

Estimation of the activation energy by DMTA: an original approach for considering biological heterogeneity

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Background and objectives

Cooking bananas and plantains represent a major starchy resource in central African and Latin American countries. One of the most common banana traditional cooking process involves boiling into water. The cooking stage (irreversible gelatinisation reaction) induces some massive water and heat transfers from the solution into the pulp and some simultaneous counter-current transfers of soluble solutes that leach from the pulp into the cooking solution.



Among thermo-physical criteria, the apparent cooking activation energy (E_a) is an important parameter used for process modelling. In order to take into account the pulp heterogeneity, E_a estimates will be investigated using differential scanning calorimetry (DSC)^{1,2,3,4} and dynamic thermomechanical analysis (DMTA).

Material and methods



> DSC and DMTA operating conditions

Green plantains (*Musa paradisiaca*) at green stage of ripeness were processed using DSC and DMTA devices :

DMTA 7e[®] nonisothermal conditions

- ✓ 20mm diameter parallel plates
- ✓ 17mm diameter grease weatherproofed cylinders
- ✓ linear viscoelastic range
- ✓ 500mN static & 450mN dynamic forces
- ✓ N= 1Hz, strain amplitude > 500µm
- ✓ 6 heating rates β_i from 25 to 120°C
- ✓ Pure indium calibration at different β_i

Measured parameters

- ✓ Tan δ versus T (°C) and t (s)

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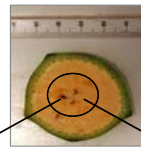


Fig 1. DMTA and DSC sampling areas

DSC 7[®] nonisothermal conditions

- ✓ Stainless steel reference and sample sealed pans
- ✓ Empty reference pan
- ✓ 14 to 20mg dry matter micro-samples
- ✓ 6 heating rates β_i from 25 to 120°C
- ✓ Pure indium calibration at different β_i

Measured parameters

- ✓ Heat flux ϕ (mW) versus T (°C) and t (s)

> Kinetic considerations

The kinetic analysis of solid state decompositions is commonly based on a single-step kinetic equation (I) which could be rearranged considering the explicit temperature dependence of the rate constant $k(T)$ into the Arrhenius equation⁵. It gives the traditional kinetic description based on A , E_a and $f(\alpha)$ which has been widely used^{1,5,6,7} for kinetic predictions (II):

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (I)$$

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (II)$$

Recent 'model-free kinetic' as an isoconversional method produces a dependence of E_a on α , without requiring knowledge of the reaction model or the preexponential factor^{1,7}. Among potential solutions in non-isothermal conditions, the equation (III) describes below the linear relationship between $\ln(\beta/T^2)$ and $1/T$ in which the apparent activation energy can be directly estimated via the slope of the straight line⁸:

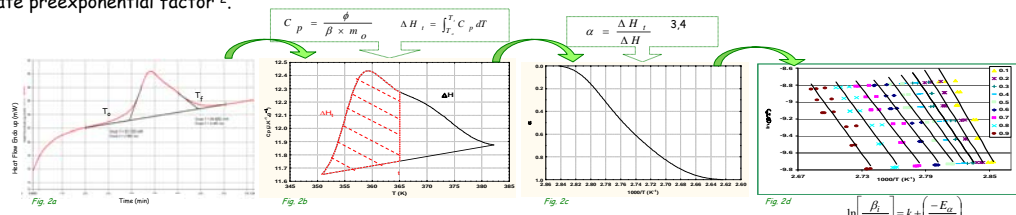
$$\ln\left[\frac{\beta_i}{T^2 \alpha_i}\right] = k + \left(\frac{-E_a}{RT \alpha_i}\right) \quad (III)$$

The equation (III) is known as "the Kissinger equation"^{4,8} here with an isoconversional form ($T_{\alpha,i}$ and E_{α} depending on the extent or degree of conversion α). The straight line Y-axis origin K may be used to estimate preexponential factor².

