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Multi-response kinetic modelling of the formation of five Strecker aldehydes during kilning of barley malt

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Introduction

- **Barley** is the fourth most important cereal crop in the world; around **30%** is used for malt production[1].
- **Kilning** process conditions (temperature gradient mostly) determine both **colour** and **aroma** of barley malts.
- This happens during the **curing stage** of kilning.
- Malt characteristic aroma is mainly due to the presence of **Strecker aldehydes** formed through the Maillard reaction.

Aims of the study

- to understand the effect of **temperature** and **time** on the formation of **aroma** compounds in malt during the curing stage of kilning,
- to develop a **mechanistic kinetic** model for the formation of Strecker aldehydes.
- to estimate **rate constants** and **activation energies** of the reactions defined in the model.

The malting process



1 steeping
- **Hydration** of barley kernels
- From 12 to at least 40% moisture

2 germination
- Activation of the production of **proteases**, **amylases** and others
- Cell wall breakdown

3 kilning
- **Drying** step: reduction of moisture
- **Curing** step: higher temperature, formation of flavour and colour.

Materials & Methods

Samples — **Two varieties of barley:** the two-row spring variety 'RGT Planet' and six-row winter variety 'Etincel'

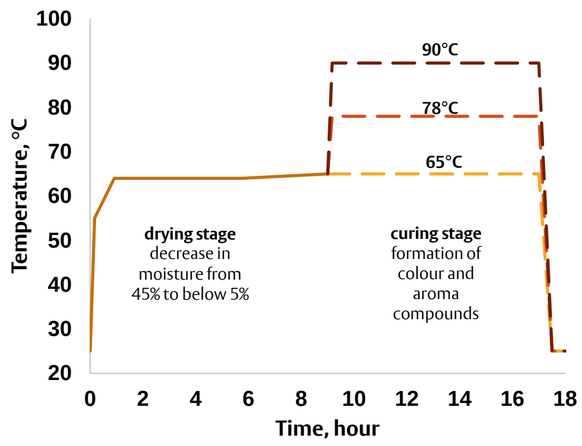
Malting trials — Experiments carried out in **duplicate** for each temperature and variety. Samples analysed in **duplicate**

Quantification of volatile and non-volatile compounds

HS-SPME-GC-MS — **Strecker aldehydes:** methional, 2-methylpropanal, 2-methylbutanal, 3-methylbutanal, phenylacetaldehyde

LC-MS/MS — **Sugars:** glucose, fructose
Amino acids: Phe, Trp, Ile, Leu, Met, Tyr, Val, Pro, Glu, Thr, Ala, Gly, Gln, Asn, Asp, Ser, His, Arg, Lys
Amadori rearrangement products: fructosyl derivatives of Val, Ile, Leu, Phe, Ala, Gly, Pro

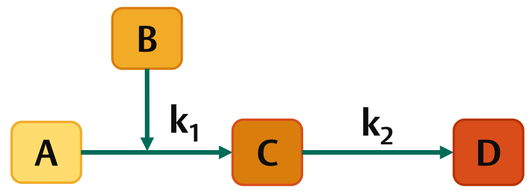
Kilning temperature programmes



The drying stage was kept constant for all experiments. Isothermal curing stage in order to understand the effect of temperature.

Multi-response kinetic modelling

A simple example of a kinetic model:

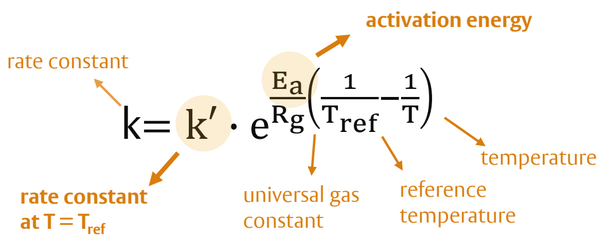


And the system of differential equations associated:

$$\frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[C]}{dt} = k_1[A][B] - k_2[C]$$

