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Acrylamide physical removal from food products

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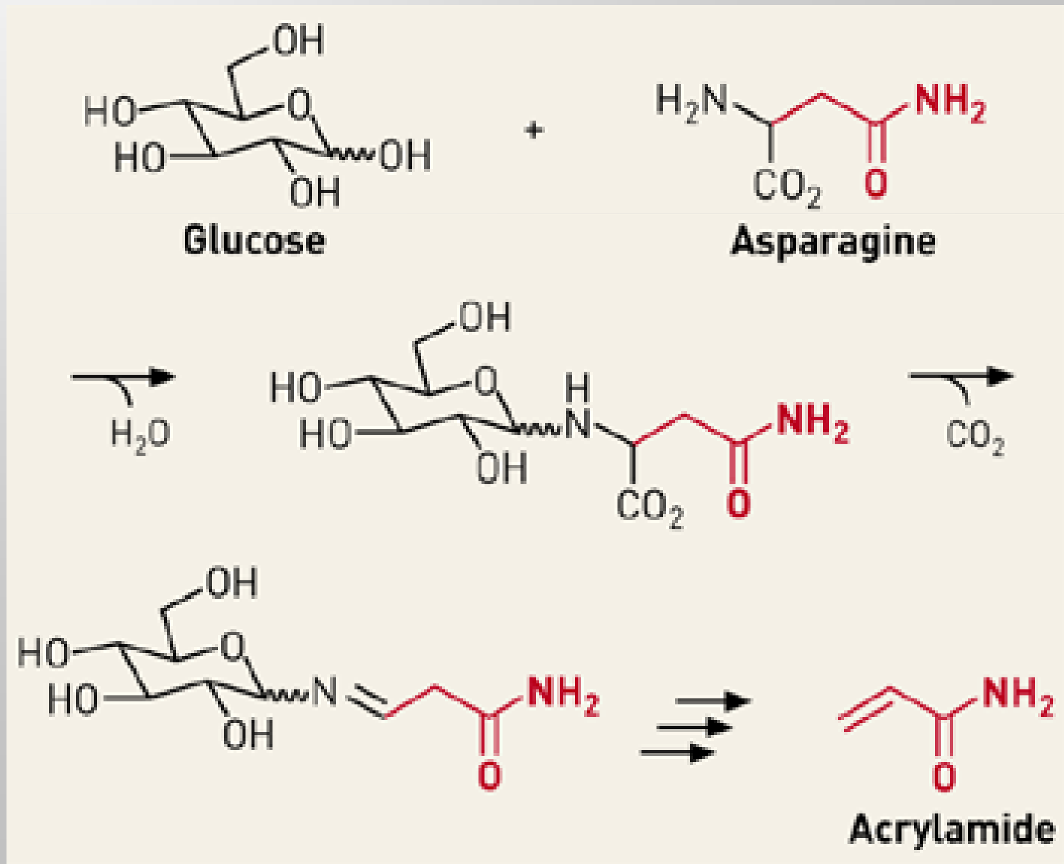
Acrylamide

- Certainly toxic molecule
- IARC (1994) has classified acrylamide as a probable carcinogenic molecule
- Diet as a source of acrylamide
- EFSA: acrylamide levels in foods must be reduced



ENVIRONMENTAL PROTECTION AGENCY

[FRL–8511–8; Docket ID No. EPA–HQ–ORD–2007–1141]

Draft Toxicological Review of Acrylamide: In Support of Summary Information on the Integrated Risk Information System (IRIS)

AGENCY: Environmental Protection Agency (EPA).

Certainly Toxic molecule

Probable carcinogenic molecule

USA Environment Protection Agency has released the draft of the report on acrylamide toxicology.

- **The Reference Dose (RfD) for noncancer effects** (peripheral degenerative nerve changes detected microscopically in animal studies) **has been raised to 0.003 mg/kg-bodyweight/day**.

- **EPA considers the mode of action for carcinogenicity to be mutagenicity.**

- **EPA used only conservative linear low-dose modeling to derive cancer potency.**
Their estimated total lifetime cancer risk from exposure to 1 µg/kg-bodyweight/day over 70 years is 8 x 10-4.

- **Carcinogen classification:** ***"likely to be carcinogenic to humans"*****.**

Certainly Toxic molecule

Probable carcinogenic molecule

Press release 26 November 2007

HEATOX project completed – brings new pieces to the Acrylamide Puzzle

The three-year project included 24 partners from 14 countries

These are conclusions of the European research project HEATOX:

-Increasing toxicological evidence suggests that acrylamide in food might be a cancer risk factor.

-Sufficient analytical methods to detect acrylamide in relevant foods are now available.

-There are ways to decrease exposure to acrylamide, but not to eliminate it.

-Acrylamide is not the only risk factor in cooked foods.

theheatoxproject

Mol. Nutr. Food Res. 2007, *51*, 000–000 DOI 10.1002/mnfr.200600253

Research Article

Importance of a canteen lunch on the dietary intake of acrylamide

Frédéric Mestdagh[1,2], Carl Lachat[1,3], Katleen Baert[1], Emmanuelle Moons[4], Patrick Kolsteren[1,3], Carlos Van Peteghem[2] and Bruno De Meulenaer[1]

[1] Department of Food Safety and Food Quality, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium
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[3] Nutrition and Child Health Unit, Department of Public Health, Prince Leopold Institute of Tropical Medicine, Antwerp, Belgium
[4] Federal Agency for the Safety of the Food Chain, Brussels, Belgium

Diet as a source of acrylamide

Table 1. Descriptive statistics of acrylamide consumption (mg/kg bw/day) and acrylamide contamination (µg/kg) for the most important food groups.

