Studies on acrylamide levels in roasting, storage and brewing of coffee

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The content of acrylamide in coffee reaches a peak early in the roasting process, reflecting occurrence of both formation and destruction of acrylamide during roasting. Levels of acrylamide in the fully roasted product are a small fraction of the peak reached earlier. Glucose and moisture in green coffee do not show a significant correlation with acrylamide in roasted coffee. Pre-roasting levels of asparagine show a correlation only in Arabica coffee. The main factors affecting the level of acrylamide in roasted coffee appear to be the Arabica/Robusta ratio, with Robusta giving higher levels; time and degree of roast, with both shorter and lighter roasting at the edges of the normal roasting range giving higher levels; storage condition and time, with clear reduction at ambient storage. This storage reduction of acrylamide followed second order reaction kinetics with an activation energy of 73 KJ/mole. The acrylamide in roasted coffee is largely extracted into the brew and stable within usual time of consumption. As these four main factors also substantially affect the sensorial characteristics of the brew, and as modifications of the process have to comply with the consumer-accepted boundaries of taste profiles, only small effects on the acrylamide level are expected to be achievable.

Keywords: Acrylamide / Brew / Coffee / Roast / Storage

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1 Introduction

Since Swedish researchers reported in April 2002 the occurrence of acrylamide in heated foods (Swedish National Food Administration, Information about Acrylamide in Food, http://www.slv.se/engdefault.asp), extensive efforts were undertaken by the different stakeholders towards mechanistic elucidation and prevention. The presence of acrylamide was confirmed in a whole range of foods and drinks, which were heated above 120°C during their processing or preparation. Acrylamide was detected in fried potatoes, bread, cookies, potato and cereal based snacks, coffee and other products. The formation of acrylamide appeared to be dependent on the composition of the food and the imposed thermal conditions. The mechanism of acrylamide formation was reported to involve reducing sugars and amino acids, predominantly asparagine [1–4].

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Abbreviation: LRU, light reflectance units

Several analytical procedures to measure acrylamide specifically in roasted coffee have been published [5–9]. The preferred methods appear now to use MS/MS. Within-lab variation coefficients of 5.1% [5] and 9.2% [7] were reported for acrylamide in the coffee matrix. Owen *et al*. [10] reported that Food Analysis Performance Assessment Scheme (FAPAS) proficiency testing yielded for a roasted coffee with 312 μg/kg acrylamide a range from 193–431 μg/kg ($z = -2$ to $z = 2$).

The European coffee industry started a comprehensive study on the fate of acrylamide during processing, storage, and brewing of coffee. The aim of the study was to investigate the influence of raw materials and processing parameters up to the brewing for their potential effects on acrylamide levels and to identify possible ways of reducing its content. In the meantime, other studies on the parts of this chain from roasting until brewing were published. During roasting of coffee the acrylamide level was found to pass through a peak value, with the level in the final roasted product being only a fraction of the peak values observed earlier during roasting [11, 12]. The same observation was made in the present study. In addition, further studies reported on effects of roasting and degree of roast [8, 9, 13].

However, their experimentally imposed thermal conditions were quite different from the actual commercial scale coffee-roasting practice. Moreover, two studies reported about instability of acrylamide during storage of roasted coffee [6, 14]. Population exposure estimates including coffee were published for a series of Western countries [8, 15–20].

The aim of the present study was to investigate acrylamide formation and its fate throughout the complete range from roasting of green coffee to brewing of the beverage, with the objective to identify possible ways for acrylamide reduction.

2 Materials and methods

2.1 Green coffees

The roasting experiments were performed with the three major types of green coffee: Arabica coffee (*Coffea arabica*) from Brazil (dry processed) and from Colombia (wet processed) and Robusta coffee (*Coffea canephora robusta*) from Vietnam (dry processed). These three cover the major types of internationally traded green coffee (dry, respectively, wet processed Arabica, and dry processed Robusta). The three countries of origin were in recent years the three largest exporters of green coffee and supplied together more than half of the international export.

In an additional check on representativity of the results obtained with these three coffees, a number of random samples of green coffee were taken and roasted, 5 Robusta's from, respectively, Cameroon (2), Cote d'Ivoire, Indonesia and Uganda, and 15 Arabica's from, respectively, Brazil (2), Colombia (2), Costa Rica, Ethiopia (2), Guatemala, Honduras, India, Kenya, Mexico, Peru, Papua New Guinea and El Salvador.

