{-8} \text{ m}^2/\text{sec at 40.00 and 38.00 degrees Celsius respectively.}
2.1.3 Thermal Conductivity (κ). The thermal conductivity, more oftentimes denoted by κ, of a foodstuff is an essential parameter employed in designs relating to the degree of transference of thermal energy. As a matter of fact, this parameter provides the quantity of thermal energy that will be transferred per unit time over a unit thickness of the material if a unit temperature difference occurs through that dimension. It is the amount of thermal energy that enters the constant-temperature area per unit time unit on the temperature incline; and characterizes the ability of a material to convey heat [52]). It measures the capability of a substance to conduct heat. As opined by Krokida et al. [53], thermal conductivity records in the literature demonstrate a wide disparity occasioned by the effect of diverse experimental procedures, discrepancy in composition of the material and variation of the configuration of the material. There is an extensive inconsistency in the size of thermal conductivity values meant for materials frequently met in food process systems. For instance, at 20°C, κwater \( \approx \) 0.597W/m-°C whereas at 25°C κpure water \( \approx \) 0.606W/m-°C, κair \( \approx \) 0.0251W/m-°C and κ for insulating materials ranges between 0.035 and 0.173 W/m-°C. A good number of high water-containing foods have thermal conductivities that approximate that value for water. Conversely, the values of thermal conductivity for porous foods when they are dried are affected by the air trapped in their pores since air has low value of the property. It is influenced intensely by the material’s structure, water content and temperature [53]. Not only does the configuration of porous substances, including foods, that influences the thermal conductivity; but also the various conditions that affect the paths through which thermal energy flows in the substance. As reported by Fikre [54], such influences include the substance’s homogeneity, void ratio, form, dimensions and void spaces arrangement and the content of the pores.

The consequential temperature variation over a specified period of time can be used to deduce thermal conductivity (Bozikova, et al., [25]. The thermal conductivity of decayed mixture of materials was determined by Waszkielis et al. [55] using TP08 probe (with a precision of about 3.00 ± 0.02%) attached to a digital multi-meter (Keithley 2700). In that work, the probe fitted with a needle 1.2 mm in diameter was place in the tube holding the material to be analyzed. Oladunmoye et al., [42] determined thermal conductivities of cassava and maize flours dough using the transit heat flow technique, by means of a thermal conductivity probe. They obtained the dough’s thermal conductivity, κ (in W/m-K) by equation (2) as shown below:

\[
κ = \frac{Q}{4πS} 
\]  
(2)

Where Q - the power supplied (in W/m length of probe) and S - the gradient of the temperature-time graph. The values of κ obtained were between 0.36 ± 0.07 and 0.39 ± 0.02 at water content between 44.14 ± 1.94 and 45.09 ± 1.26 % (db) for wheat-maize mixture and thermal conductivity of 0.362 ± 0.13 to 0.473 ± 0.12 at water content ranging from 44.02 ± 2.04 to 51.31 ± 2.99 % (db) for the wheat-cassava flour blend.

In a similar manner, thermal conductivity value for kernel of sheanut was determined by Aviara and Haque [44] using a guarded hot-plate apparatus with the steady-state heat flow method. However, Sanni et al., [56] adopted the model of Choi and Okos [57] as shown in equation (3) to compute the thermal conductivity of cassava meal.

\[
κ = \Sigma Y_i
\]  
(3)

Thermal conductivities of food materials increased with increasing moisture content [24] and [58].

2.1.4 Enthalpy (H). The enthalpy of a material is the amount of energy in the material that can be converted into work. It can also be referred to as Heat Content or Total Heat in the material. The total enthalpy of a material is unknown, but variations in enthalpy can be measured with calorimetric procedures described by [59]. The change in a food’s enthalpy can be used to evaluate the energy that must be added or extracted to effect a temperature change. Calorimetric methods that are used to determine phase transitions include the Differential Scanning Calorimetry (DSC), which measures temperatures and heat flows associated with thermal transitions in a material. Customarily, a calorimeter quantifies the amount of heat that goes into or out of a test sample. On the other hand, a differential calorimeter quantifies the thermal energy of a test sample as a comparison to some reference. However a DSC does these two in addition to heating the
specimen such that the temperature ramps up linearly. DSC is a procedure in which the variance in the amount of thermal energy necessary to raise the temperature of a specimen as well as that of the reference are quantified as temperature-dependent. It is the most extensively applied thermal analytical practice on record in food research and it has a pronounced effectiveness in quality assurance of food and largely because of its speed, simplicity, and availability [60]. It has the advantage of offering a direct estimate of the complete enthalpy change of transitions without calling for the understanding of the thermodynamic mechanism. Guadarrama-Lezama et al., [61] and Perez et al. [62] used a DSC to determine the enthalpy of sponge cake batters, and got values ranging from 1.70 ± 0.03 to 4.60 ± 0.07 J/g.

3. Conclusions
Abundance of scientific confirmation have been found that indicates the efficacy of using cassava flour in producing diverse bread formulae. The prospective returns in the utilization of cassava flour for dough making include; savings on foreign exchange due to importation of wheat or its flour, better earnings for farmers, and enhancement in food security and rural development by way of encouraging production of cassava. Thermal changes which could either be a heat absorption or revolution are inevitable in food processes. Knowledge of these properties helps in designing thermal processes and calculating thermal loads for canning, sterilization, pasteurization, cooking and such other processes. This has attracted researchers whose interests are in development of healthful wheat-based products by swapping, at in part, wheat with cassava flour, especially HQCF.

Studies have been carried out, and are still being done in the area of thermal characteristics of food materials; but more is required on HQCF. Such characteristics include; thermal conductivity, thermal diffusivity and specific heat which are essential in designing heat treatment systems for processing of the flour into other products. It has also been discovered that these properties are affected to a great extent by moisture content and temperature of food materials. Thermal properties were found to increase with moisture content at a given temperature, and increase with temperature for a particular moisture content. Food industries and researchers have mutually found DSC to stand out as a suitable technique in predicting post-processing changes in the dietetic and physico-chemical attributes of foodstuffs after using dissimilar heat and non-heat processing. Various scientific reports on thermal properties procedures, especially DSC have revealed their benefits in envisaging the alterations such as starch gelatinization in carbohydrates, denaturation of proteins and oxidation of lipids that can occur in the course of food processing. The industrial application of DSC for food manufacture is highly encouraging as it will be able to contribute to boosting the circumstances encountered in processing, thereby decreasing the temperature and time that would be required in such activity. This will of course lead to a decline in energy and general production cost. However, at this juncture, there is a great necessity for more prediction models to be developed.

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