Addressing the Challenge of Acrylamide in the Bakery Sector

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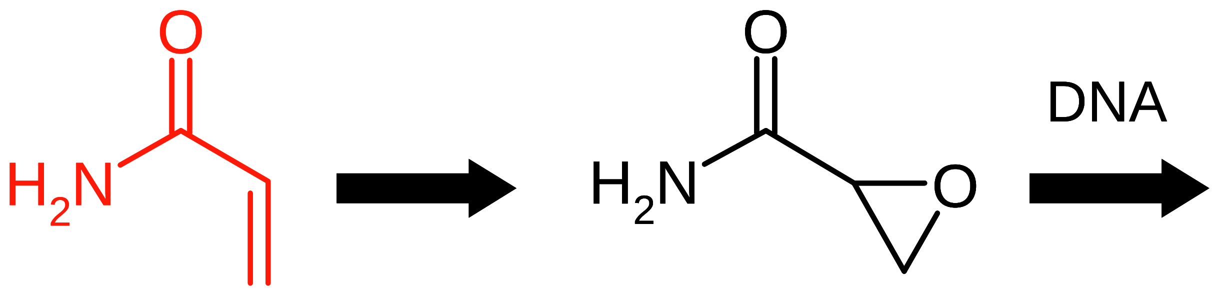
Outline

- Why acrylamide is important and how it is formed
- Reduction options (pilot scale)
  - Raw material selection
  - Changes in key precursors during processing
  - Pilot scale reduction in sweet biscuit and cracker systems
    - Effects of ingredients/additives
  - Interactions with other contaminants
- Conclusions

Why is Acrylamide Important?

- Neurotoxic (repeated high dose in humans)
    - Long term low level exposure?
- Mutagenic & carcinogenic observed in rats
- Evidence for genotoxic mechanism of carcinogenicity (mediated by glycidamide) increasing



Acrylamide glycidamide

PREMIER FOODS

Why is Acrylamide Important?

- JECFA estimate pastry & sweet biscuits contribute 10 – 20% exposure[1]

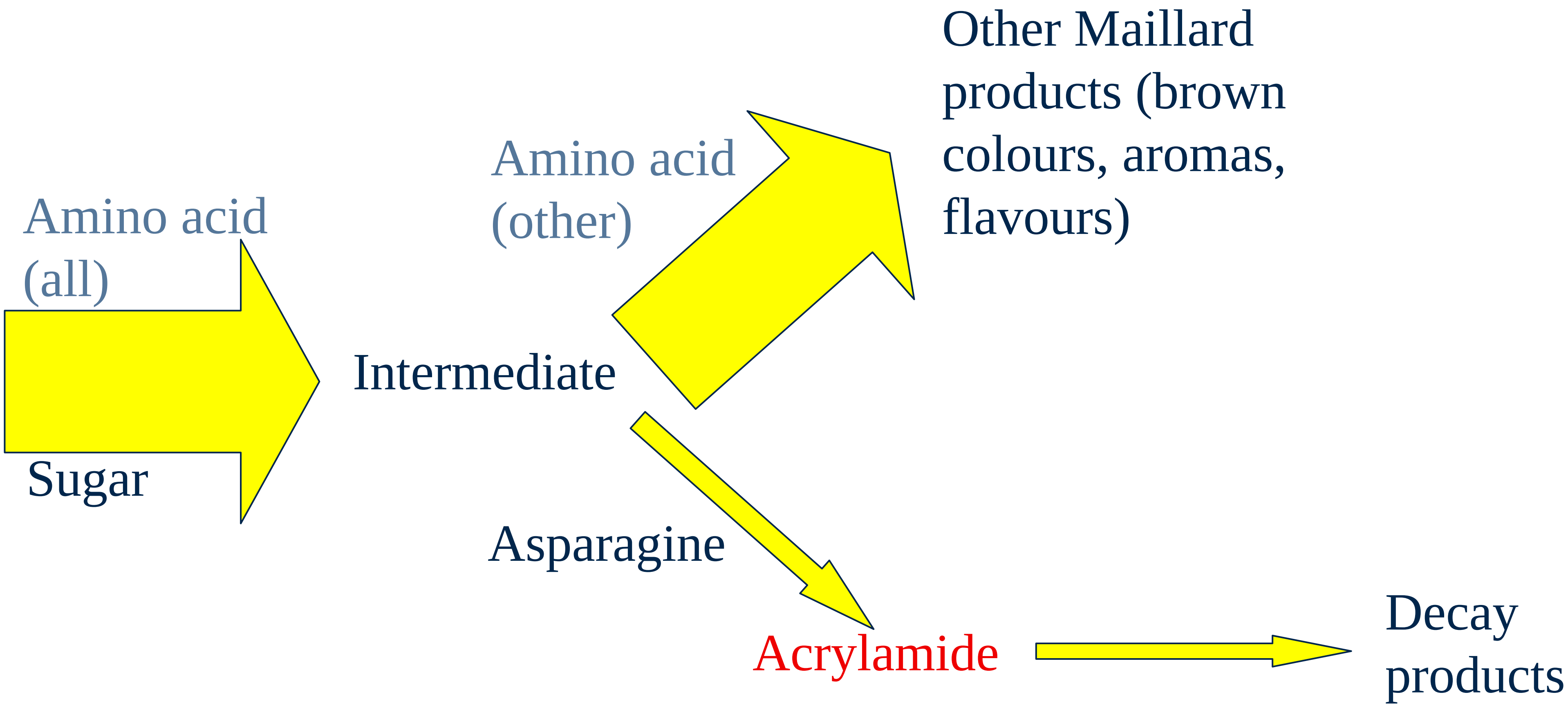
	Biscuits[2]	Crispbread[2]	Gingerbread[2]	Other bakery ware[2]
Total number	899	413	1009	192
	µg/kg	**µg/kg**	**µg/kg**	**µg/kg**
Min	**5**	**5**	**5**	**5**
25%	68	80	137	15
Median	**165**	**165**	**244**	**30**
75%	381	501	669	163
95%	920	1389	1805	740
Max	**3324**	**2838**	**7834**	**1300**

- MOEs for both morphological nerve changes and carcinogenicity are relatively low (<10000 = concern for substances which are mutagenic & carcinogenic)[1]
- …"efforts to reduce acrylamide should be continued" ALARP

1) 64th JECFA

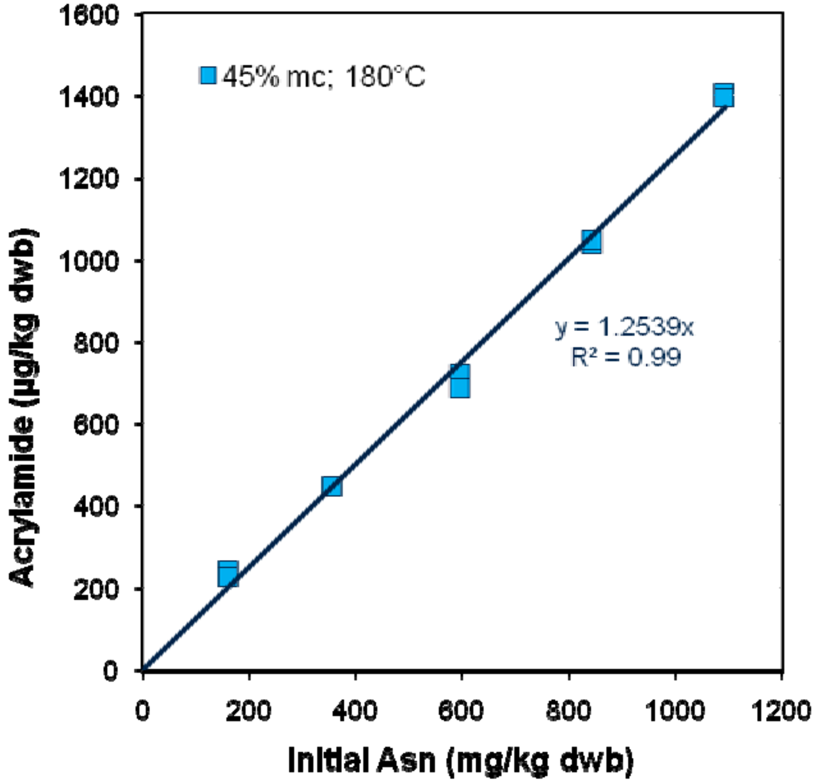
2) Data from http://irmm.jrc.ec.europa.eu/

Outline Chemistry



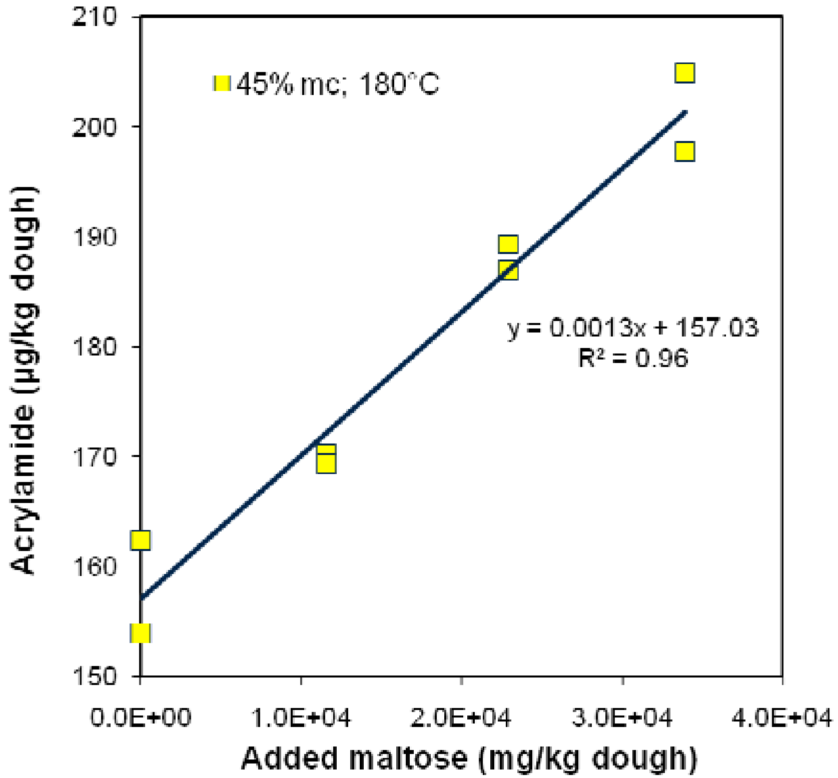
Acrylamide is formed from asparagine (Asn) in a reaction mediated by sugars

Asn is the key determinant of acrylamide in cereals



- Yield of acrylamide from added Asn in dough is circa 0.1 g/100g

- Yield of acrylamide from added sugars in dough is circa 0.01 – 0.001 g/100g



Mitigation options

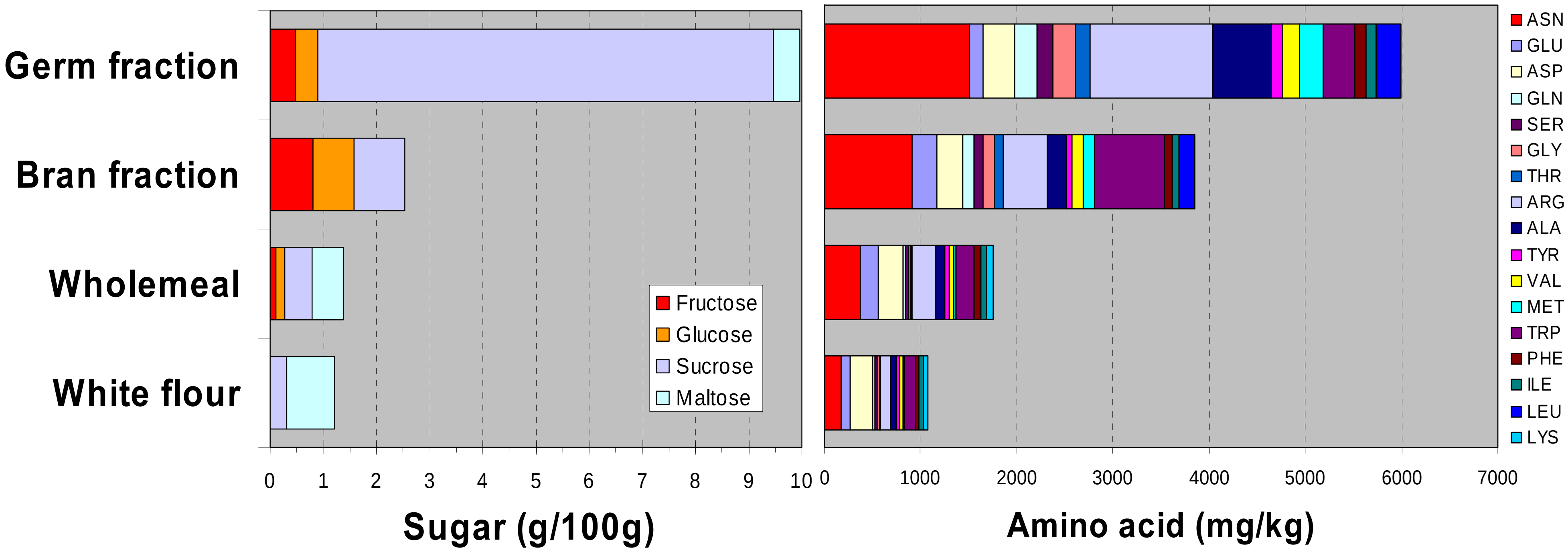
- Asn reduction by
  - Raw material selection
  - Yeast fermentation
  - Complexing agents
  - Asparaginase
- Reaction mechanism
  - Amino acid addition (competitive inhibition, decay)
  - pH adjustment (Maillard)
  - Ammonium salt replacement (reactive intermediates)

