Acrylamide Formation in Potato Products
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SUMMARY

Acrylamide, a substance classified as a potential carcinogen, occurs in heated starchy foods at concentrations many times in excess of levels permitted in drinking water. Early surveys indicated that levels of acrylamide in potato products such as French fries and potato crisps were the highest of the foodstuffs investigated. The present project addressed this issue by determining levels of acrylamide precursors (asparagine and reducing sugars) in raw potatoes and levels of acrylamide in (i) potato products from different storage regimes, (ii) spot-sampled potatoes purchased from a local supermarket, (iii) samples that received pre-treatments and were fried at different temperatures and (iv) French fries reheated in different ovens. A risk assessment of the estimated acrylamide intake from potato products for various cohorts of the Irish population was also conducted.

A significant accumulation of reducing sugars occurred in Lady Clare potatoes (a crisping variety) stored at 3°C as opposed to 8°C (Trial 1). Asparagine contents in potatoes at 3°C were relatively constant over the storage period but a gradual increase in levels occurred in samples stored at 8°C. However, the mean asparagine contents of potatoes stored at 3 or 8°C were not significantly different. In Lady Clare potato crisps, acrylamide content was highly correlated with glucose (0.84), fructose (0.83) and total reducing sugar (0.84) contents but not with content of asparagine (0.06) or other amino acids. The mean acrylamide content in Lady Clare potato crisps was 1781 µg/kg fresh weight.

Reducing sugar and asparagine contents in Maris Piper potatoes (a French fry variety) stored in a commercial storage facility were monitored on thirteen occasions between November 2004 and July 2005 (Trial 2). A small accumulation of reducing sugars occurred in the early stages but levels were constant over the later stages of storage. Asparagine levels were constant over the storage period and no trend was observed. The acrylamide content of the resulting French fries was highly correlated with glucose (0.92), fructose (0.90) and total reducing sugar (0.92) contents but not with asparagine.
content (0.06). A acrylamide content was inversely correlated with the lightness of French fries (as measured by Hunter L values) indicating that as the fries became darker, acrylamide formation increased. The mean acrylamide content in Maris Piper French fries was 313 \( \mu \)g/kg fresh weight.

Reducing sugar contents varied widely in spot samples of Rooster, Record and Oilean potatoes obtained on fourteen occasions between October 2004 and November 2005; asparagine contents were relatively stable (Trial 3). Fructose and glucose contents of the tubers were positively correlated with acrylamide content (0.78 and 0.81 respectively). Acrylamide concentrations in the French fries prepared from these ware potatoes were negatively correlated with Hunter L and b values (0.71 and -0.54 respectively) indicating that as French fries became darker, acrylamide content increased. The mean acrylamide contents for French fries prepared from Rooster, Record and Oilean potatoes were 1284, 1276 and 1188 \( \mu \)g/kg fresh weight respectively.

In Trial 4, a combination of soaking in dilute citric acid solution (2% w/v) and blanching in oil produced the lowest level of reducing sugars in Rooster potatoes prior to frying and also the lowest level of acrylamide in the fried samples. Frying temperature had a marked effect on acrylamide content of the French fries with values of 243 (150°C) to 401 (170°C) to 761 (190°C) \( \mu \)g/kg fresh weight. Acid-soaking of samples resulted in lighter-coloured French fries as compared to water-soaked samples (55.3 vs 51.9 L) while increasing the frying temperature resulted in darker fries (62.1 vs 54.7 vs 44.0 L). Puncture force values were influenced by acid pre-treatment (lower force) and oil blanching (higher force) but not by frying temperature.

Re-heating method [none, microwave (MW) or convection oven (CO)] did not have a significant effect on acrylamide content of Maris Piper or Rooster potatoes. Both microwaved and convection oven-reheated samples were significantly darker than non-reheated samples while puncture force values for microwaved samples were lower than for convection heated or non-reheated samples (Trial 5).
A Monte Carlo risk assessment model indicated that human exposure to acrylamide through intake of French fries was 0.32µg/kg bw/day for Irish males and 0.26 µg/kg bw/day for Irish females. This is below the WHO recommended daily intake limit set at 1µg/kg bw/day but it does represent 26 - 32% of the limit for males and females. The model also indicated that the level of exposure from potato crisps was significantly less than that estimated for French fries (0.052 and 0.064µg/kg bw/day for males and females respectively). The level of acrylamide in French fries made in the home is likely to be high with a mean simulated value of 1073µg/kg. Simulated human exposure to acrylamide from one portion of homemade French fries is also high (0.94 and 0.69µg/kg bw/portion for males and females respectively).