> Computation

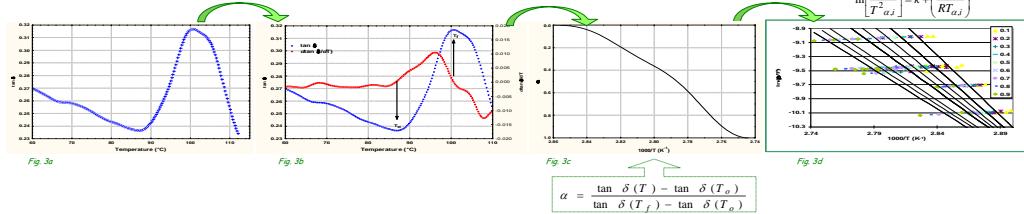
DSC procedure in 4 steps

- Fig 2a Correction of $\phi(T)$ lags with β_i and determination in $[T_0, T_f]$ range
- Fig 2b Computation of heat capacity (C_p) with real β values and computation of ΔH in $[T_0, T_f]$ range
- Fig 2c Computation of α
- Fig 2d Kissinger equation plot



DMTA procedure in 4 steps

- Fig 3a Correction of tan $\delta(T)$ lags with β_i
- Fig 3b Numeric determination of $[T_0, T_f]$
- Fig 3c Computation of α by tan δ normalisation
- Fig 3d Kissinger equation plot



Results

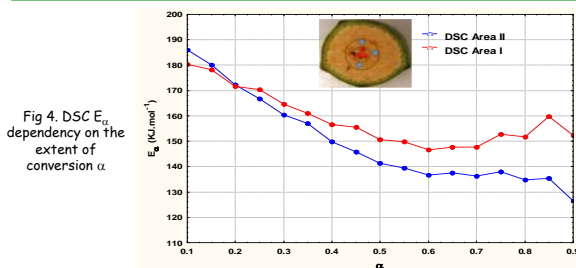


Fig 4. DSC E_a dependency on the extent of conversion α

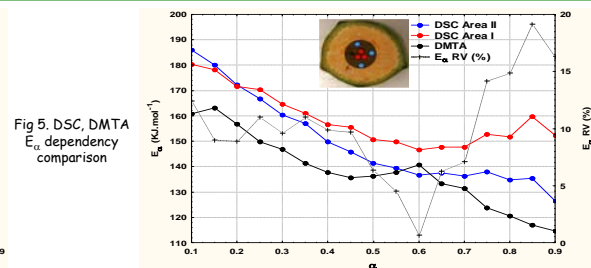


Fig 5. DSC, DMTA E_a dependency comparison

$$\ln\left[\frac{\beta_i}{T^2 \alpha_i}\right] = k + \left(\frac{-E_a}{RT \alpha_i}\right) \quad (IV)$$

E_a relative variation % :

$$E_a \text{ RV (\%)} = \left(\frac{E_{a \text{ DSC}} - E_{a \text{ DMTA}}}{E_{a \text{ DSC}}}\right)$$

where

$$E_{a \text{ DSC}} = \text{Mean DSC } E_a$$

Estimated DSC E_a seemed to depend on the sampling area (Fig 4), probably due to the raw material heterogeneity (water gradient). A continuous decrease in E_a was observed while α rise using both DSC and DMTA methods (Fig 4 & 5), suggesting a multi-steps process of different E_a ^{1,7}. Nevertheless, 'the kinetic scheme of the process' did not correspond to one of the most characteristic $E_a(\alpha)$ dependency shapes reviewed¹. E_a Relative Variation percentage (IV) between DSC and DMTA was relatively low in the 0.1 - 0.8 α range (below 15%).

Higher differences in E_a estimates at $\alpha > 0.8$ were probably due to some shrinkage of grease weatherproofed samples and to the systematic error induced by Arrhenius computation with 'DMTA estimated sample temperature' (thermocouple acquired temperature is distant from the sample).

Conclusion and perspectives

- An estimation of E_a during the irreversible gelatinization process could then be obtained using a thermo-mechanical nonisothermal isoconversional approach.
- E_a estimated differences between DSC and DMTA were relatively low in the 0.1 - 0.8 α range (< 25 KJ.mol⁻¹);
- Such estimation could be sufficient for later process modelling with decouple transfers;
- A better estimation of E_a may be later obtained using some recent numerical algorithms^{5,7}. It may help to determine the contribution of the individual steps to the overall reaction rate and getting a better comprehension of the complex gelatinization process.

References

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