Other

- Dilution (surface area/volume effect)
- Oven profiling/RF heating

Precursors in Wheat Berry Fractions

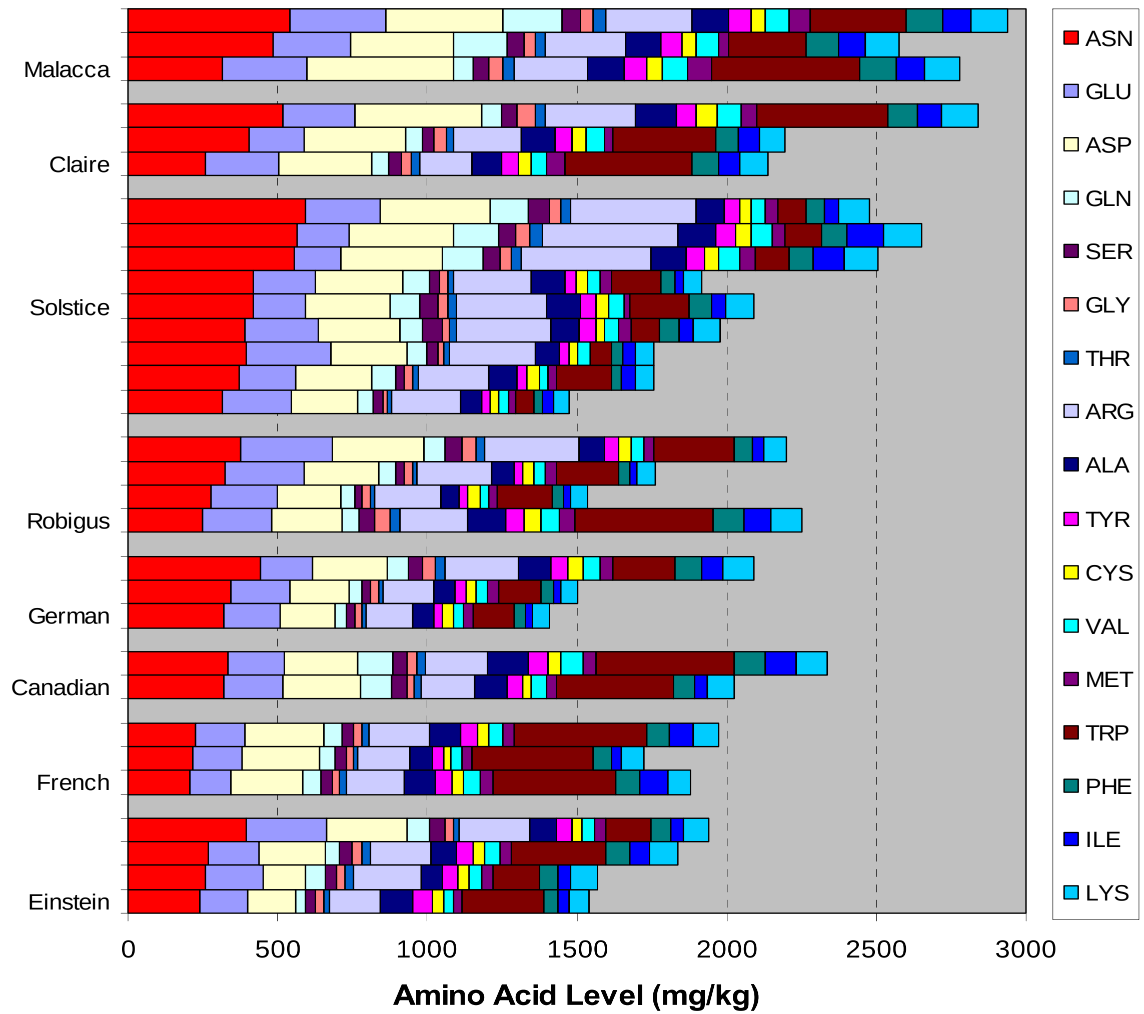
- Highest levels of both sugars and Asn are found in the germ and bran



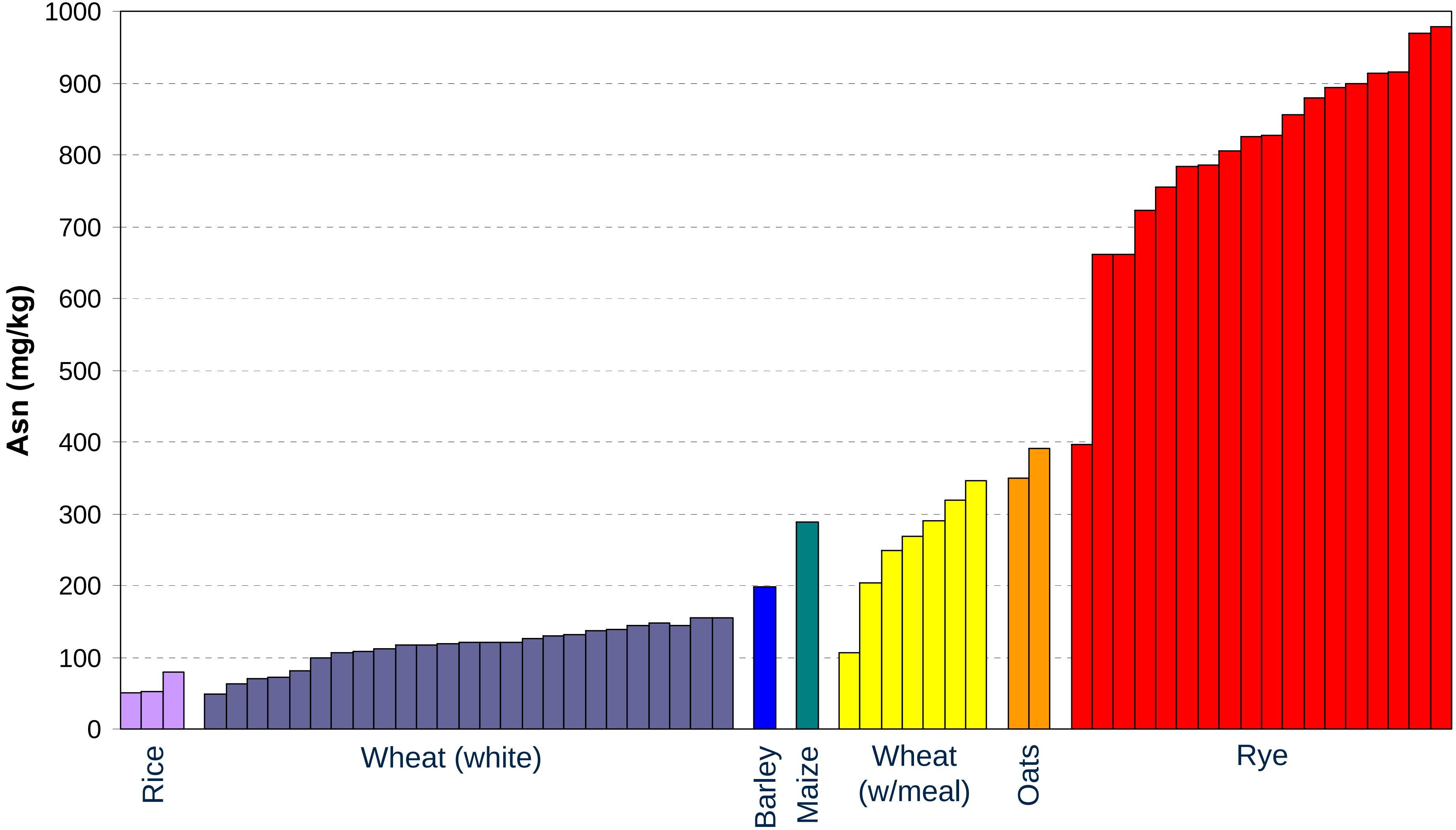
- So more refined flours give less acrylamide (but at the price of other health benefits)
- Asn accumulates in plants under conditions of stress, so it is a variable source of acrylamide

Amino Acids in Commercial Bread Wheat Flours

- Roughly ordered by total amino acid levels then Asn
- Asn was as variable within as between varieties
- No link with the total free amino acid levels
- Selection by growing variety is not enough



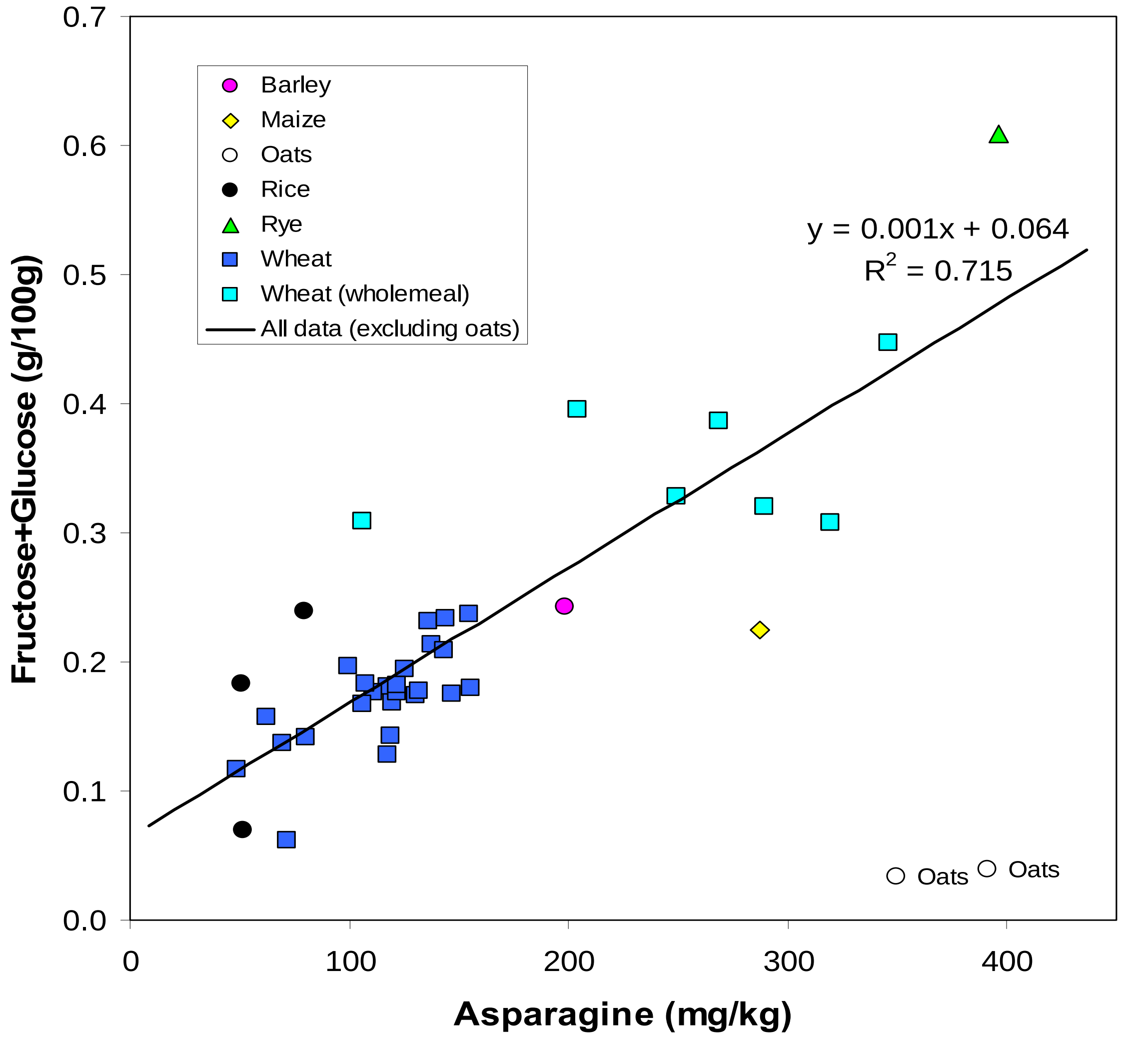
Asn variation in other flours



Biscuit/confectionery Flours: Asn v Reducing Sugars

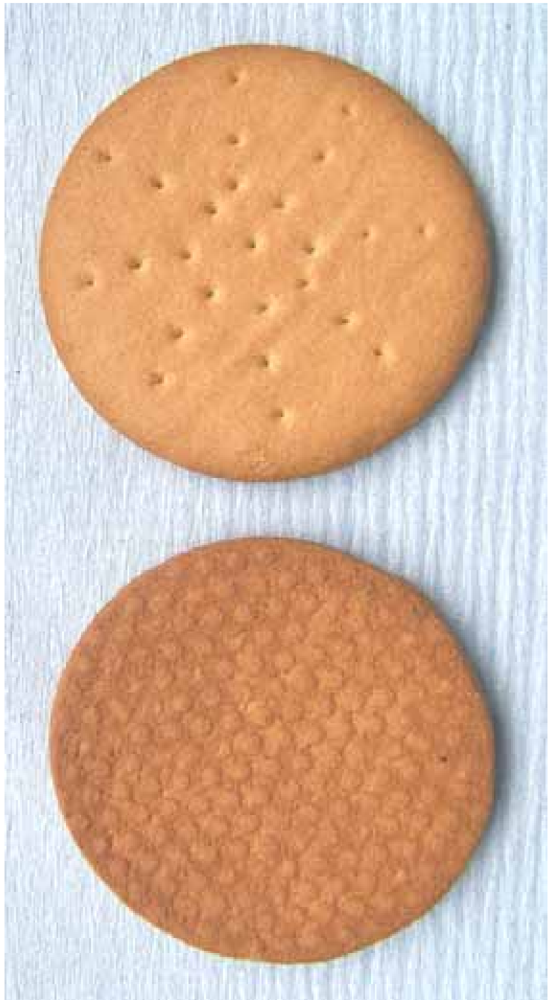
- Reducing sugars and Asn vary in tandem
- Oats is outlier, but only 2 samples
- Grist selection may offer opportunities for acrylamide reduction