INTRODUCTION

Acrylamide is a substance classified as a potential carcinogen and it occurs in heated starchy foods at concentrations many times above levels permitted in drinking water. Formation of acrylamide occurs via the reaction of reducing sugars such as fructose or glucose with the amino acid asparagine at high temperatures and low water activity (Stadler et al., 2002). Since potatoes may contain relatively high levels of both asparagine and reducing sugars, this is the most likely route to acrylamide formation in French fries and potato crisps. Therefore, factors which affect the concentration of precursors such as variety (Hebeisen et al., 2005), storage temperature and time (Amrein et al., 2004) and level of nitrogen and phosphorous in the soil (Heuser et al., 2005) affect acrylamide formation in the cooked product. For example, storage of tubers at temperatures of 3-5°C promotes acrylamide formation by causing an accumulation of reducing sugars (Noti et al., 2003). This is known as ‘cold-sweetening’ and can be reversed by reconditioning the tubers for two to three weeks prior to frying (De Wilde et al., 2005). The chemical reaction leading to acrylamide formation is also responsible for the development of fry colour in many French fries and potato crisps and correlations between instrumental colour parameters and levels of acrylamide in cooked potato products have
been demonstrated (Pedreschi et al., 2006). Both the temperature and duration of heating have a significant influence on acrylamide levels in French fries and crisps. Rydberg et al. (2003) found that acrylamide levels increased in French fries as the oven temperature increased from 100 to 220°C and Pedreschi et al. (2004) reported similar increases as the frying temperature rose from 150 to 190°C. An inverse relationship between acrylamide and moisture content of a foodstuff has been reported (Elmore et al., 2005). Soaking or blanching prior to frying can reduce acrylamide formation (Grob et al., 2003). The current project therefore addressed:

- Current developments affecting acrylamide formation in cooked potato products
- Determination of levels of acrylamide precursors (reducing sugars and asparagine) in commercial Irish potato cultivars stored under different temperature conditions for up to 10 months
- Determination of levels of acrylamide precursors in ware potatoes spot sampled from Irish supermarkets over a 10 month period
- Determination of levels of acrylamide in selected fried potato from the trials outlined above
- Risk assessment (based on Irish consumption data for potato products) of the estimated intake of acrylamide in various cohorts of the Irish population.

MATERIALS AND METHODS

Preparation of French fries and potato crisps
Tubers were peeled and placed in a 0.25% sodium metabisulphite solution to prevent enzymatic browning. For the production of French fries, potatoes were then chipped using a manual French fry press and the chipped potatoes
placed in the metabisulphite solution for 5 minutes. Samples for crisp production were sliced to a thickness of 1.4 - 1.5mm using a mechanical slicer and placed in the metabisulfite solution for 1 minute. French fry samples were cooked in 220g lots at a temperature of 190°C in sunflower oil for 6 minutes using a domestic deep fat fryer. Potato crisps were fried in 150g lots at 185°C for 3 minutes. After frying, excess oil was removed from the surface of the samples and they were vacuum-packed and stored at -20°C for subsequent acrylamide analysis.

Potatoes for crisp production (Trial 1)

Samples of Lady Clare potatoes were obtained locally and stored at 4 or 8°C from September 2004 to July 2005. The experimental design was 1 variety x 2 treatments (conditioned at 8°C vs storage at 4°C) x 13 test periods x 2 replicates. Two supplementary trials were also conducted. Supplementary (a): Samples of Lady Rosetta and Premier potatoes were obtained directly from a potato grower and tested over a 2 month period from August to mid-September 2005. Supplementary (b) was identical to Trial 1 except that samples were stored for a short period (mid September to end-November 2005). Unfried samples were tested for colour and content of reducing sugars, asparagine and dry matter. Fried samples were tested for acrylamide content (excluding supplementary trials) and colour.