	Contamination (µg/kg foodstuff)*			Consumption (mg/kg bw/day) – P 50–P 95** (Mean)		
	N	Mean	P 50 (P 0–P 100)	Total (*N* = 160)	Male (*N* = 60)	Female (*N* = 100)
Biscuits	1130	276	142 (<5–6798)	404–1727 (589)	375–1801 (576)	483–1658 (598)
Bread	119	27	15 (<7–150)	1639–3708 (1768)	1868–4083 (2063)	1589–3168 (1592)
Breakfast cereals	380	125	70 (<5–1649)	0–1294 (291)	0–1313 (267)	0–1204 (305)
Chocolate	43	190	130 (<8–626)	142–618 (215)	88–618 (196)	163–624 (226)
Coffee drink	262	14	12 (<0.5–59)	0–6362 (1381)	0–4768 (1107)	0–6632 (1546)
Crisp bread	557	329	182 (<5–2838)	0–523 (88)	0–312 (46)	0–576 (113)
French fries (outside canteen)	538	377	220 (<5–3300)	0–1127 (125)	0–1134 (123)	0–1113 (126)
French fries (canteen data)	10	58	50 (32–116)	814–2349 (813)	892–2362 (980)	629–2286 (713)
Potato crisps	925	707	522 (<5–4215)	0–547 (98)	0–599 (137)	0–521 (75)
Gingerbread	1025	556	308 (<5–7834)	0–206 (24)	0–217 (35)	0–5 (17)
Sweet spiced biscuit	47	353	277 (<15–1234)	0–399 (75)	0–406 (76)	0–295 (74)

* For values below the LOD and LOQ, LOD/2 and LOQ/2 were respectively used.
** 50th and 95th percentile.
N, number of observed values.

RECOMMENDATIONS

COMMISSION

COMMISSION RECOMMENDATION

of 3 May 2007

on the monitoring of acrylamide levels in food

(notified under document number C(2007) 1873)

(Text with EEA relevance)

(2007/331/EC)

efsa
European Food Safety Authority

Parma, 26 October 2007
EFSA/DATEX/004

Request for data on acrylamide levels in food

The EFSA Scientific Panel on Contaminants in the Food Chain adopted on 19 April 2005 a statement in which it endorsed the risk assessment on acrylamide in food carried out by the Joint Food and Agriculture Organisation/World Health Organisation Expert Committee on Food Additives (JECFA) in February 2005. In that assessment JECFA concluded that the margins of exposure for average and high consumers were low for a compound that is genotoxic and carcinogenic and that this may indicate a human health concern. Therefore, appropriate efforts to reduce acrylamide concentrations in foodstuffs should continue.

The European Commission thus issued on 3 May 2007 a Recommendation to Member States for the monitoring of acrylamide levels in food (2007/331/EC). The recommendation contains detailed sampling requirements and specification of products to be tested in respective Member State. Results should be reported to EFSA by 1 June each year for three years. For details see:
http://eur-lex.europa.eu/LexUriServ/site/en/oj/2007/l_123/l_12320070512en00330040.pdf

EFSA says acrylamide levels are rising not falling.(INTERNATIONAL)

18 May 2009 Food Chemical News

ISSN: 0015-6337; Volume 51; Issue 12

Levels of acrylamide, a suspected carcinogen that forms during high-temperature cooking, are increasing rather than decreasing in key food products, according to a new survey published last week by the European Food Safety Authority.

EFSA raises a question mark over voluntary initiatives undertaken by the food industry to reduce the levels of acrylamide using the toolbox promoted by the Confederation of European Food and Drink Industries (CIAA). Cookies had 243 [micro]g/kg acrylamide in 2003-6, rising to 317 [micro]g/kg by 2007. Acrylamide in breakfast cereals rose from 116 [micro]g/kg in 2003-6 to 156 [micro]g/kg in 2007. Acrylamide in french fries rose from 284 [micro]g/kg in 2003-6 to 350 [micro]g/kg in 2007.

EFSA says the reduction in acrylamide in bread could be partly due to changes in processing of crisp bread products, where acrylamide has been reduced in non-fermented products by 25-75%.

"There seems to be an overall trend towards lower acrylamide values over time," EFSA concludes, cautioning that reduction isn't consistent across all food groups and that many food categories show an increase. "It is not clear if the acrylamide toolbox has achieved its effects," the report says.

The report is based on data from member-states, with Germany supplying the lion's share of the samples for 2007. The report follows the commission recommendation that member-states monitor acrylamide in foodstuffs in 2007, 2008 and 2009.

EFSA: acrylamide levels in foods must be reduced

JECFA/72/SC

Food and Agriculture Organization
of the United Nations

World Health
Organization

JOINT FAO/WHO EXPERT COMMITTEE ON FOOD ADDITIVES
Seventy-second meeting
Rome, 16–25 February 2010

SUMMARY AND CONCLUSIONS
Issued 9 March 2010

1.1 Acrylamide

Dietary exposure estimates:
Mean 0.001 mg/kg body weight (bw) per day
High 0.004 mg/kg bw per day

Effect	NOAEL/BMDL$_{10}$ (mg/kg bw per day)	MOE at Mean dietary exposure	MOE at High dietary exposure	Conclusion/comments
Morphological changes in nerves in rats	0.2 (NOAEL)	200	50	The Committee noted that while adverse neurological effects are unlikely at the estimated average exposure, morphological changes in nerves cannot be excluded for individuals with a high dietary exposure to acrylamide.
Mammary tumours in rats	0.31 (BMDL$_{10}$)	310	78	The Committee considered that for a compound that is both genotoxic and carcinogenic, these MOEs indicate a health concern.
Harderian gland tumours in mice	0.18 (BMDL$_{10}$)	180	45	

BMDL$_{10}$, lower limit on the benchmark dose for a 10% response; bw, body weight; MOE, margin of exposure; NOAEL, no-observed-adverse-effect level.