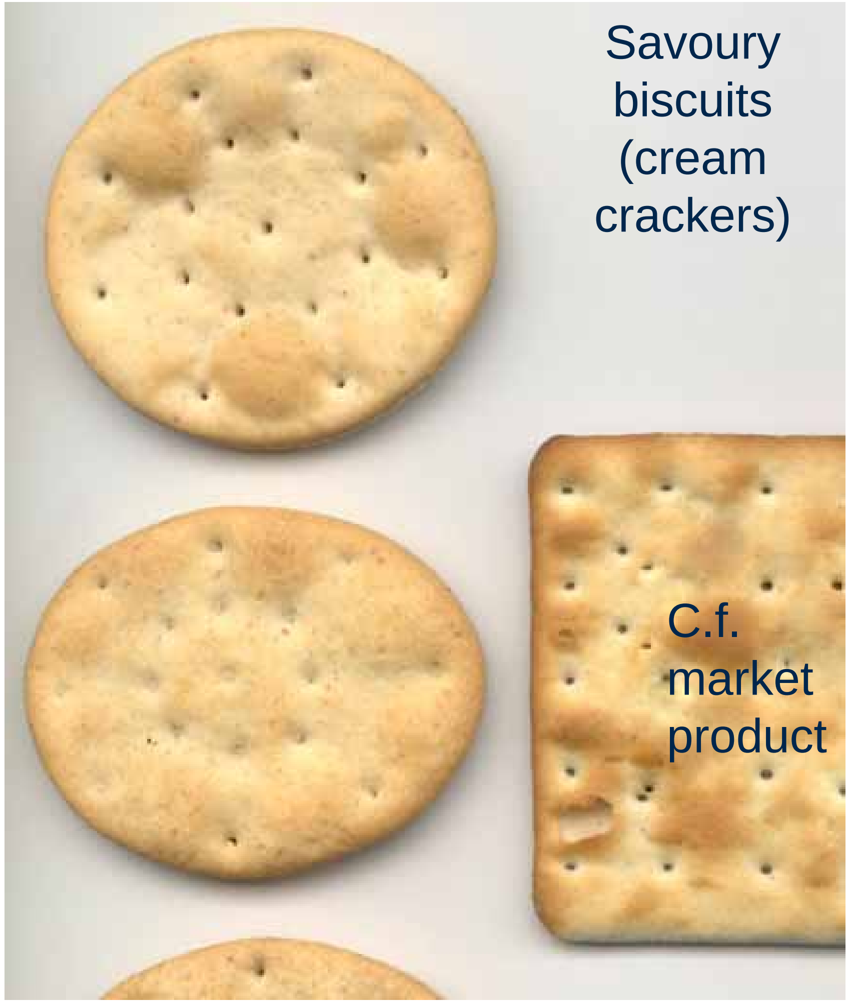
- *But not for bread flours,* possibly due to selection on protein quality/quantity.



Products Produced (kg scale)

Sweet biscuits





Recipes

	Short dough biscuit	Straight dough cracker	Sponge & dough cracker	
			Sponge	dough
Flour				
Strong	1000	750	500	500
Soft	-	250	-	-
Salt	10.8	12.6	-	12.6
Water	138	360	232.5	145
Fat	300	150	-	140
Yeast	-	13.5	5.4	3.6
Castor sugar	320	-	-	-
Invert syrup	20	-	-	-
$NaHCO_3$	4	-	-	-
HN_4HCO_3	2.7	-	-	-
Tartaric acid	0.9	-	-	-

- Simplified commercial recipes[1]
- Invert syrup was 36% glucose, 32% fructose
- Other additives:
  - $CaCl_2$, $CaCO_3$
  - Ca propionate (0.38-0.75%, 2-4x standard level when used as a preservative)
  - Phytic acid (0.5-1%, comparable to the levels found in wheat)
  - Propionic acid

1. Derived from: Whitely, P. R., (1971), Biscuit manufacture; fundamentals of in-line production. London: Elsevier Publishing Company Ltd.

Pilot Scale Manufacturing Processes

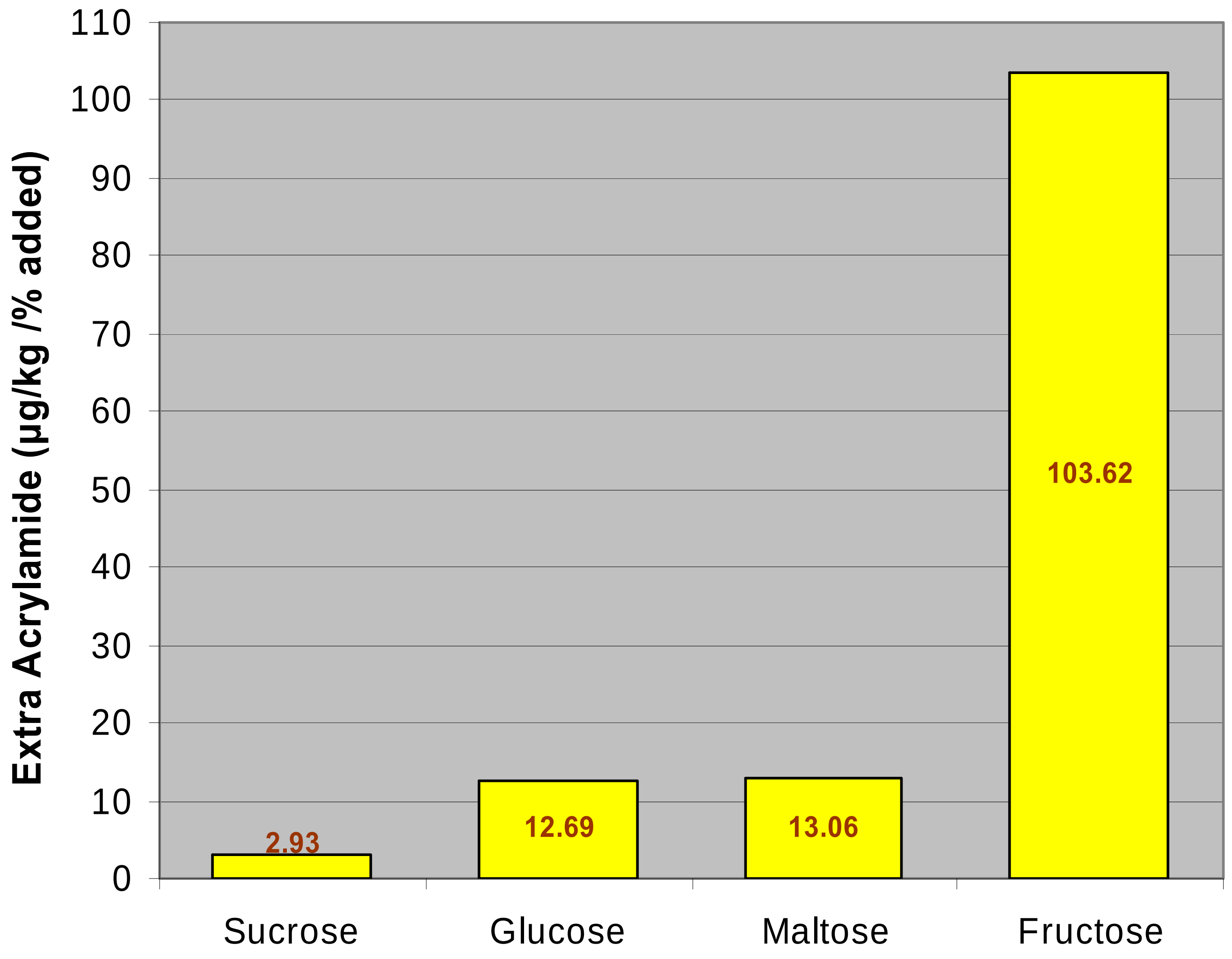
- Short dough biscuits
  - Doughs z-blade mixed, sheeted to 3 mm and docked
  - Baked in pilot commercial oven with control doughs as sets of 3x3 on stainless steel mesh (rising oven profile)

- Crackers (straight dough/sponge & dough processes)
  - Doughs spiral mixed, proved, laminated, sheeted to 3mm and docked
  - Baked in pilot commercial oven with control doughs as sets of 3x3 on stainless steel mesh (rising oven profile)

- Measured final moisture, pH, acrylamide

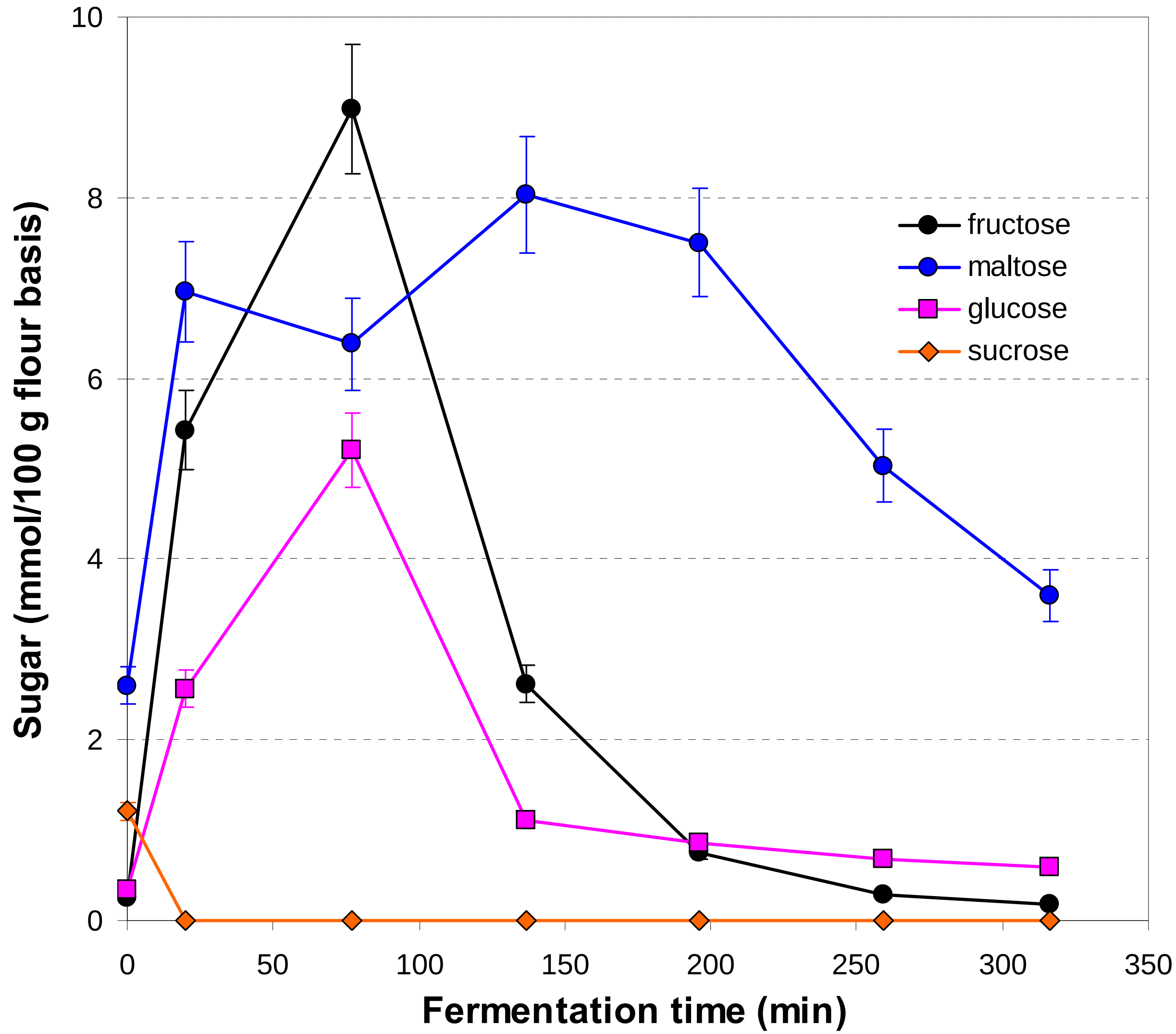
Relative Reactivity of Sugars

- Data from sugar add back experiments on model bread doughs
- As expected monomers are most reactive
- Fructose could be created in situ by inversion of sucrose in acid conditions