To investigate a possible effect of the initial moisture content, green coffees were either pre-dried in an air stream of 40°C to 7% moisture, or wetted by spraying water to 14% moisture.

2.2 Roasting equipment

The roasting experiments were executed in the following three roasters: Roaster A (Probat RT 3SY/Emmerich/Germany), a fluidized bed roaster with mechanical supported movement of the coffee beans, with heat transfer predominantly by convection and a batch size of 2 kg green coffee; Roaster B (Neuhaus Neotec RFB6/Reinbek/Germany), a rotating fluidized bed roaster with heat transfer by convection and a batch size of 2 kg green coffee and Roaster C (Probat PRG500/Emmerich/Germany), a drum roaster with heat transfer mainly by conductivity and a batch size of 0.5 kg green coffee.

The process conditions in the roasting experiments were varied beyond the normal commercial range, *i.e.* from under-roasted to over-roasted. The roast degree, as measured by light reflectance using a Lange colorimeter, was varied from very light roast, 100–110 LRU (Lange reflectance units) corresponding to 4–6% dry-weight-loss, to very dark roast, 40–50 LRU and 9–11% dry-weight-loss. The roasting time was varied from very fast roast (1.5 min) to very slow roast (16 min). Before the execution of the storage trials, the samples of roasted coffee were analyzed for acrylamide within 1 week or stored at –18°C until analysis.

To ensure that representative results were obtained with these three roasters, 51 roasted coffee samples were drawn from different types of commercial scale roasting equipment operated by 17 different European partners in this study.

The storage trials for roasted coffee were done with vacuum-packed roast and ground coffee produced 2 weeks before and stored at 4°C until onset of the storage study, that was carried out at four different temperatures: –18°C, +4°C, room temperature and at +37°C. Samples taken under the standardized storage conditions were analyzed for acrylamide on the next day.

Brewing experiments were carried out using several brewing machines widely used in Europe. The tested brewing strengths ranged from 46 to 146 g coffee/L water.

2.3 Analyses

The degree of roast was measured both by light reflectance (LRU, measured with colorimeter of Hach-Lange/Düsseldorf/Germany) and by measurement of the dry-weight-loss. The acrylamide analyses were performed by the lab of Eurofins scientific GmbH, Hamburg, using LC-MS/MS with deuterium-labeled acrylamide as an internal standard. For coffee with a content of 282 µg/kg acrylamide, the method is reported to have SD of 25.9 µg/kg (= 9%). [7] The analysis of asparagine and reducing sugars was performed by the Institute of Plant Biology, Technical University Braunschweig, using the OPA method [21] for asparagine and a DIONEX® BIO-LC HPAEC-PAD for the (reducing) sugars.

3 Results and discussion

The general characteristics and in particular the sensorial characteristics of roasted coffee largely depend on the blend

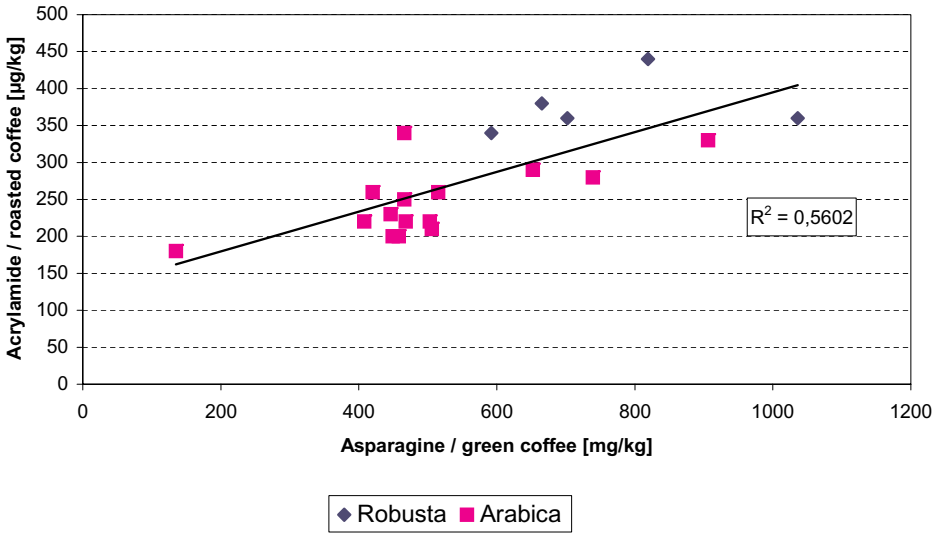

Figure 1. Asparagine levels in green coffees versus acrylamide level in corresponding roasted coffee (roaster B, medium roast time and medium degree of roast).