Potatoes for French fry production (Trial 2)

Samples of Maris Piper potatoes were stored in a commercial potato store at 8°C from September 2004 to July 2005. The experimental design was 1 variety x 15 test periods x 3 replicates. Supplementary (c): Maris Piper potatoes imported weekly from the UK and supplied by Sam Dennigan & Co. Ltd. were tested from August to mid-September 2005. Supplementary (d) was identical to the initial Trial 2 except that samples were stored from mid-September to end-November 2005. Un-fried samples were tested for reducing sugars, asparagine, dry matter content and colour. Fried samples were tested for acrylamide content (excluding supplementary trials) and colour.
Potatoes from ware trade (Trial 3)

Rooster, Record and Oilean varieties were sampled monthly in a supermarket in the period from September 2004 to July 2005. The design was 3 varieties x 14 testing dates x 2 duplicates. Two supplementary trials were also conducted. Supplementary (e): Queens and Homeguard potatoes supplied by Sam D'ennigan & Co. Ltd. were tested from August to mid-September 2005. Supplementary (f) was identical to Trial 2 except potatoes were sampled from mid-September to end-November 2005. Unfried samples were tested for colour and content of reducing sugars, asparagine and dry matter. Fried samples were tested for acrylamide content (excluding supplementary trials) and colour.

Frying Tests (Trials 4 and 5)

**Trial 4**: The effect of pre-treatments and frying temperatures on the quality and the acrylamide content of French fried Rooster potatoes was investigated. The experimental design was 2 soaking methods (water vs citric acid, 1 hr, 15°C) x 2 blanching methods (water (3.5 min, 85°C) vs sunflower oil (45 sec, 150°C)) x 3 frying temperatures (150, 170, 190°C for 6 min). Un-fried samples of the pre-treated/blanched chipped potatoes were tested for reducing sugars, asparagine, dry matter contents and colour. The fried samples were tested for acrylamide content, colour and texture (by texture profile analysis, TPA).

**Trial 5**: The effect of post-fry reheating on the acrylamide content and quality of French fries prepared from Rooster and Maris Piper potatoes was investigated. Samples were chipped, fried (170°C for 6 min), divided into three lots and blast frozen (-35°C). Lot 1 was thawed while lots 2 and 3 were re-heated in microwave (1000W for 3 min) and convection ovens (175°C for 7 min). The experimental design was 2 varieties x 3 finishing treatments (none, microwave and oven) x 3 replicates. The fried samples were tested for acrylamide content, colour and texture (TPA).
Methods of analysis

Ethanolic extracts of sugars and amino acids were prepared from the potato samples using the method described by Brunton et al. (2007a). Dry matter content of the tubers was measured prior to frying as described by Fagan, Gormley and Uí Mhuircheartaigh (2003). Colour was measured in the unfried and fried samples using a Hunter Lab colorimeter as described by Brunton et al. (2007a). Glucose, fructose and amino acid contents of the ethanolic extracts were measured by gas chromatography (GC) and high performance liquid chromatography (HPLC) as described by Murray et al. (2007) and Brunton et al. (2007b) respectively. Acrylamide contents of French fries and potato crisps were measured by liquid chromatography-mass spectrometry (LC-MS) as described by Minihan et al. (2005). Texture profile analysis (TPA) of French fried samples was measured using a TAXT 2i (Stable Micro Systems) system (Bourne, 1978).

Development of risk assessment model

Data for the various stages in the crisp and chip making processes were collated from the scientific literature and values also taken from the current study. These were modelled regarding their impact on reducing sugar levels and consequently on acrylamide formation using a Monte Carlo simulation model. Data for the consumption of fried potato products in Ireland was taken from the Irish Universities Nutrition Alliance survey (2001). Flow diagrams of the fried potato chip and crisp processes modelled in this study are given in appendices 1 and 2.