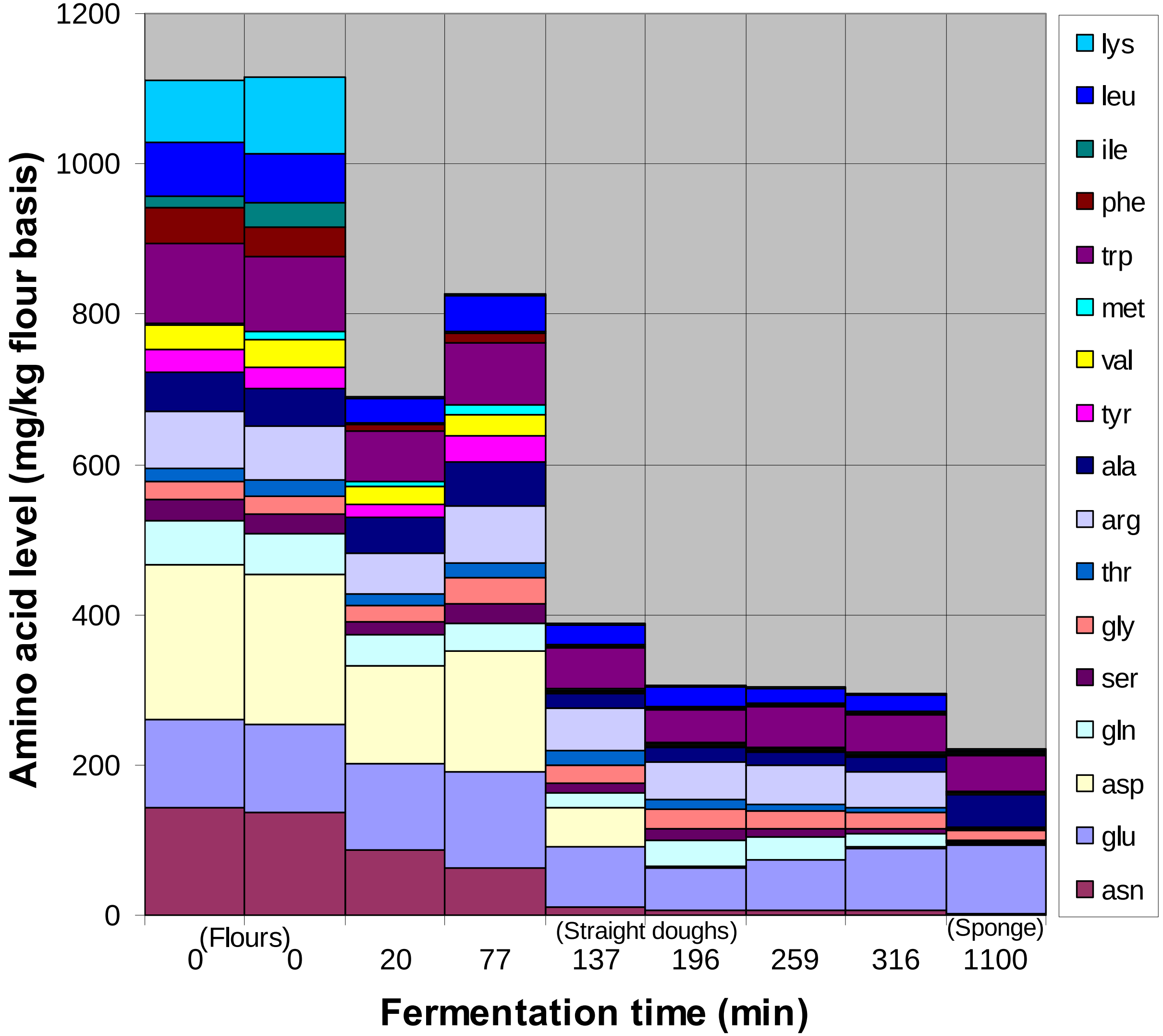
Release of Sugars in Fermented Cracker Doughs

- Sucrose rapidly consumed by yeast
- More fructose produced than corresponding loss of sucrose (glucofructans?)
- Glucose and maltose rise as expected (starch damage + yeast action)
- Virtually all sugars gone after 18hrs (0.1% total) e.g. in sponge process



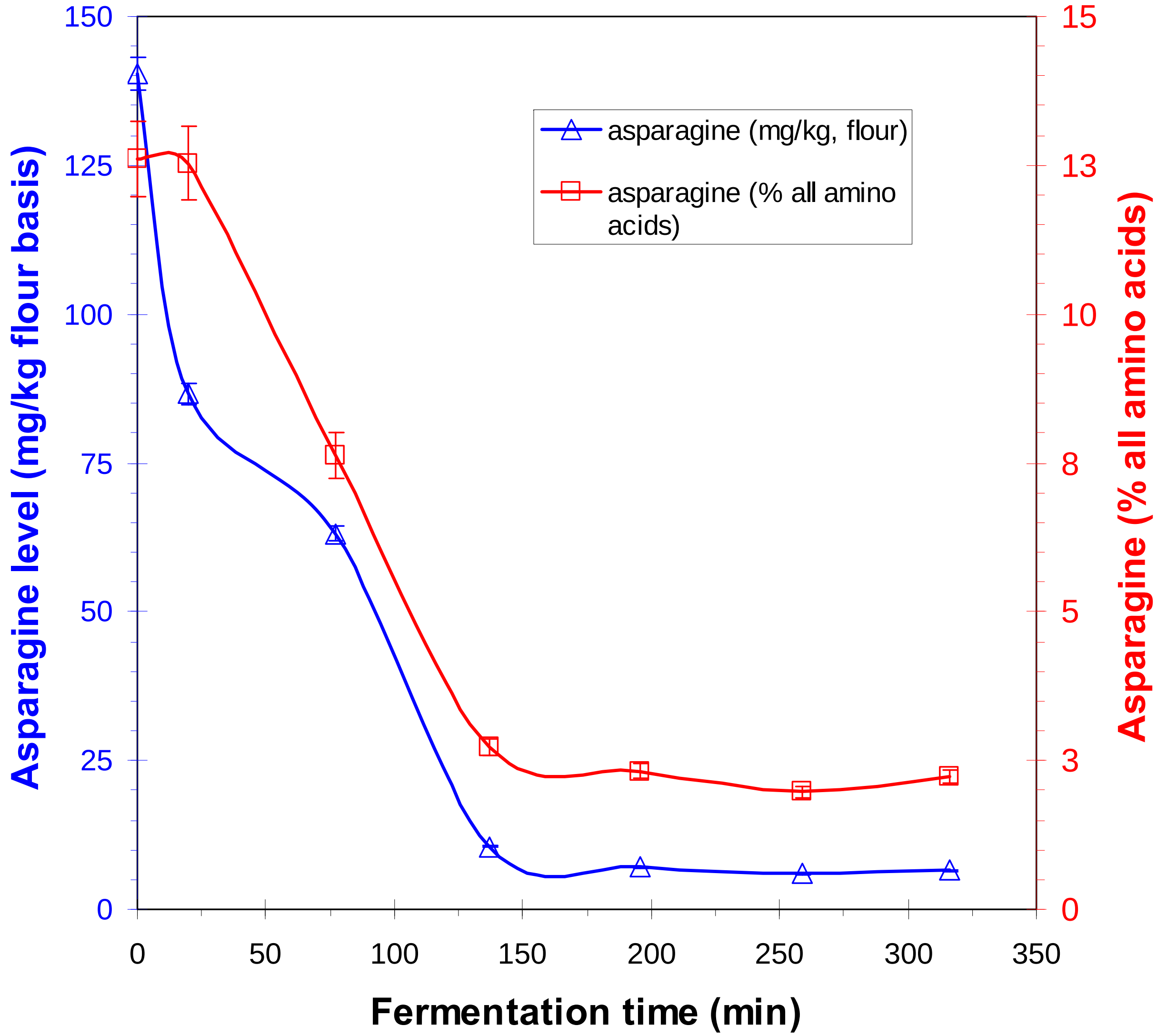
Effect of Yeast on AAs in Cracker Doughs

- Levels of all amino acids fall during proof
- However…..



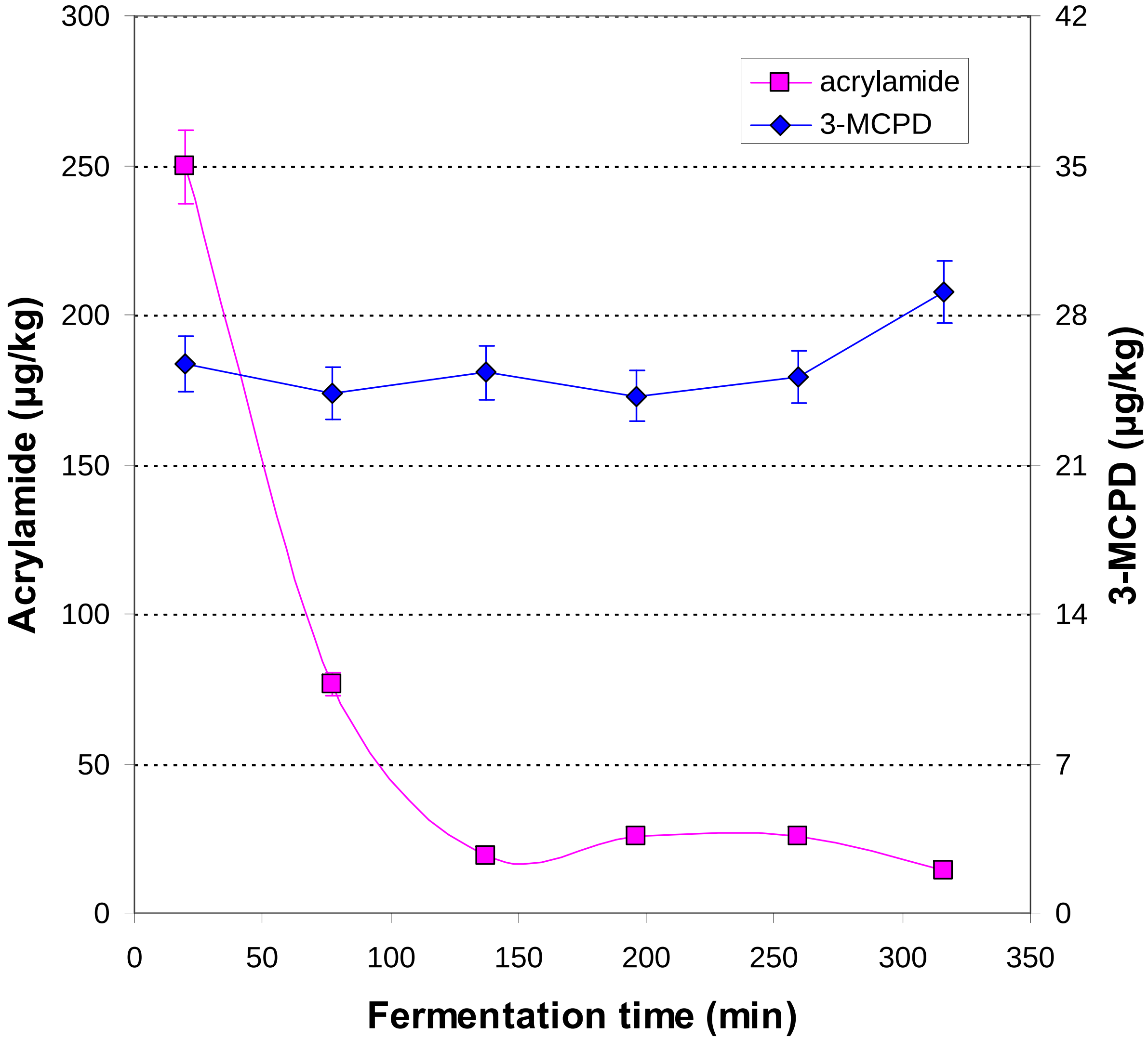
Effect of Yeast on AAs in Cracker Doughs

- Levels of all amino acids fall during proof
- However, yeast selectively consumes Asn
- After extended fermentation times (c.18h) all the Asn was consumed (not shown)



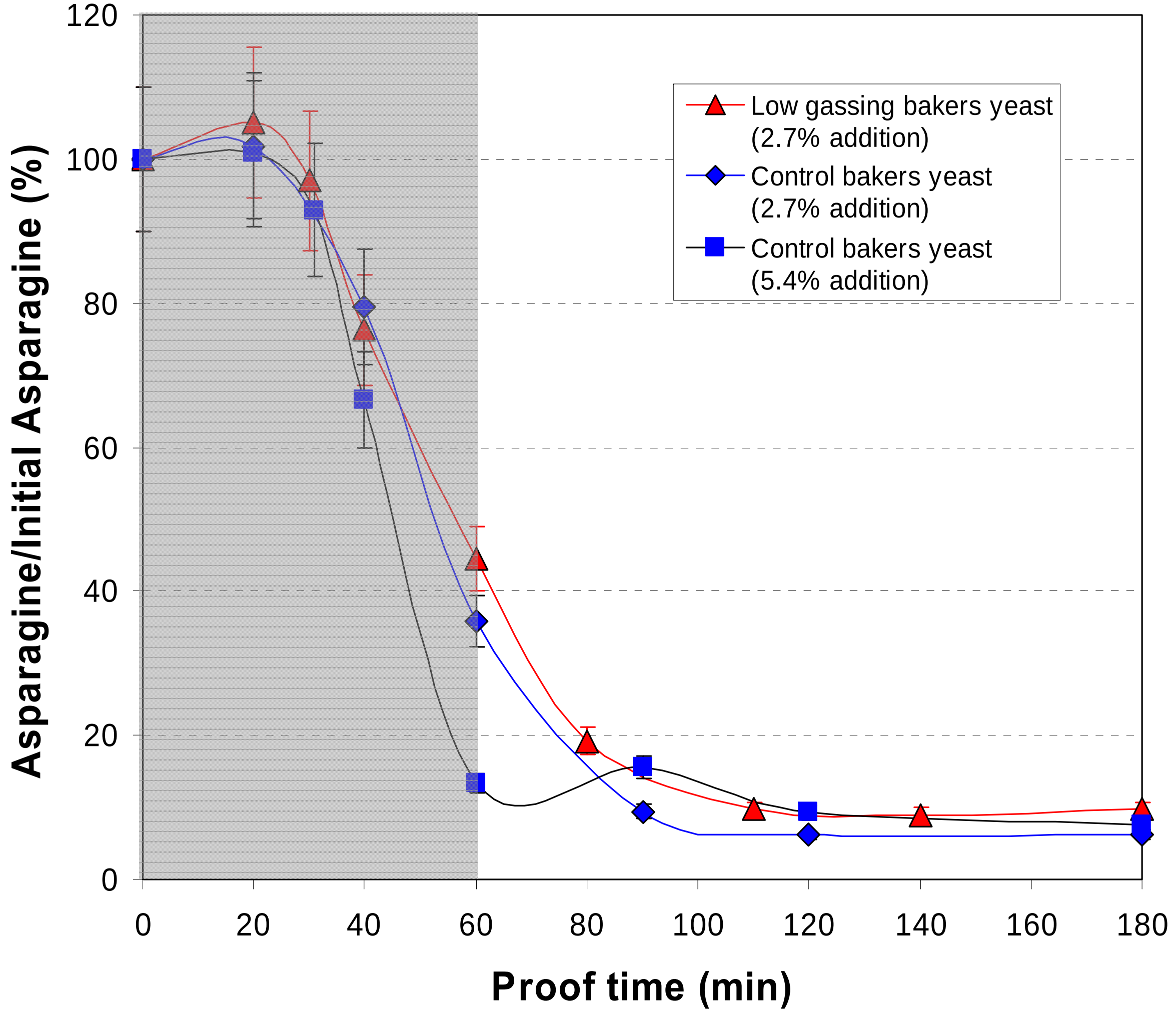
Effect of Yeast on acrylamide in Cracker Doughs