Milano, 24/02/2010
Circ. n.: u186/10 AP/mc

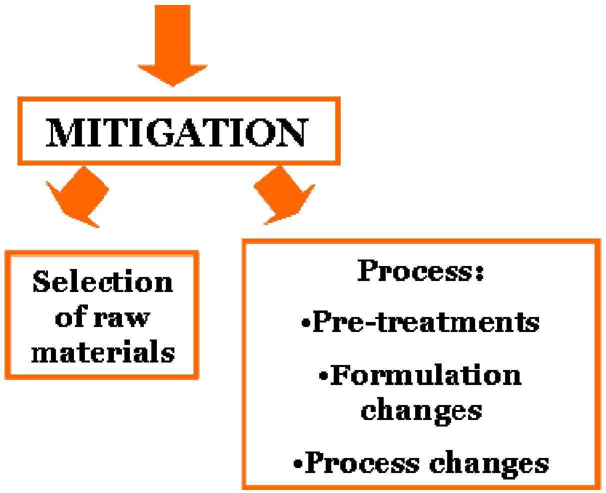
OGGETTO: **Acrilamide: proposta di valori guida in alcune categorie di prodotti alimentari**

Nel corso della riunione del Gruppo di Lavoro di esperti degli Stati Membri "Industrial and Environmental Contaminants" del 19 febbraio scorso, sono stati considerati i seguenti livelli guida di acrilamide in alcune categorie di prodotti alimentari.

Foodstuff	Guidance level in mg/kg
French fries ready to eat	0,6
Potato crisps	1,0
Crisp bread	0,5
Breakfast cereals	0,3
Biscuits	0,55
Infant biscuits	0,25
Ginger Bread	1,0
Processed cereal based baby foods	0,1
Roasted coffee	0,35
Instant coffee	0,85
Coffee substitutes	1,0

EU Members \ JECFA
…latest news!

Main technological interventions aimed to reduce acrylamide concentration in foods



At present only mitigation interventions are available

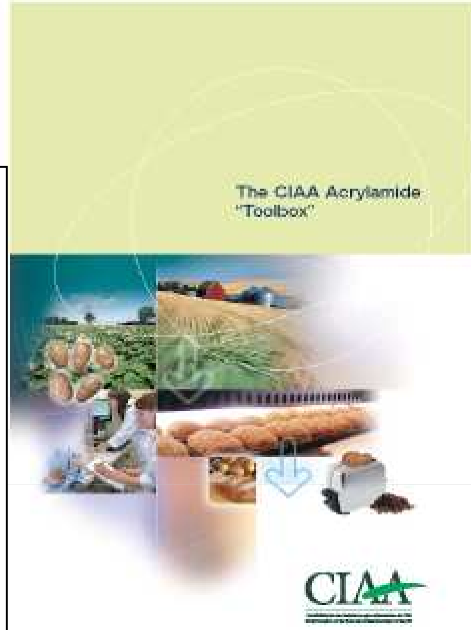
Most mitigation strategies are reported in the CIAA Toolbox

Pre-treatment	✓chemical: dipping in additive solutions ✓physical: thermal treatment ✓biotechnological: yeast or lactic acid fermentation, use of asparaginase ✓combinations
Formulation change	✓substitution of acrylamide-promoting ingredients ✓addition of acrylamide-inhibiting ingredients
Process change	✓reduction of thermal input ✓increase of relative humidity during heating ✓modality of heat transfer ✓rapid chilling

Michele Suman

CIAA Acrylamide Toolbox

- CIAA Acrylamide Toolbox updated February 2009



Biscuit sector brochure recommends for biscuits crackers and crispbread:

- Ammonium bicarbonate (ABC) replacement,
- Fructose replacement in recipes with ABC,
- Substitution with more highly refined flour,
- Bake to lower colour, same moisture,
- Extended bake at lower temperature to same moisture

CIAA Toolbox also includes potential measures for some applications:

- Agronomical developments (sulphur application, crop selection)
- Substitution with lower asparagine cereals or non-cereal components
- Amino Acids (glycine)/Calcium/pH
- Rework reduction
- Extended fermentation
- Reduced resting time for unfermented dough
- Asparaginase.
- Oven profile optimisation,
- Bake to higher moisture

Main technological interventions aimed to reduce acrylamide concentration in foods

MITIGATION

Selection of raw materials

Process:
- **Pre-treatments**
- **Formulation changes**
- **Process changes**

Pre-treatment	✓chemical: dipping in additive solutions ✓physical: thermal treatment ✓biotechnological: yeast or lactic acid fermentation, use of asparaginase ✓combinations
Formulation change	✓substitution of acrylamide-promoting ingredients ✓addition of acrylamide-inhibiting ingredients
Process change	✓reduction of thermal input ✓increase of relative humidity during heating ✓modality of heat transfer ✓rapid chilling

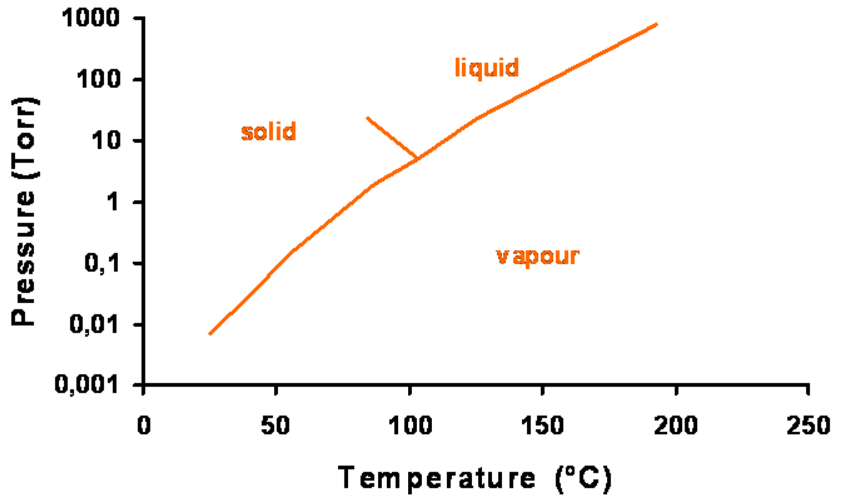
Michele Suman

Acrylamide removal: preamble

By virtue of its low molecular weight one can plausibly think that acrylamide can be removed from foods by exploiting its physicochemical properties

Combinations of pressure, temperature and time were chosen on the basis of literature data relevant to the physical properties of acrylamide as well as the results of preliminary trials.