Statistical analysis

Data were analysed by one-way analysis of variance using Gen-Stat (Version 3.2, VSN International Ltd., Hemel Hempstead, U.K.). Pearson correlation coefficients were calculated using SAS (Version 6.12, SAS Institute Inc., Cary, NC, USA).
RESULTS AND DISCUSSION

Potatoes for crisp production (Trial 1)

Lady Clare potatoes stored from November 2004 to July 2005 at 3°C had higher mean glucose (GLU) and fructose (FRU) contents than those stored at 8°C (430.2 vs 110.3 µgGLU/g fresh weight, 399.9 vs. 110.7 µgFRU/g fresh weight). Potatoes stored at 3°C showed a steady increase (115 to 1237 µg/g fresh weight) in reducing sugar contents over the storage period (Figure 1). Such accumulation at low temperatures is referred to as ‘cold sweetening’ (Copp et al., 2000). A number of other studies have also reported that storage of potatoes at low temperatures represents a significant risk for acrylamide formation in French fries and potato crisps (De Wilde et al., 2005).

Asparagine contents in potatoes stored at 3°C were relatively constant but a gradual increase in asparagine levels occurred in potatoes stored at 8°C (Figure 1).

Figure 1. The effect of storage at 3°C on glucose, fructose and asparagine levels in Lady Clare potato tubers.

A number of other studies have also reported that storage of potatoes at low temperatures represents a significant risk for acrylamide formation in French fries and potato crisps (De Wilde et al., 2005).
2). The reason for the increase at 8°C is unclear and Amrein et al. (2004) reported that longterm storage of potatoes had little effect on levels of free amino acids. Acrylamide content was highly correlated with glucose (0.84), fructose (0.83) and total reducing sugar (0.84) contents (Figure 3) but not...
with asparagine content (0.06) or with that of other amino acids. The equation of the line (12 data points) predicting the acrylamide content of crisps from reducing sugar content of raw Lady Clare potatoes was \( y = 2.274x + 271.92 \) (\( R^2 = 0.697 \)) with a standard error of prediction of 708 (Figure 3).

**Potatoes for French fry production (Trial 2)**

During the early stages of storage, significant increases in reducing sugar levels occurred in Maris Piper potatoes stored from November 2004 to July 2005 in a commercial potato storage facility at 8°C. Levels were relatively constant during the later stages of storage (Figure 4). Some authors have reported that storage at this temperature results in relatively constant levels of reducing sugars (De Wilde et al., 2005) and others have reported a significant accumulation at temperatures up to 12°C. Asparagine levels were relatively constant over the storage period and no trend was noted (Figure 4). The acrylamide content of fries produced from these potatoes was highly

**Figure 4.** The effect of storage at 3°C on glucose, fructose and asparagine levels in Maris Piper potato tubers.

constant over the storage period and no trend was noted (Figure 4). The acrylamide content of fries produced from these potatoes was highly
Figure 5. Relationship between total reducing sugar and acrylamide levels in French fries prepared from Maris Piper potatoes.

Figure 6. The relationship between the Hunter L value and the acrylamide content of French fries prepared from Maris Piper potatoes.
correlated with glucose (0.92), fructose (0.90) and total reducing sugar (Figure 5, 0.92) contents but not with content of asparagine (0.06) or other amino acids. The equation of the line (12 data points) relating acrylamide and reducing sugar contents in the un-fried Maris Piper potatoes was $y = 0.125x + 109.83$ ($R^2 = 0.832$) with a standard error of prediction of 75.8. Fry colour (Hunter L) became darker as acrylamide concentration increased (-0.87, Figure 6).

Potatoes for ware trade (Trial 3)

A wide variation in levels of total reducing sugars (sum of glucose and fructose levels) from September 2004 to July 2005 was observed (ranges were 152-12286, 301-8812 and 279-7881 µg/g fresh weight) for Rooster, Record and Oilean potatoes respectively (Figures 7-9). The potatoes in this study were purchased from a supermarket and thus their storage history was

![Figure 7](image_url)

*Figure 7.* Concentrations of glucose, fructose and asparagine in Rooster potatoes purchased between September 2004 and July 2005.
unknown. Asparagine contents were relatively constant for the three varieties over the test period and no trend in asparagine levels was noted (Figures 7-9). However, increases in asparagine contents were apparent at certain collection

Figure 8. Concentrations of fructose, glucose and asparagine in Record potatoes purchased between September 2004 and July 2005.