- Despite initial fructose "surge" early in fermentation, acrylamide levels fall rapidly
- 3-MCPD, generated from yeast glycerol, does not increase with time
- Glycerol formation may be limited by sugars availability



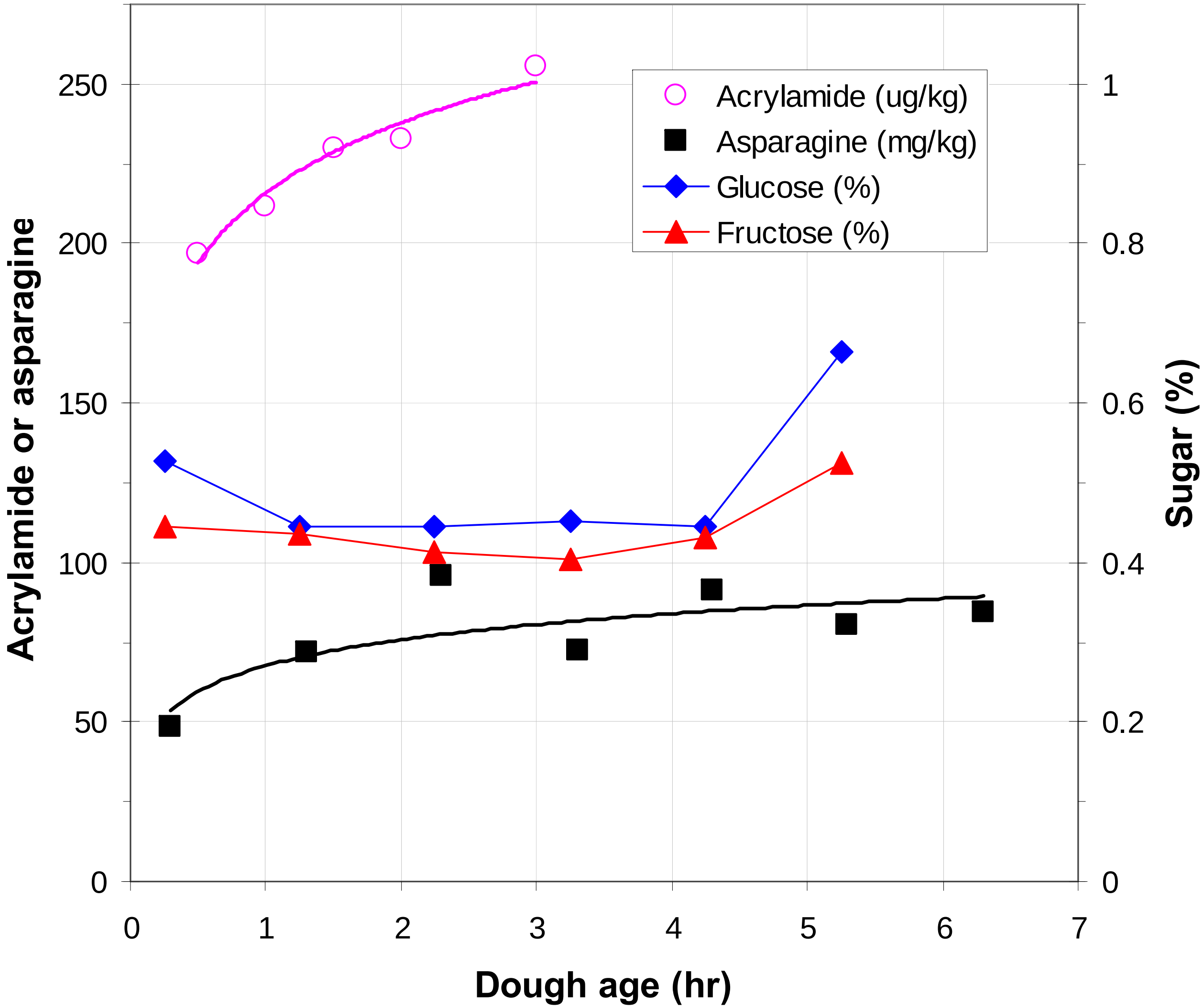
Low Gassing Yeast in (Bread) Dough

- For short fermentation products, doubling yeast significantly cuts Asn after 1 h
- Low gassing bakers yeast is almost as effective as the standard in consuming Asn
- May be possible to optimise yeast addition / gassing and Asn reduction



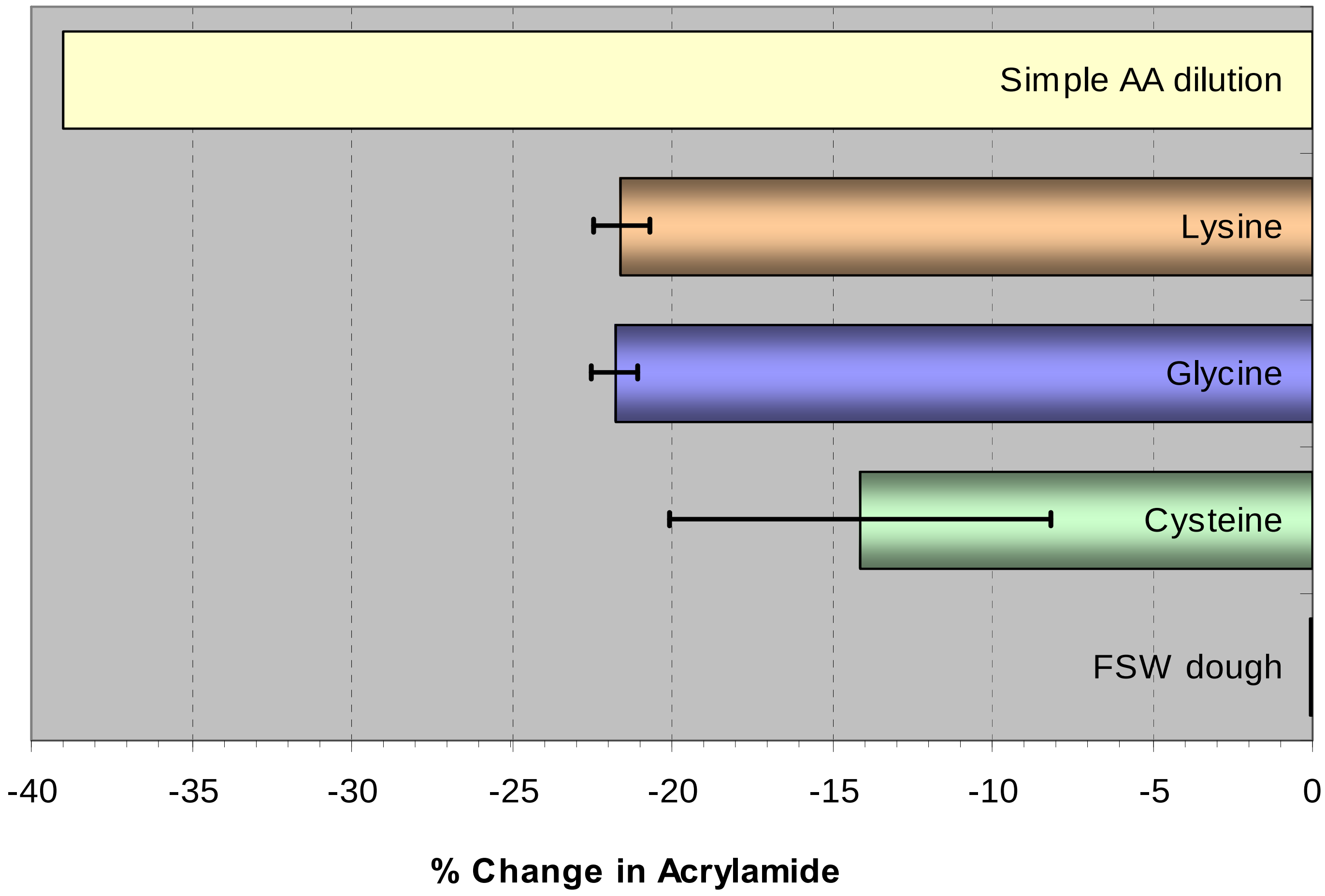
Effect of Dough Age in Sweet Biscuits

- More acrylamide is formed in doughs which have been allowed to age
- Increase is ~35% over three hours
- Extra acrylamide is not due to a rise in sugar levels
- Amino acid levels rise with age for at least the first hour after mixing
- Increase in Asn is enough to explain the extra acrylamide



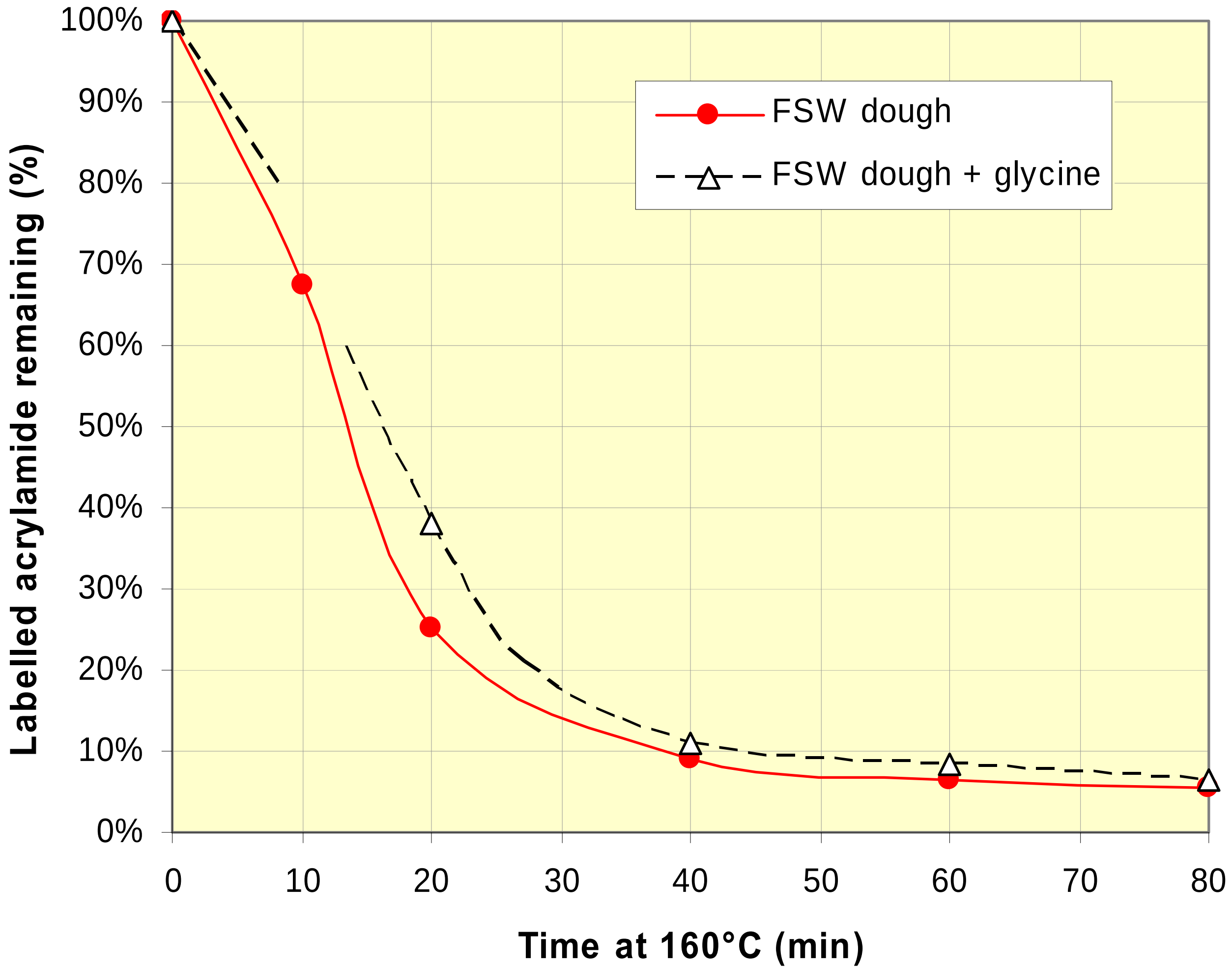
Effect of Amino Acid Addition on Savoury Biscuits

- 5.6 µmol/kg of three amino acids added separately to basic recipe (0.04-0.08%)
- Severe (c.40%) dilution of amino acids
- 15-20% drop in acrylamide formation