Table 1. Effect of Arabica versus Robusta coffees on acrylamide levels (roasted in 2.5 min to a medium roast)

	Number of samples	Acrylamide mean (µg/kg)	Standard deviation	Variation (%)
Robusta	6	378	32	8
Arabica	17	251	45	18

(Arabica/Robusta), on the amount of heat effectively transferred into the coffee beans during roasting, and on the roasting time. Arabica and Robusta coffee are botanically different species and they are distinctly different in sensorial properties. The amount of transferred heat is largely dependent on the temperature of the hot air used to roast, on the applied coffee/air ratio and on the achieved heat transfer rate. A larger amount of transferred heat results in a darker roast. The roasting experiments were designed to cover the three main factors, Arabica/Robusta, roasting time, and degree of roast.

Roasting of the 23 different green coffees in roaster B for 2.5 min to a medium roast (80 LRU) revealed a difference between the two botanical different species, Arabica and Robusta coffee, with Robusta producing on average a higher acrylamide level (see Table 1). No difference appeared for the two different ways of processing (dry *versus* wet processing) Arabica coffee cherries to green coffee beans (data not shown).

The 20 additional green coffees (5 Robusta and 15 Arabica) were also analyzed for aspartic acid, glutamic acid, asparagine, glucose, fructose and sucrose. A weak positive correlation ($R^2 = 0.56$) for the asparagine level in green coffees and the acrylamide in the corresponding roasted coffee is apparent from Fig. 1. This applies to the Arabica coffees as well as to the combined Arabica plus Robusta coffees. Taking the 5 Robusta's samples separately, a correlation is not evident. In addition, glucose levels in the green coffees did not show a clear correlation with the acrylamide in the roasted coffees (data not shown). It is very well possible that correlations between green coffee components and acrylamide formation in the beginning of the roasting process are obscured by the reduction of acrylamide in the second stage of the roasting.

In contrast to potatoes and potato chips, where a rather stringent correlation is evident between the precursors asparagine and reducing carbohydrates and acrylamide content in the final product, for coffee, there is an only rather weak positive correlation observed between asparagine in green and acrylamide in roasted coffee.

Moreover, lowering or raising the moisture content of the green coffee (to 7, respectively, 14%) before roasting did not result in a significant difference of acrylamide in the roasted coffees (data not shown).

To study the acrylamide formation during the roasting process, partial roasting was applied by prematurely stopping the roasting process. This confirmed that both, formation and reduction of acrylamide, occurred during roasting. Figure 2 shows a typical curve for the formation and reduction of acrylamide during roasting up to medium roast.

Similar patterns of acrylamide formation and reduction were observed in other studies [9, 11]. Heating experiments with portions of 3 g ground green coffee in a sealed headspace vial in a laboratory oven, without forced cooling