Phase diagram of acrylamide



Adapted from Budavari et al., 1989

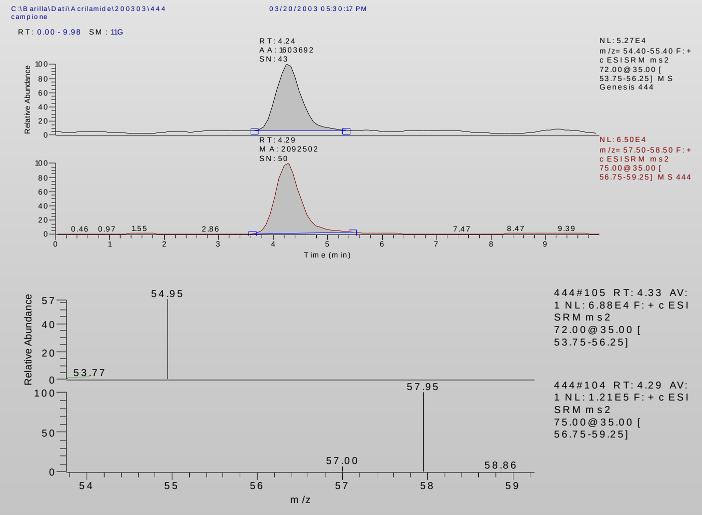
Michele Suman

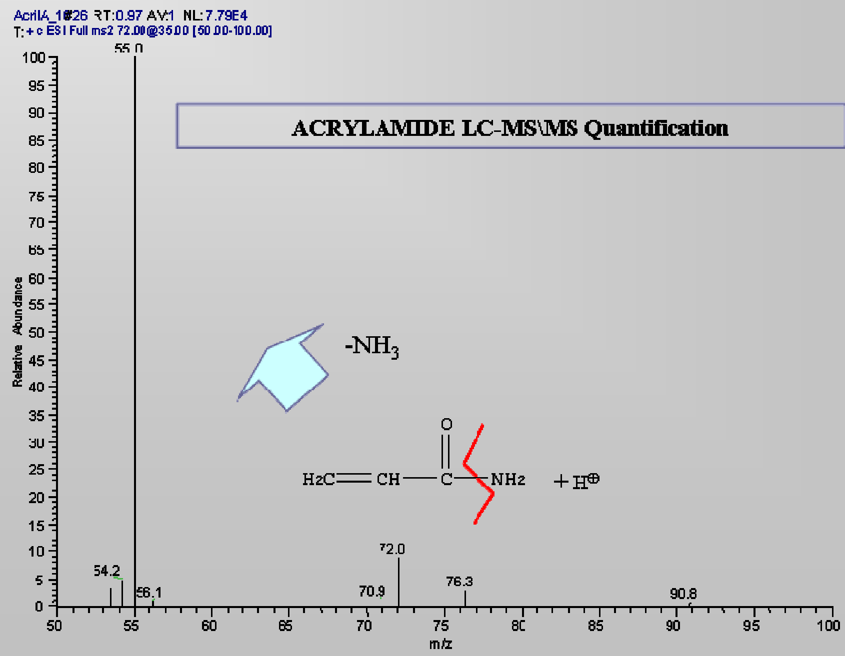
Samples preparation & analysis

Previously ground samples were subjected to the vacuum treatment.

Also, aliquots of the ground samples were hydrated before the vacuum treatment. Weighed Petri dishes containing approximately 5 g of sample were introduced in vacuum desiccators saturated with water vapor. Samples were left in the desiccators for the time (varying from 1 to 24 h) necessary to reach different water activities.

Acrylamide determination was carried out following an LC-MS\MS strategy by the adoption of acrylamide (d3 -acrylamide) as internal standard (water extraction\centrifugation\SPE clean up previously executed).





Samples treatment

•pure acrylamide
•cookies
•potato chips

were subjected to treatments.
After the treatments, samples were immediately removed from the oven, wrapped in aluminum foil and stored in desiccators until analyses were performed (within 24 h)

Experiments of acrylamide removal were made by using an apparatus consisting of an oven (5Pascal, VS-25 SC), connected to a rotary vacuum pump (BOC Edwards, E2M40) able to achieve a pressure of 0.133 Pa in few seconds when the oven was empty.

Source:
Nicoli, M. C., & Anese, M. (2006).
A process for removing acrylamide from foods.
Patent N°PD2006A000332.

Results – some examples

Average composition of commercial biscuits and potato chips, as reported in the respective labels.

Food component	Cookies (g/100 g)	Potato chips (g/100 g)
Protein	7	5
Carbohydrate	65	72
of which sucrose	25	3
Fat	21	12
Water	2	2

Acrylamide concentration of cookies and potato chips subjected to treatments at 6.67 Pa and 60 °C for increasing lengths of time.