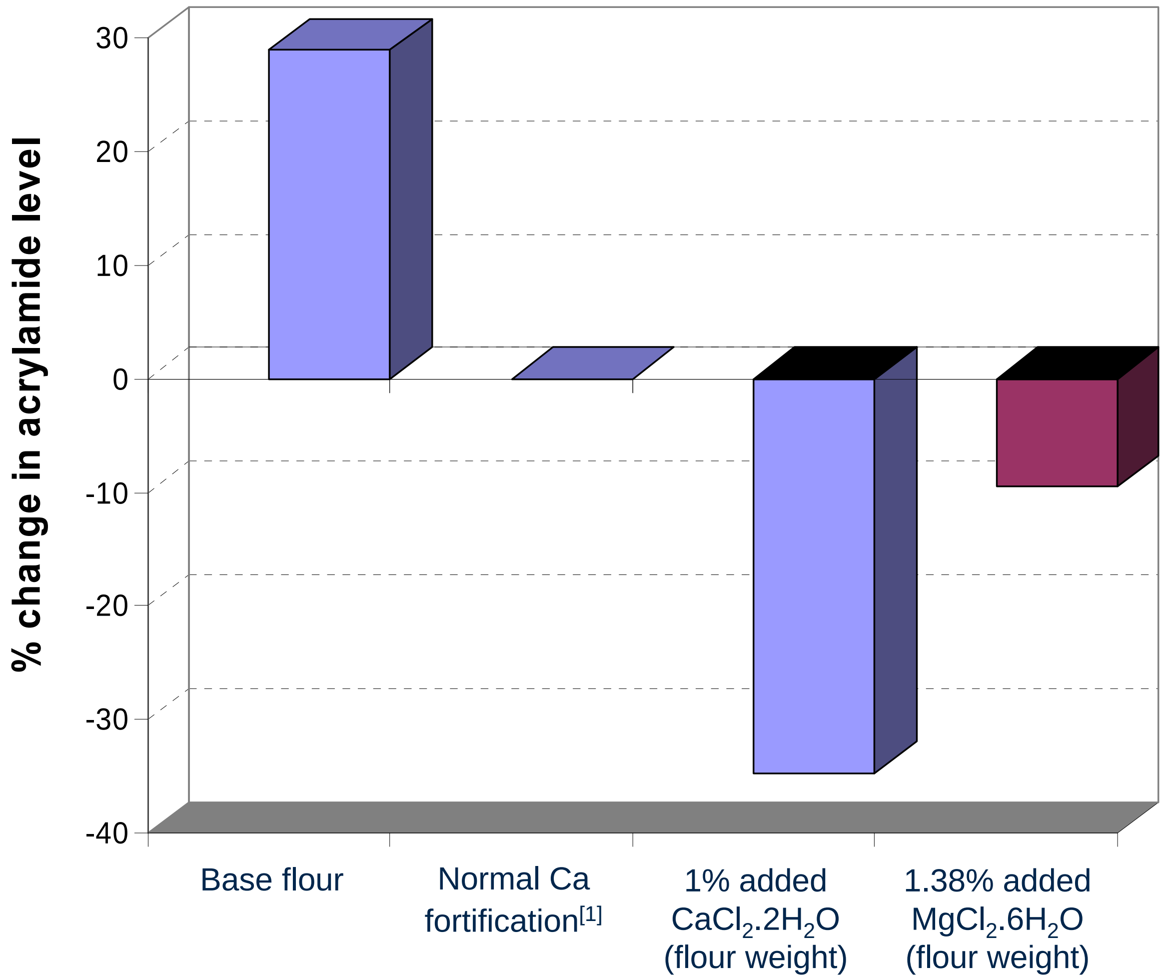
Effect of Amino Acid Addition on Savoury Biscuits II

- Dough spiked with 626ppm $^{13}C_3$ acrylamide
- No loss of acrylamide during bench proof (six hours @ 20°C)
- 1556 mg/kg glycine added to FSW recipe
- Cooked at 160°C for 10-80min
- Decay of the ^{13}C labelled acrylamide was slightly slowed by the extra glycine



Effect of Metal Ions in Savoury Biscuits

- Doughs made from pure flour compared to (UK) normal and enhanced calcium fortification when cooked
- Acrylamide levels fell with both increasing calcium and magnesium concentration
- Both metals produced comparable effects for equal quantities of their metal ions

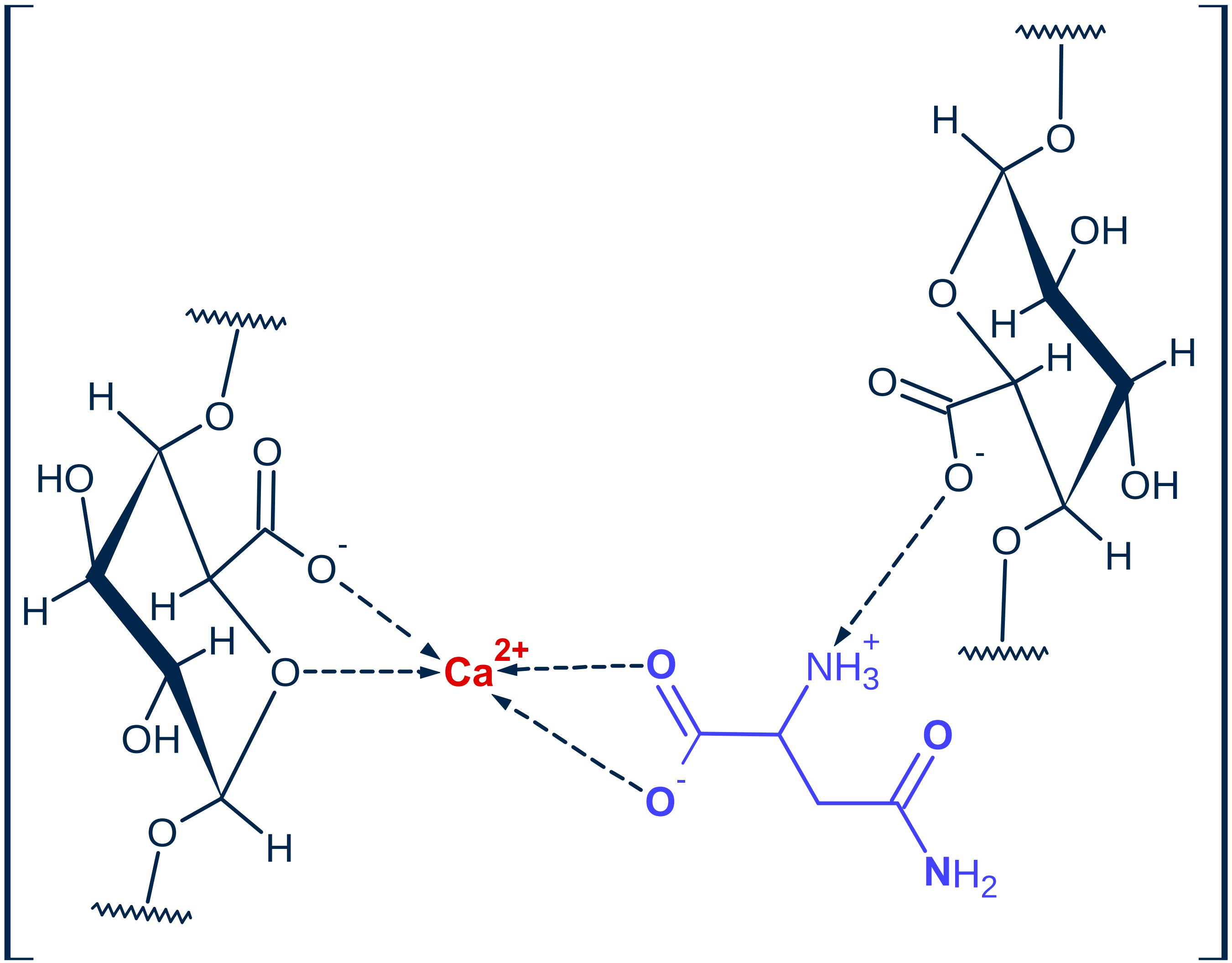


Ca+Mg (%)	0.022	0.098	0.198	0.123

[1] SI 1998 No 141: 0.24-0.29 g/100g $CaCO_3$

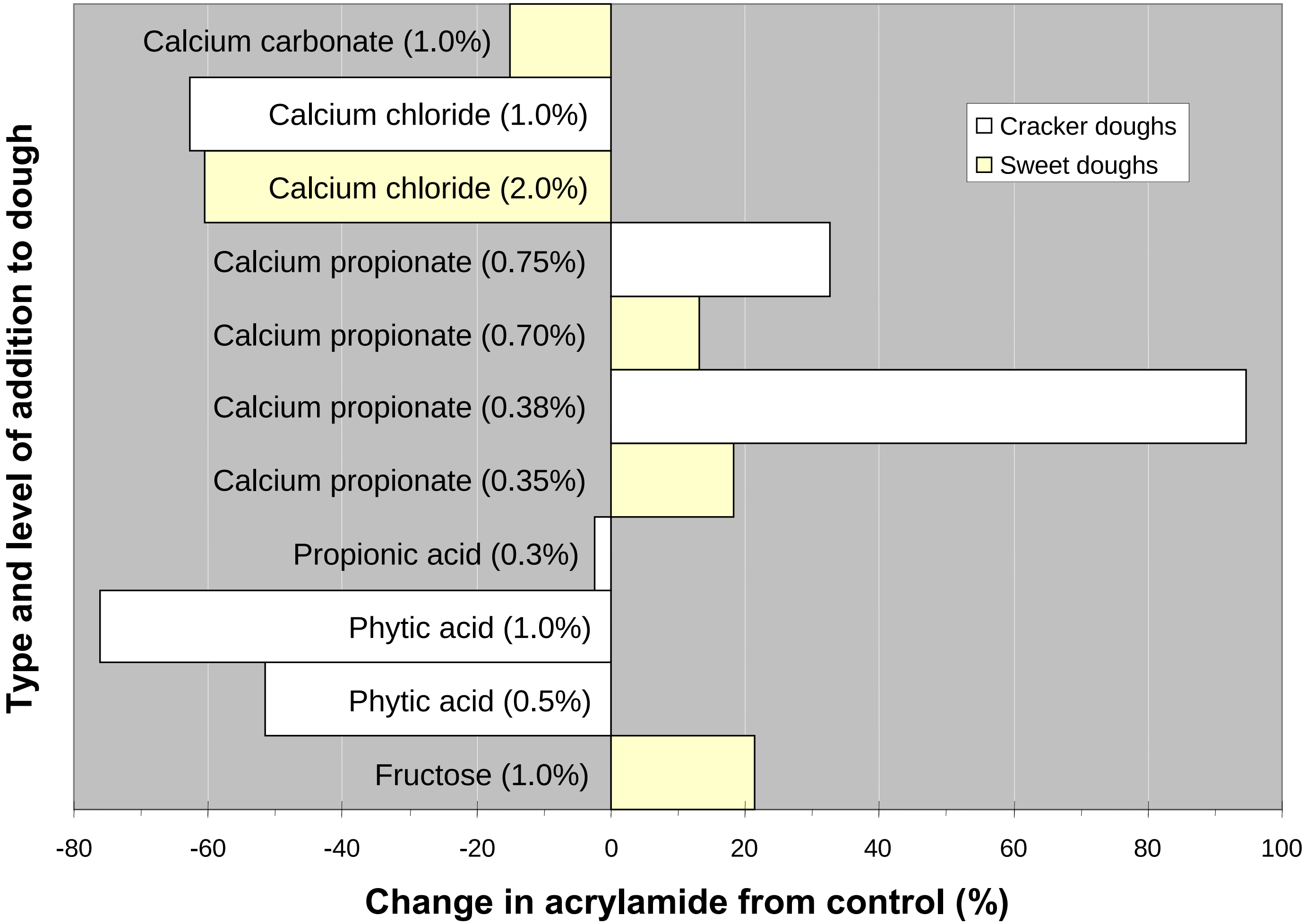
Effect of Metal Ions: Theory

- Multivalent cation crosslinking / ionic interactions
- Reduce solubility of Asn
- Stabilise complexes at high temperature

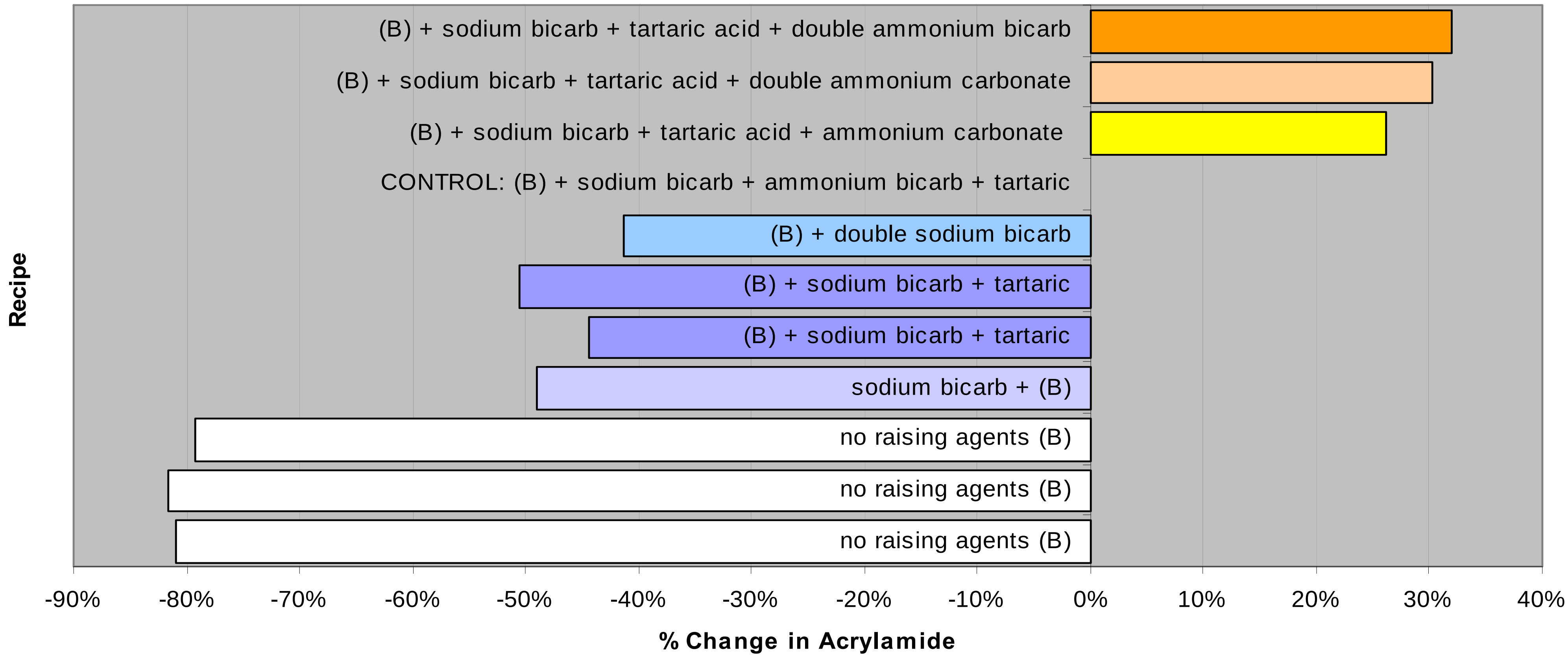


Effect of Additions on Sweet and Savoury Biscuits

- Phytic acid and calcium reduced acrylamide as expected
- Calcium propionate was NOT beneficial
- Propionate alone had little effect
- Cracker doughs were typically twice as sensitive to additions as sweet doughs