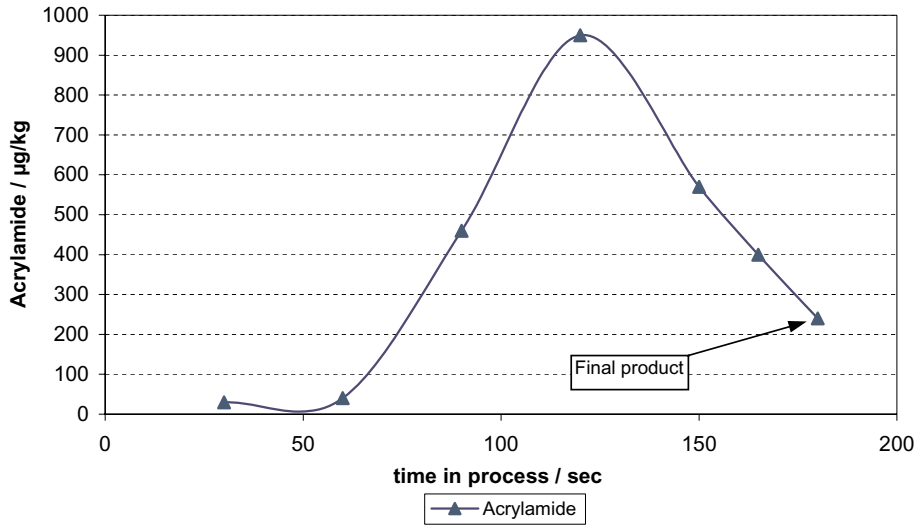

Figure 2. Acrylamide levels of partially roasted coffees, by prematurely stopping the process of roasting (Colombia coffee up to medium roast in 3 min).

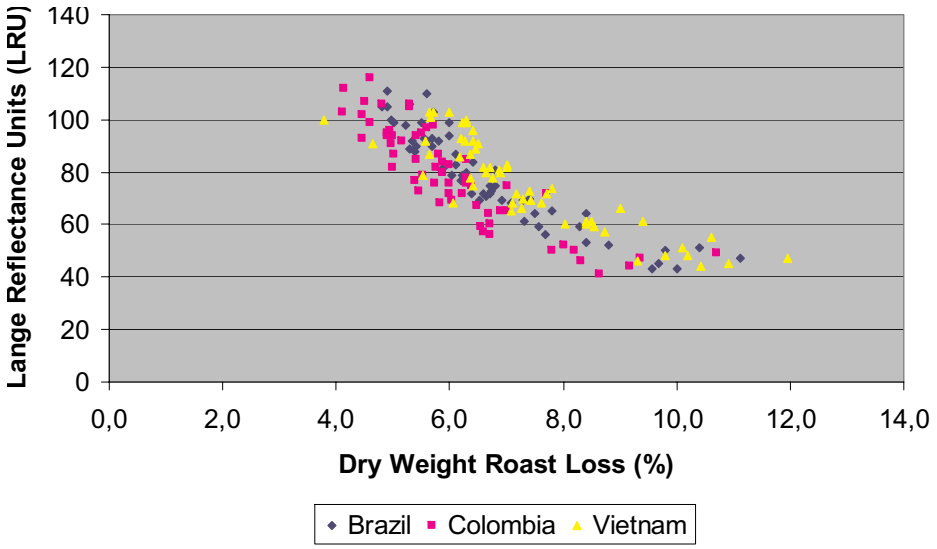

Figure 3. Relation between dry-weight-loss during roasting and degree of roast measured as light reflectance.

afterwards, indicated that the acrylamide content reached a maximum of about 300 µg/kg [9]. Taeymans *et al.* [11] reported that peak levels of around 2000 µg/kg had been observed early in the process of roasting coffee beans. Differences in observed absolute maximum values might be partly attributable to the type of green coffee and the way of roasting. However, differences in the ways of cooling of the (partially) roasted coffees might be of major importance. Senyuva *et al.* [9] did not apply any forced cooling. In the present study, the roasting process was stopped prematurely and the full batch of coffee cooled down by forced air-cooling. The results reported by Taeymans *et al.* [11] were based on samples taken directly during the process of roasting. Cooling down of such smaller samples can be achieved in a shorter time than the cooling of a full batch of coffee. Even small differences in the cooling efficacy might result in the process to be "frozen" in a quite different state. Compared with the very short "time in process" for these partially roasted coffees (50 to 180 s) the duration of the cooling step could affect the balance of the acrylamide formation and reduction reactions to a major extent. At least, this would make the observed variation in early roasting acrylamide peak values plausible.

The degree of roast is usually measured by reflectance of light. In the present study, it is expressed as reflectance units measured in a Lange colorimeter. The relation between LRU and percentages loss of dry weight of the coffees is shown in Fig. 3. In the first phase of roasting, the overall weight loss of the green coffee is mainly through evaporation of moisture. In the later phases of the process, loss of dry-weight, browning, taste and aroma development occur.