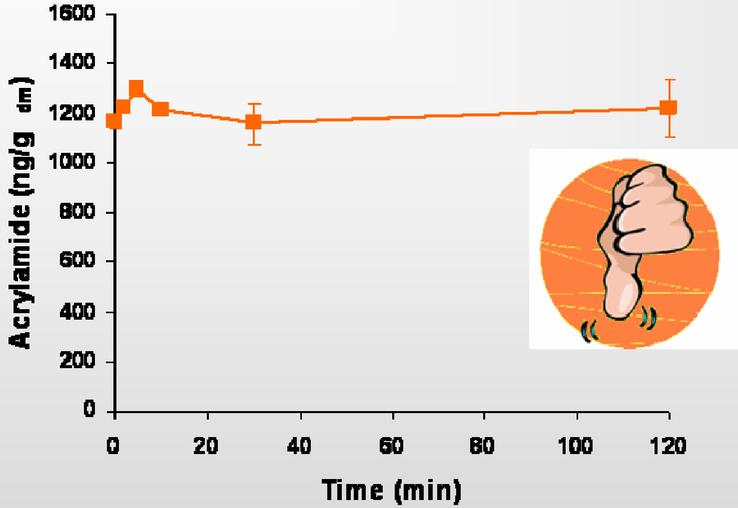
Food	Time (min)	Acrylamide (ng/g_{dm})
Cookies	0	1166 ± 30^a
	2	1230 ± 8^a
	10	1216 ± 29^a
	30	1158 ± 82^a
	120	1222 ± 113^a
Potato chips	0	366 ± 4^b
	5	323 ± 10^b
	15	340 ± 23^b
	30	335 ± 5^b
	60	345 ± 12^b

Different letters within each food category indicate significant difference ($P < 0.05$) by Tukey test.

Source:
Anese, M.; Suman, M.; Nicoli, M.C.
"Acrylamide removal from heated foods"
Food Chemistry 2010, Vol 119, pp. 791-794.