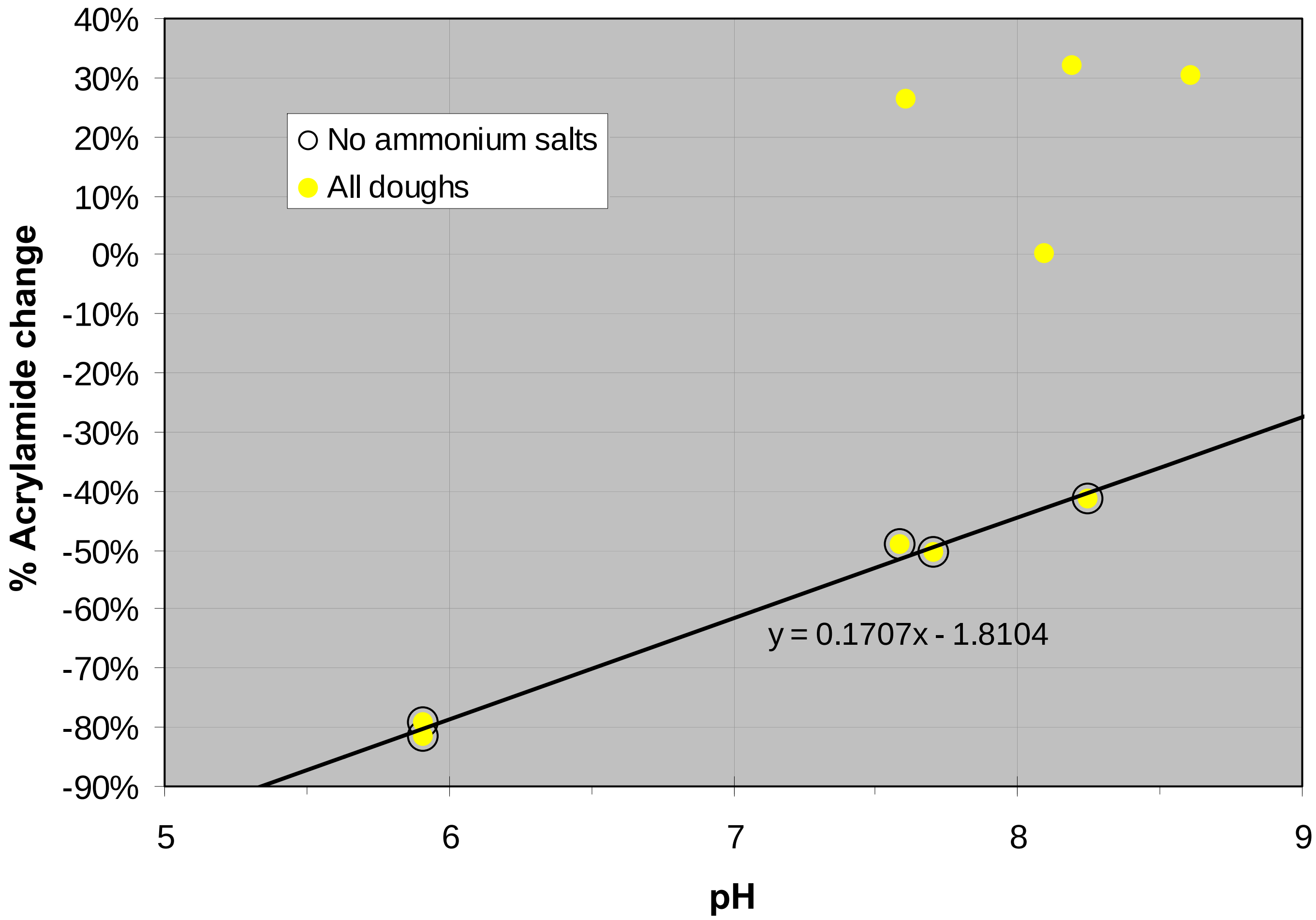
Effect of Raising Agents in Sweet Biscuits



- Any raising agent increases acrylamide, but ammonium based agents are worst

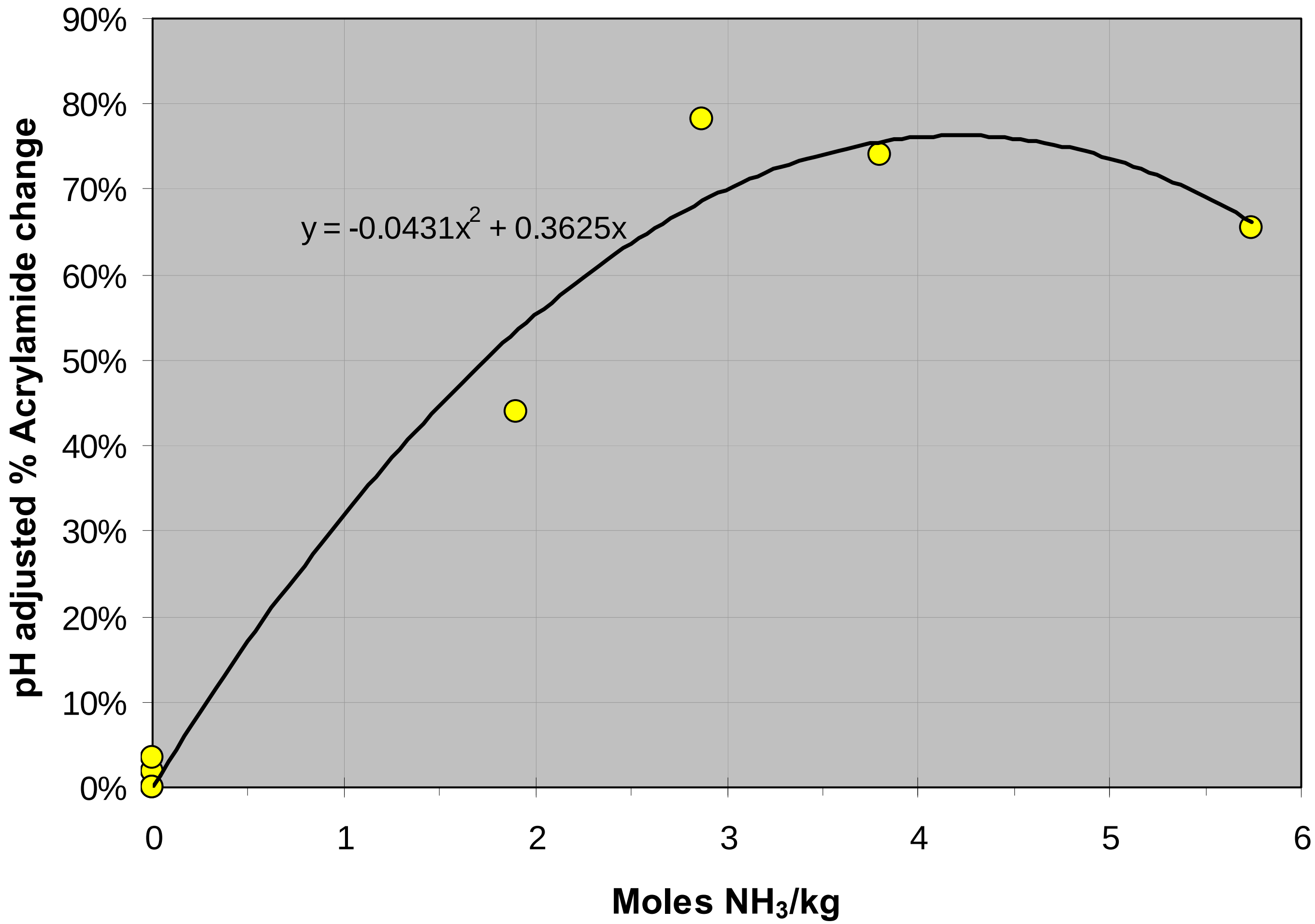
Effect of pH and NH_3 in Sweet Biscuits

- pH shifts can explain non NH_3 raised data
- Effect of pH is linear and in line with work on bread (17% vs 12%)



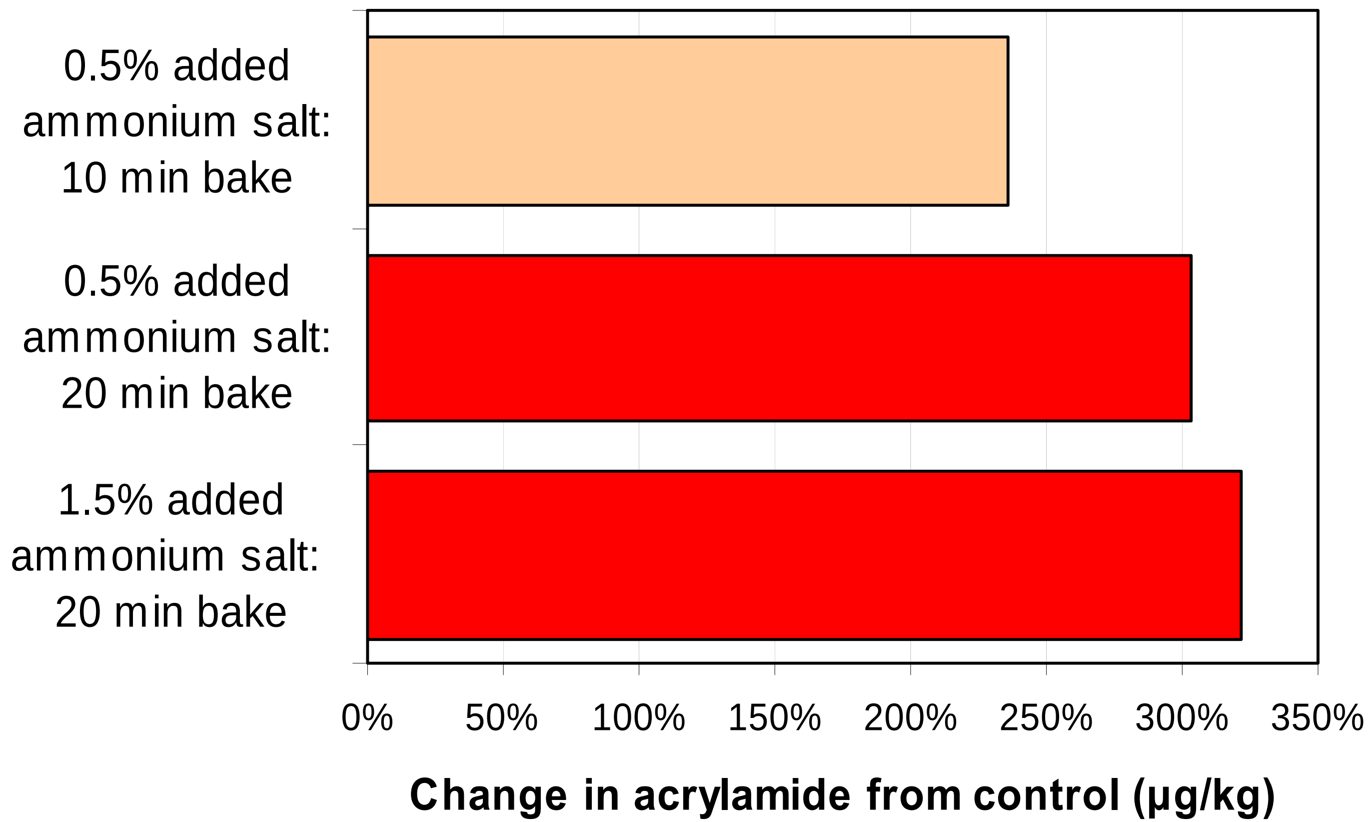
Effect of NH_3 in Sweet Biscuits

- Effect of pH removed
- As expected NH_3 strongly increased acrylamide
- Plateau in acrylamide possibly due to increased decay at high NH_3 levels