Figure 9. Concentrations of fructose, glucose and asparagine in Oilean potatoes purchased between October 2004 and July 2005.
Increases in free amino acid contents, including asparagine, occur as a result of an increase in protein degradation brought about by sprout formation (Brierley et al., 1997).

A positive, linear correlation between total reducing sugars and acrylamide content was found for French fries made from the three potato varieties \[ y = 0.1799x + 547.51, \quad R^2 = 0.6758 \; \text{Figure 10} \] but no significant correlation was
found between asparagine in the potatoes and acrylamide levels in the French fries. Acrylamide concentrations in the French fries were correlated with Hunter L (-0.71) and b values (-0.54) indicating that as French fries became darker acrylamide content increased. This relationship is described by the equation $y = -43.01x + 3652.4$ ($R^2 = 0.621$) and indicates that L values may be reliable indicators of acrylamide content in potato products.

Frying tests (Trials 4 and 5)

Trial 4 investigated the effect of different pre-treatments on the concentrations of acrylamide precursors in raw potatoes and the influence of frying temperature on acrylamide content in French fried Rooster potatoes. Figure 12 illustrates reducing sugar levels in raw, chipped potatoes following different combinations of soaking (acid or water) and blanching (water or oil) prior to frying. The acid soak resulted in a lower level of reducing sugars than the water soak (2819 vs 3391 µg/g fresh weight) while the oil blanch produced lower levels of reducing sugars relative to the water blanch (2674 vs 3109 µg/g fresh weight). Combining soaking in citric acid with blanching oil gave the lowest level of reducing sugars prior to frying (Figure 12, 2051 µg/g fresh weight). This combination also gave the lowest level of asparagine in the raw,
chipped potatoes (Figure 13, effect not significant) and the lowest level of acrylamide in the fried samples (Figure 14). Frying temperature had a marked effect on acrylamide content with values increasing from 243 to 401 to 761 µg/kg fresh weight at 150, 170 and 190 °C respectively (Figure 14). The effect of pre-treatments and frying temperature on the quality of French fries

**Figure 13.** Effect of pre-treatments on average asparagine contents in chipped Rooster potatoes.

**Figure 14.** The effect of cooking temperature and pre-treatments on acrylamide contents in French fries made from Rooster potatoes.
was also examined. Acid-soaking of samples resulted in a lighter coloured French fry compared to water-soaking (55.3 vs 51.9 Hunter L) while increasing the frying temperature resulted in darker fries (62.1 vs 54.7 vs 44.0 Hunter L). Puncture force values were influenced by acid pre-treatment (lower force), oil blanching (higher force) but not by frying temperature.

Trial 5 examined the effect of microwave (MW) and convection oven (CO) reheating on levels of acrylamide and quality of French fries made from Maris Piper and Rooster potatoes. Reheating method had no effect on acrylamide content for either cultivar (Figure 15). Both MW and CO reheated samples were darker than non-reheated (Figure 16). Puncture force values for MW reheated samples were lower than for CO or non-reheated samples (Figure 17).

**Figure 15.** The effect of reheating method on acrylamide content in French fries made from Rooster and Maris Piper potatoes.
Two risk assessment models were developed during this study. One focused on the formation of acrylamide during French fry production and the other...
related to the production of crisps and the impact of the crisp production process on acrylamide formation. The simulated mean level of acrylamide formation was estimated at 317µg/kg for French fries and 720µg/kg for potato crisps. The models indicated that human exposure to acrylamide through intake of French fries may be as high as 0.3 µg/kg bw/day for males and 0.26µg/kg bw/day for females (Figure 18). This is below the WHO recommended daily limit of 1µg/kg bw/day but it does represent 26-32% of the recommended limit for males and females. The level of exposure from potato crisps was less than that estimated for French fries (0.052µg/kg bw/day and 0.064µg/kg bw/day for males and females respectively; Figure 19). The level of acrylamide in French fries made in the home is likely to be high with a mean simulated level of 1073µg/kg. The level of reducing sugars was the most important parameter identified in the sensitivity analysis in both the French fry (correlation coefficients 0.54 and 0.52 for glucose and fructose respectively) and crisp models (correlation coefficients 0.58 and 0.57 for glucose and fructose respectively) and highlights that the level of reducing sugars
sugars in the raw tubers is a strong determinant for acrylamide formation in fried potatoes.