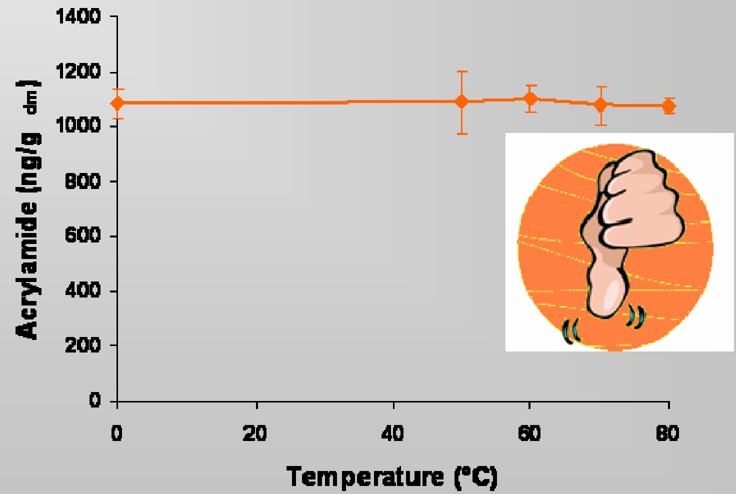
Potato chips

P=0.05 Torr; T=60°C



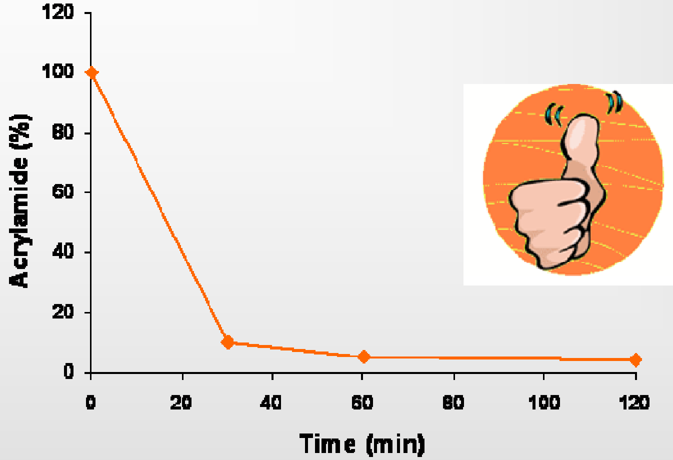
Potato chips

P=0.02 Torr; t=1 h



Pure acrylamide

P=0.05 Torr; T=60°C

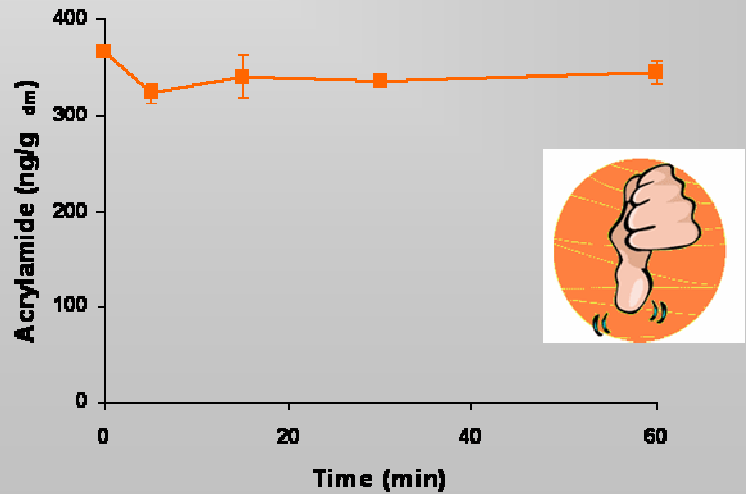


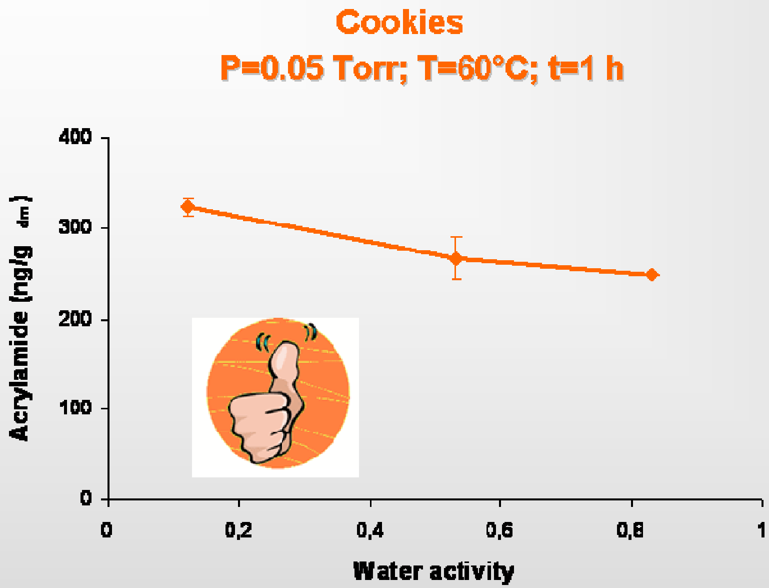
Why acrylamide can be quickly removed from the model systems but not so easily from the foods?

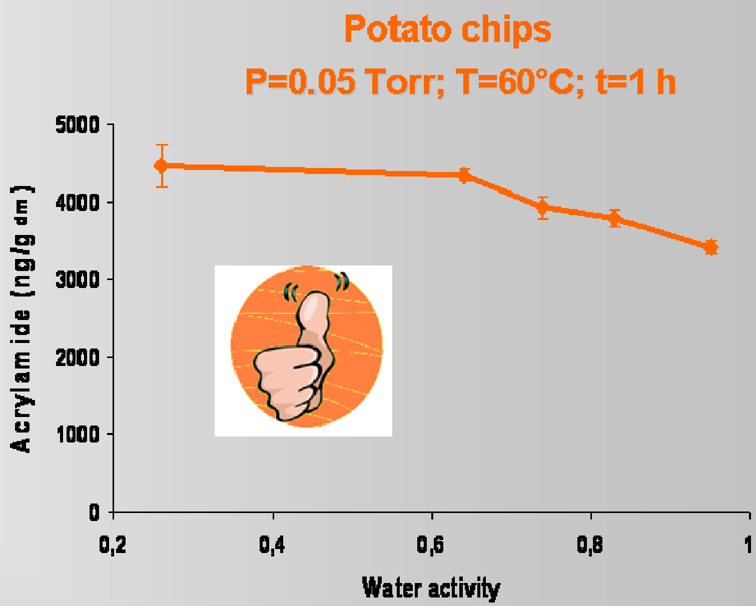
Possible role of water?

Cookies

P=0.05 Torr; T=60°C







Percentage of acrylamide removal from cookies and potato chips having different water activity values, subjected to treatment at 6.67 Pa and 60 °C for 1 h.

Food	Water activity	Acrylamide removed (%)
Cookies	0.12	12
	0.53	27
	0.83	32
Potato chips	0.26	0
	0.64	0
	0.74	4
	0.83	11
	0.95	20

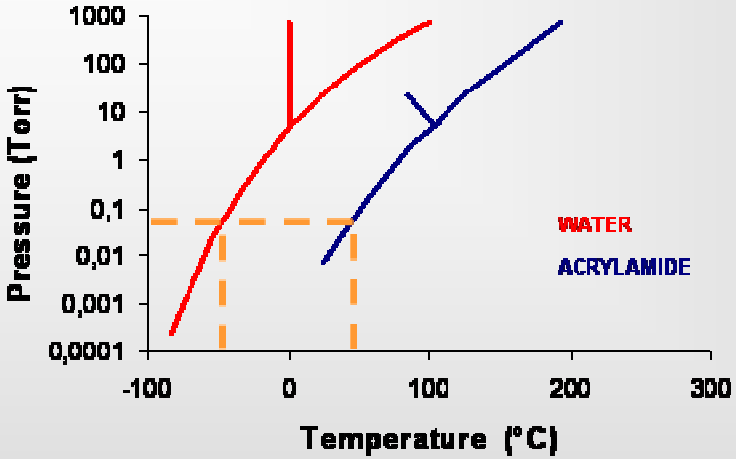
Acrylamide removal is favored by high water activity values

(volatile compounds entrapped into the low moisture matrix and released during moistening: structural collapse of the system)

- lipid film on the product surface that determines a physic impediment to acrylamide evaporation?

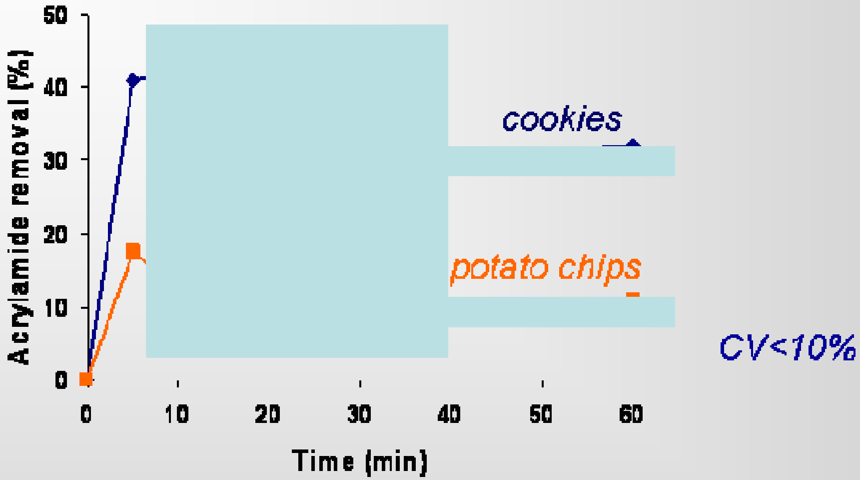
- modulated interactions between acrylamide and some endogenous polar components?