The extreme values in reflectance reached in the full experimental range, were on the light "roasted" side 116 LRU and on the dark side 41 LRU (both with Colombia coffee). In

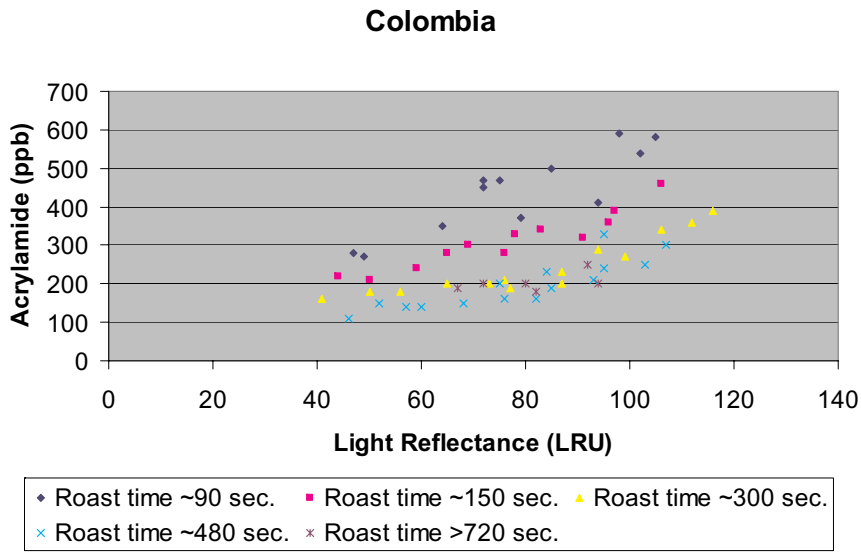

Figure 4. Effect of the degree of roast on acrylamide in Colombia coffee as measured over the full experimental range, from under- to over-roasted coffee.

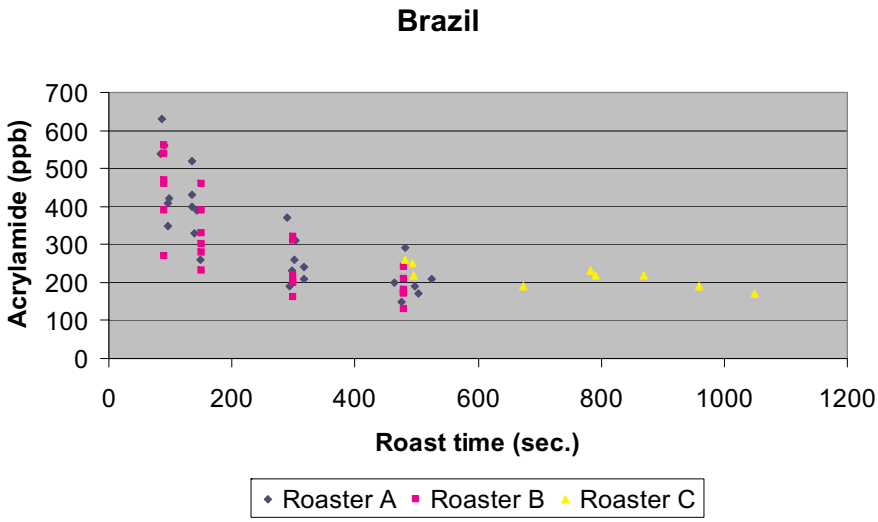

Figure 5. Effect of the roast time on acrylamide in Brazil coffee as measured over the full experimental range, from under- to over-roasted coffee.

practice, however, the range of the roast degree for the roasted coffees in Europe is from 55 to 105 LRU. In Scandinavia predominantly light roasted Arabica coffees are consumed (105 – 95 LRU), whereas darkest roasting is usually practiced in many Mediterranean countries (*e.g.* Italy, 65 – 55 LRU). The color bandwidth of roasting in a specific country is usually about 10 LRU, whereas the sensorial bandwidth of an individual brand of roasted coffee is not more than 5 LRU. Differences larger than that reflect products with clearly different sensorial characteristics. The effect of the degree of roast is shown in Fig. 4, over the full experimental range from under- to over-roasted (116 to 41 LRU).

Granby *et al.* and Senyuva *et al* [8, 9] reported market samples of roasted coffee, respectively, the corresponding brews to show lower levels of acrylamide for the darker roasted coffees. This was similar seen in the present study encompassing 51 samples of commercially roasted coffees from across Europe, showing that darker roasts had on average lower levels of acrylamide (data not shown).