The results of this risk model could impact on policy-making decisions, particularly in relation to the potato industry. For example, a policy governing the use of particular cultivars with low reducing sugar levels in the French fry and crisp trade could be implemented. Alternatively, a strict policy on the inclusion of particular process stages (e.g., blanching and soaking) for cultivars with known high sugar levels could be introduced to help reduce the formation of acrylamide in fried potato products. It is accepted that the costs associated with the implementation of a new process step (e.g., blanching, soaking) may be high and would impose an additional cost on the chip and crisp industry. However, the monetary cost associated with any process change in this study has not been quantified.

Figure 19. Acrylamide daily exposure for males and females resulting from the consumption of fried potato crisps in Ireland
CONCLUSIONS

● Storage of Lady Clare potatoes (crisp variety) at 3°C resulted in a significant accumulation of reducing sugars as compared to samples stored at 8°C. This resulted in higher concentrations of acrylamide in potato crisps made from potatoes stored at 3°C. Asparagine concentrations were relatively constant at 3°C but increased at 8°C.

● Reducing sugar concentrations increased slightly in the initial stages of storage but leveled off thereafter in Maris Piper potatoes (French fry variety) stored at 8°C in a commercial potato storage facility.

● Acrylamide content of French fries made from Maris Piper was positively correlated with reducing sugar content of the un-fried potatoes and negatively correlated with lightness of fry colour.

● Reducing sugar contents in spot sampled ware potatoes purchased in supermarkets varied widely during the study. In comparison, asparagine contents were relatively stable. However, significant increases did occur at some sampling dates.

● Reducing sugar content and fry colour may serve as reliable predictors of acrylamide content in potato crisps and French fries.

● A combination of soaking in a solution of citric acid and blanching in oil prior to frying reduced acrylamide content in French fries made from Rooster potatoes as did frying at lower temperatures.

● Reheating French fries made from Maris Piper and Rooster potatoes did not influence acrylamide content.

● The mean intake of acrylamide from French fries determined using a Monte Carlo simulation model was 0.32µg/kg bw/day for males and 0.26µg/kg bw/day for females. Mean intakes were lower for potato crisps as a result of lower consumption levels of this item in the Irish diet. Daily
intakes of acrylamide from potato products accounted for up to 25% of the WHO limit of 1µg/kg bw/day.

RECOMMENDATIONS TO INDUSTRY

● Use potatoes that have been stored at 8°C for fry and crisp production. The current (and other) studies indicate that conditioning at this temperature minimises the content of reducing sugars in tubers and hence the acrylamide content of the chips on frying. This storage temperature also limits sprout formation and moisture loss. In practice this means that when potatoes are stored for long periods, storage temperatures should be closely monitored and controlled. This practice should be continued up to the point of sale.

● Recondition potatoes prior to sale if they have been stored at low temperatures for a significant period (up to 2 weeks). This involves storing the tubers for a period of not less than 3 weeks at 15°C. This reduces the levels of reducing sugars in the tubers to acceptable levels.

● Use varieties that are well recognised by the trade for French fry and crisp production and ensure that the potatoes have been stored (conditioned) at 8°C. Select potato varieties with a low natural propensity to accumulate reducing sugars.

● Blanch raw chips in oil at 150°C for 40 seconds. This pre-treatment reduces the levels of acrylamide precursors (reducing sugars and asparagine) in the chips and acrylamide in the fully-fried product.

● Fry to a light colour at a lower temperature i.e. 150-160°C rather than 170-180°C. The current (and other) studies have shown that this reduces acrylamide formation in French fries.
ACKNOWLEDGEMENTS

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LIST OF PUBLICATIONS FROM THIS PROJECT


REFERENCES


Appendix 1
Flow diagram of French fry production. Stages in oval indicate those which may significantly impact on acrylamide formation; rectangle indicates negligible impact.
Appendix 2.
Flow diagram of fried potato crisp production. Stages in oval indicate those which may significantly impact on acrylamide formation; rectangle indicates negligible impact.
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