Water stripping effect



Acrylamide and water competition for polar sites

aw=0.83, P=0.05 Torr, T=60°C

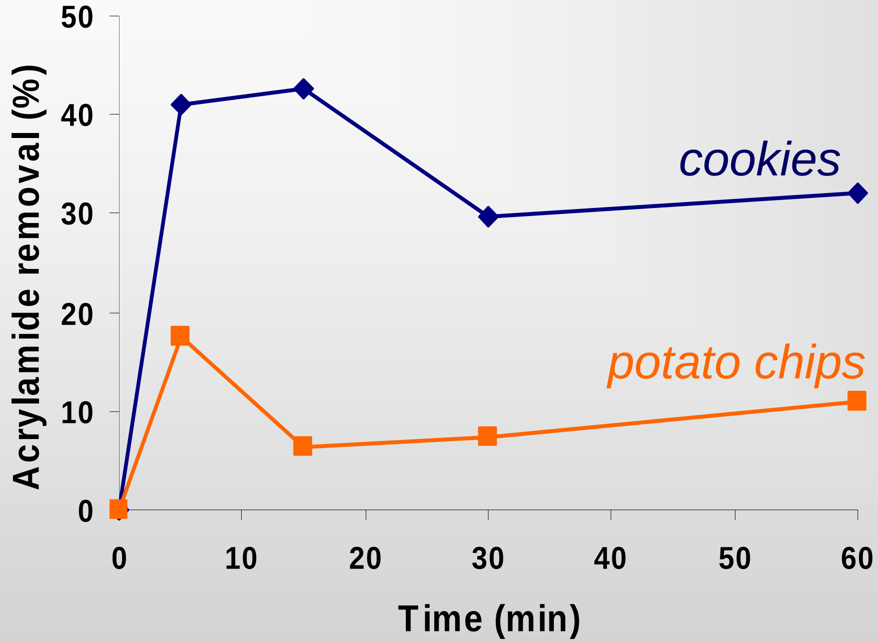


Only partial acrylamide removal

Higher acrylamide removal from cookies than from potato chips

- The superficial lipid film hurdles acrylamide removal
- Acrylamide-food components interactions

aw=0.83, P=0.05 Torr, T=60℃

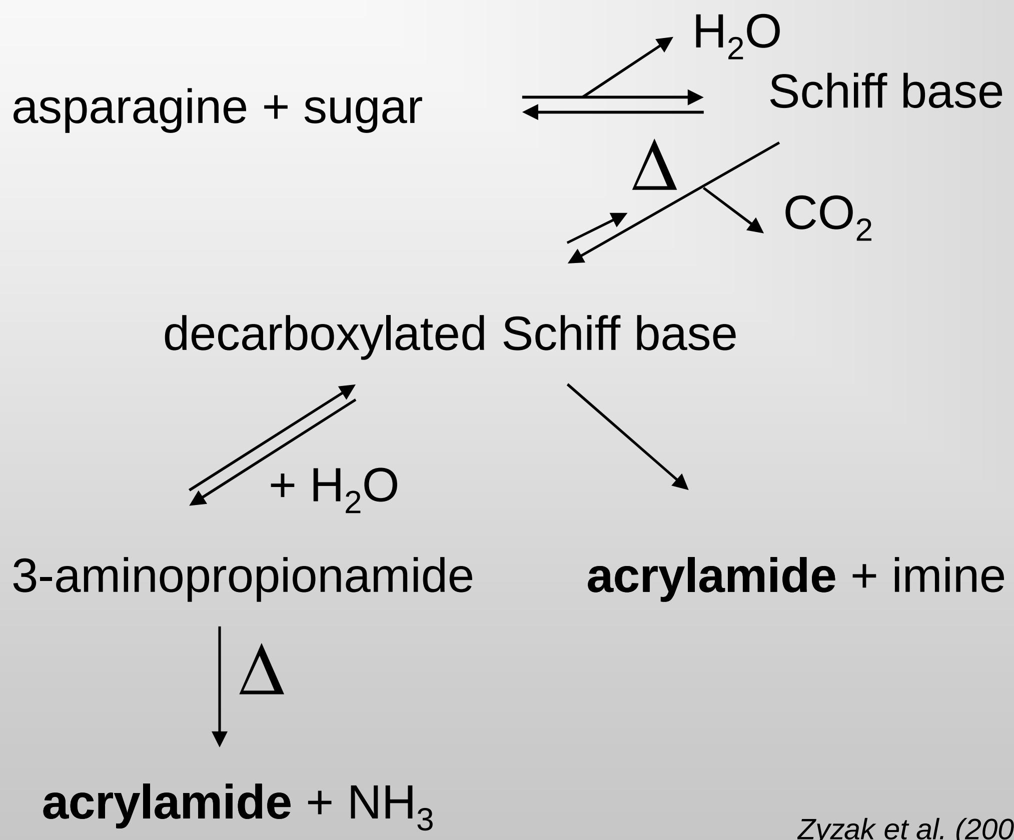


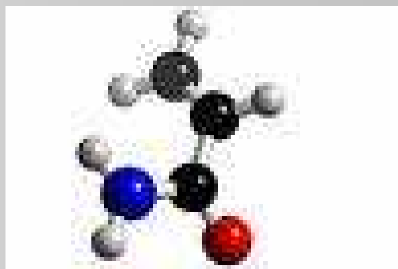
CV<10%

Higher acrylamide removal at short process times

➡ Possible formation of acrylamide?