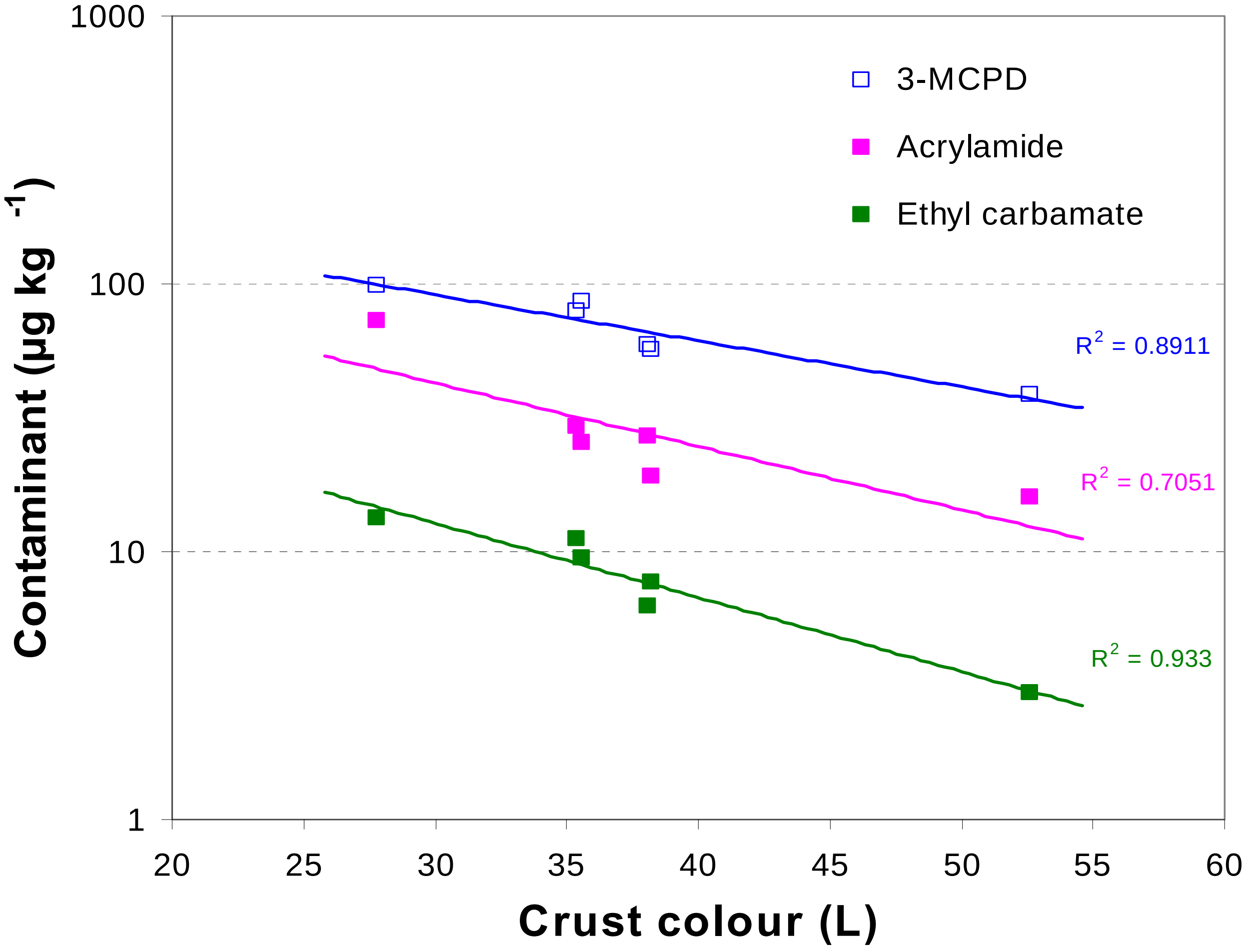
Effect of NH_3 in Savoury Biscuits

- Ammonium bicarbonate added to savoury biscuit formulation
- Acrylamide levels again more sensitive than with sweet doughs
- Increase was insensitive to bake time or addition level



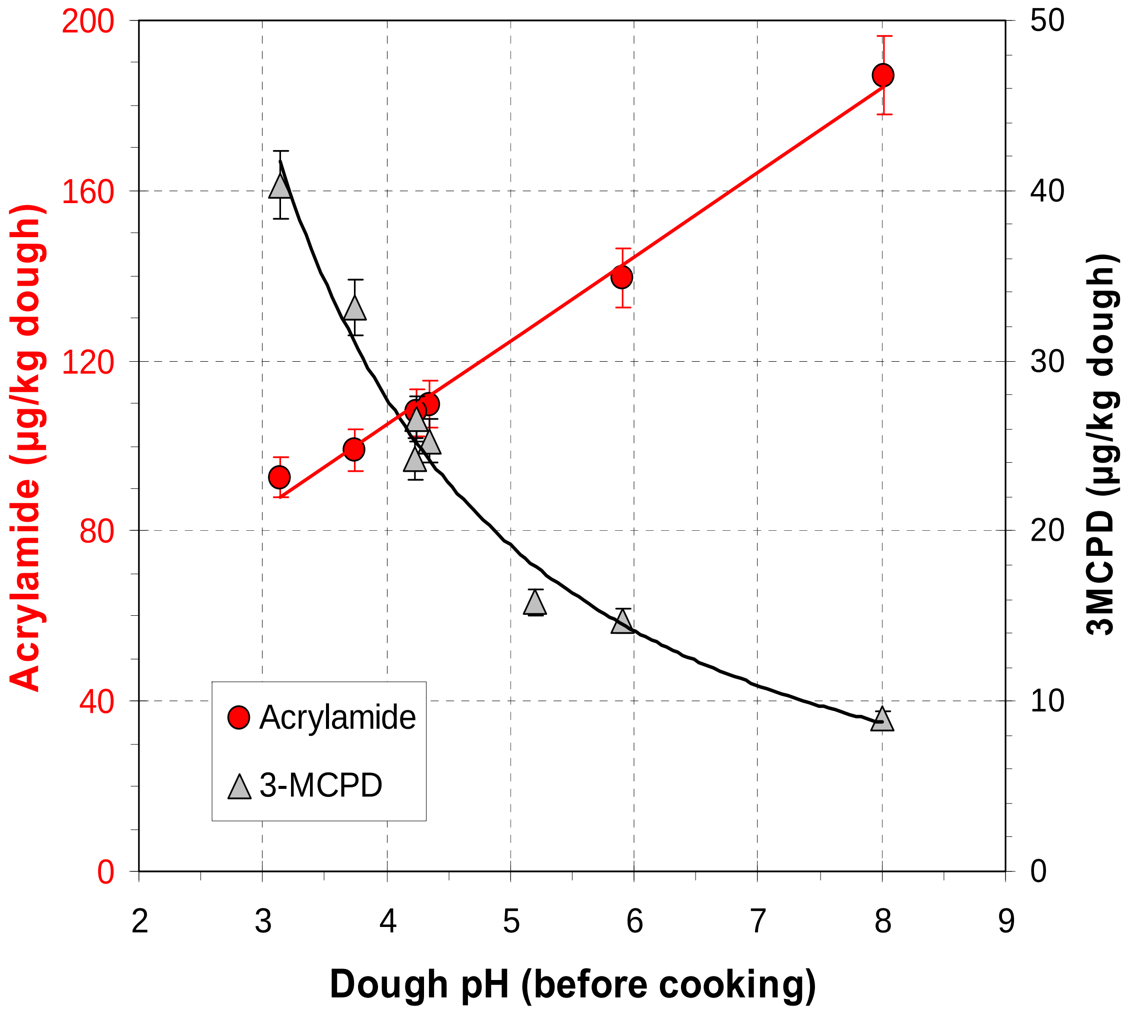
Crust Colour v Contaminants (in Bread)

- Data from loaves made in breadmaking machines, but similar results seen in other processes
- Crust colour (L) is a good indicator for all contaminants
- Hence oven profiling (where the heat is put into the product early and the end of the oven is run cooler) can be helpful.



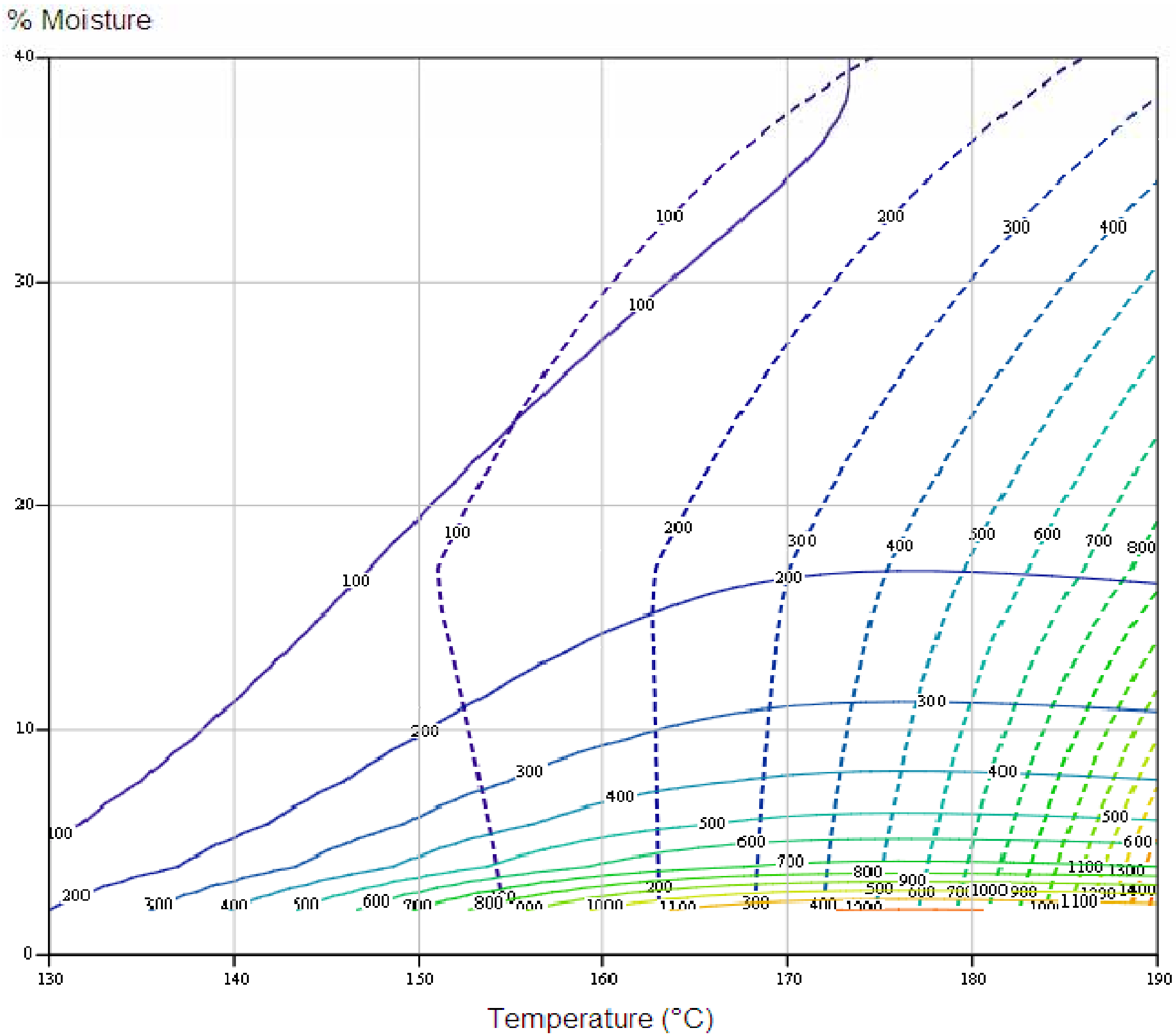
Effect of Dough pH (bread)

- Low pH is beneficial for acrylamide
- But not for 3-MCPD
- Practical pH range is small
- Similar trends with cracker doughs



Predicted Acrylamide v 3-MCPD (in Bread)

- 3-MCPD levels (dashed contours) are static or reduced whenever acrylamide is reduced (solid contours)
- Hence baking changes such as modified oven profiles are safe



Acrylamide Reduction Methods: Conclusions

- Raw material selection may be helpful for (low sugar) products
- In real bakery processes yeast has a protective effect giving lower levels of acrylamide in the final food than would be expected from the ingredients
- Recipe or process changes which affect yeast may have unexpected effects on final acrylamide levels as it is a filter/amplifier for acrylamide precursors
  - Sugars can be released or consumed
  - Asn can be consumed
- Low gassing bakers yeasts may offer a reduction route in some cases
- Extra amino acids have a modest effect on acrylamide at commercial levels
- Best practice should avoid allowing sweet biscuit doughs to age
- Calcium supplementation is beneficial (statutory fortification), but interactions with other ingredients (especially propionate) need investigation
- Ammonium salt replacement is the priority for chemically raised products
- Low pH is beneficial for acrylamide, *but*
  - limited by dough buffering
  - low pHs promote 3-MCPD formation
- Temperature and moisture changes to reduce acrylamide will not promote 3-MCPD

Acknowledgements

- The support of the UK Foods Standards Agency for this work is gratefully acknowledged

For more information see:

Updated (17/2/09) CIAA toolbox (incorporating information from GMA members) & pamphlets[1]

Hamlet,C.G.; Sadd,P.A.; Liang,L. Correlations between the amounts of free asparagine and saccharides present in commercial cereal flours in the united kingdom and the generation of acrylamide during cooking. *J. Agric. Food Chem*., **56** (15), 6145–6153 (2008)

Sadd,P.A.; Hamlet,C.G.; Liang,L. Effectiveness of methods for reducing acrylamide in bakery products. *J. Agric. Food Chem*., **56** (15), 6154–6161 (2008)

Konings, E.J.M., Ashby, P., Hamlet, C.G., Thompson, G.A.K., (2007) Acrylamide in cereal and cereal products: a review on progress in mitigation. *Food Addit. Contam*., 24(S1), 47-59.

Sadd,P.A.; Hamlet,C.G. *The Formation of Acrylamide in UK Cereal Products* in: Chemistry and Safety of Acrylamide in Food, M.Friedman and D.S.Mottram, Editors, Springer, New York; Advances in Experimental Medicine and Biology, Vol. 561, pp. 415-430. (2005)

[1] available at: http://www.ciaa.be/asp/index.asp