$$\frac{d[B]}{dt} = -k_1[B] \qquad \frac{d[D]}{dt} = k_2[C]$$

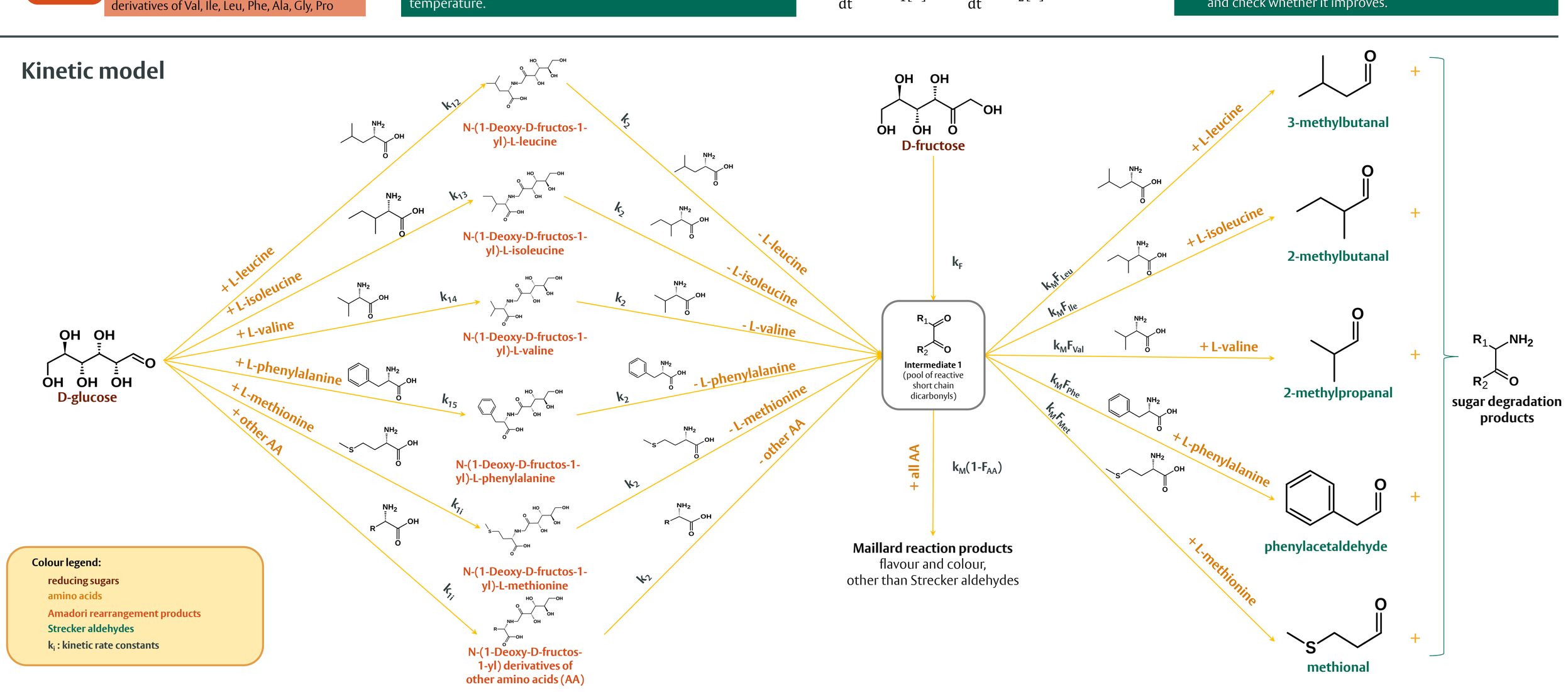
Re-parametrised Arrhenius equation
Unknowns: k', E_a



How to develop a kinetic model:
1. Propose a model based on the known chemistry of the process.
2. Solve the model. The estimated values for k' and E_a will be the ones that make the predicted model fit the observed values the best.
3. Modify the model (add or remove compounds and steps) and check whether it improves.

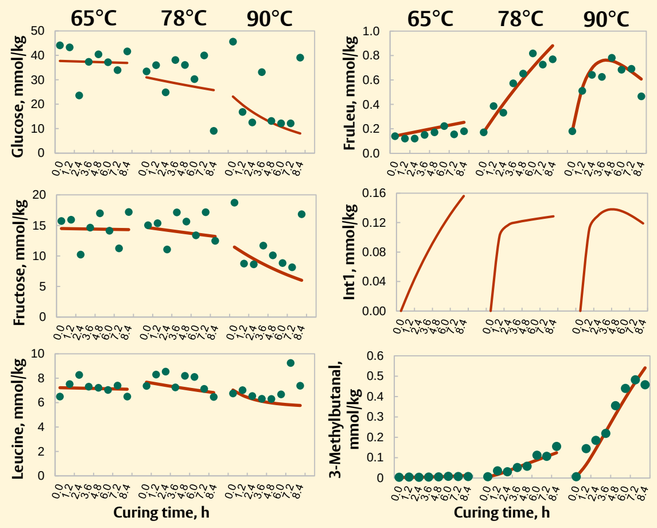
Results & Discussion

Kinetic model

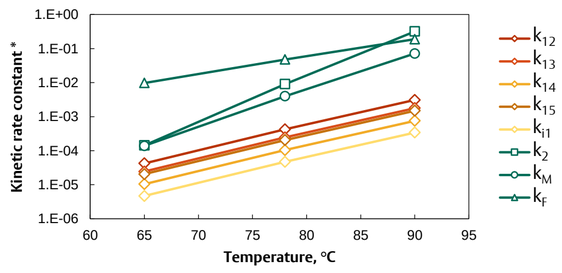


Colour legend:
reducing sugars
amino acids
Amadori rearrangement products
Strecker aldehydes
k_i : kinetic rate constants

An example of the trends for the compounds involved in the formation of **3-methylbutanal** (observed — predicted).



- There was a clear dependence of the concentration of Strecker aldehydes and curing temperature, with the **highest values reached at 90 °C**.
- The model was based on previous studies about the formation of Strecker aldehydes in other foods[2].
- 'Intermediate 1' represents a pool of reactive intermediates that once they are formed, they react rapidly to other compounds.
- No significant differences were found between spring and winter barleys.



Effect of temperature on the kinetic rate constants.
(*) k_{12}, k_{13}, k_{14}, k_{15}, k_{1i} and k_M in kg mmol^{-1} h^{-1}; k_2 and k_F in h^{-1}.

- Higher activation energies (steeper slopes in the graph above) mean that a temperature rise brings about **larger increases in kinetic rate constants** in relation to lower activation energies.
- k_2 and k_M (degradation of Amadori rearrangement products and 'Intermediate 1', respectively) had higher activation energies Ea than other reactions (steeper slopes); the **intermediate compounds degradation** rate increased to a larger extend than the degradation rate of the precursors. These intermediates are more sensitive to temperature rises than the precursors in the reaction.

Conclusions

- This model can **successfully predict** the final amount of these important flavour compounds in malt, and in consequence the **organoleptic quality** of the malt.
- It is possible to **control the kilning process** by manipulating the raw materials and their precursor concentration, as well as the time/temperature kilning profile.

References
1. Akar et al. (2004). *Barley. Post-harvest Operations.*
2. Balagiannis et al. (2009). *J Agric Food Chem*, 57(21), 9916-9922.

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