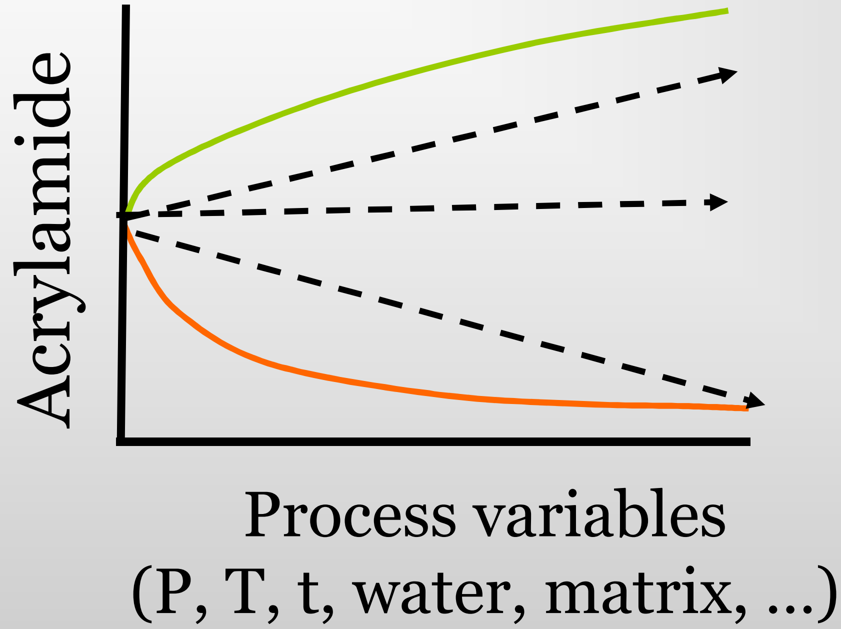
Possible mechanism for acrylamide formation during the low pressure treatment





Source:
Zyzak et al. (2003). Acrylamide formation mechanism in heated foods. Journal of Agricultural and Food Chemistry, 51, 4782–4787.

Acrylamide removal = f (food matrix; process conditions)



Ambivalent role of pressure ?

a) It affects acrylamide removal

b) It affects acrylamide formation

Source:
Anese, M.; Suman, M.; Nicoli, M.C.
" Technological Strategies to Reduce Acrylamide Levels in Heated Foods"
Food Engineering Reviews 2009, Vol-1(2), pp. 169-179.

Conclusions

- Treatment efficacy is dependent on products characteristics:
  - Cookies treated at 0.05 and 2 torr gave a final reduction of 43% and 33 %, respectively
  - Cereals biscuit\bar and Chips showed lower reduction percentages, between 17- 20 %

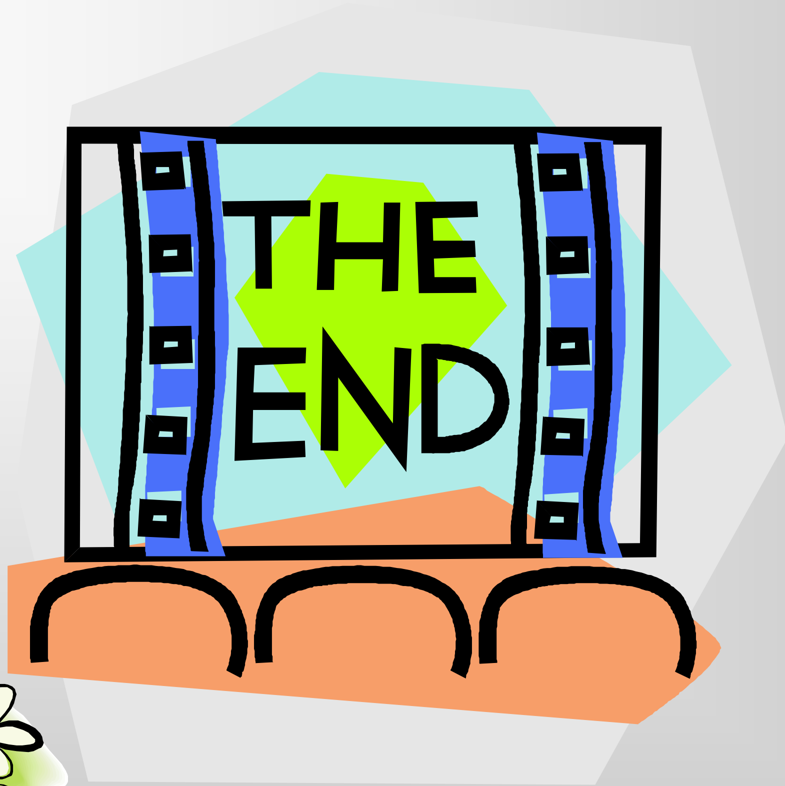
- Treatments at 0.05 or 2 torr have complete different impact in terms of scale-up costs & similar efficacy

- Preliminary sensory trials after the treatment trials showed that when the vacuum treatment was carried out for short-medium lengths of time the product's volatiles profile and flavor were not or only slightly affected.

- This technology would represent a promising and alternative strategy to mitigation interventions aimed at reducing acrylamide levels in foods.

Further areas of investigation

- Better understanding of "matrix effect" to maximize acrylamide stripping
- Better understanding of the role of each variable to maximize acrylamide removal while minimizing its formation by means of the vacuum process
- As acrylamide mainly forms in the surface, it is likely that (to be confirmed by ad hoc experiments) the vacuum treatment can be carried out on the whole product instead of on the ground one
- Evaluation of technology scale-up to verify its potential sustainability as a future solution for example in new production lines (e.g. hydration step after the ovens followed by a vacuum step where both acrylamide and the excess of water are removed…) and complete compatibility on the sensory properties of the treated foods



Acknowledgements:

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