The effect of roasting time as observed in the roasting experiments is shown in Fig. 5. In this graph, the experimental range goes beyond the commercially practiced range.

European commercial scale roasting practices roasting times from 2 to 15 min. Shorter roast times tend to induce higher levels of water extractable solids, making a stronger tasting brew [22]. This means that customers will use less coffee per cup. At very short roast times (<2.5 min) the acrylamide reduction is still progressing and the level is still going down. Figure 5 shows the results obtained with the three different roasters separately. Different types of roast equipment are capable of imposing different roast condi-

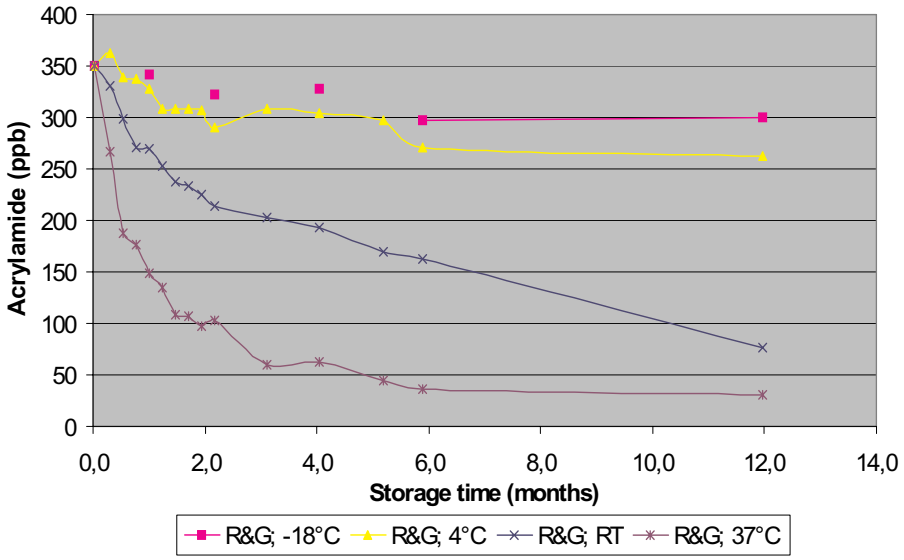

Figure 6. Reduction of acrylamide in vacuum-packed roast and ground coffee during storage.

tions on this coffee. However, under the same conditions, they do not differ with respect to the resulting acrylamide levels.

Bagdonaite *et al.* [13] reported two different series of experiments. In one series, they used a lab-scale roaster (batch size 80 g.) and observed that Robusta coffees produced higher acrylamide levels at roasting than Arabica's did. In their second series, they used pre-heated glass dishes in a lab-oven. Their results indicated that longer roasting resulted in lower acrylamide levels. For both series, there were no measurements of the degree of roast reported. The lacking of information on the degree of roast makes it impossible to draw conclusions from their results for coffee for actual consumption.

As both under-roasted and over-roasted coffees do not constitute consumable products, options to reduce acrylamide are restricted to the variation achievable within the normal sensorial range for consumption. The combined effects for degree of roast (range 105–55 LRU) and roast time (range 2–15 min) are shown in Table 2.

Table 2 used the pooled Arabica (Brazil and Colombia) results from 69 individual roast trials, as no significant difference between these two types of coffee had been observed (see Table 1). Table 2 presents the mean acrylamide levels per roast-time/degree cell. The cell with the largest number of results (cell 460–525 s/75–85 LRU) contains the results of seven independent roast trials with a mean acrylamide level of 196 µg/kg with SD of 33 µg/kg.

Except for the very short roast time (<2.5 min), the differences in acrylamide between adjacent cells are small. Along the roast time axis (range 290–870 s) the mean difference between adjacent cells in the three cell-columns is 13.5 µg/kg. Along the roast degree axis the mean difference between adjacent cells in the same cell-columns is 26 µg/kg. Both differences are smaller than the SD for similarly roasted coffees (see also Table 1). In addition, it has to be taken into account that shifting from one cell to the adjacent cell along the degree of roast axis as well as along the time axis stands for a considerable change in taste (size of difference between national taste preferences in European countries).

Table 2. Combined effects of degree of roast and roast time on average acrylamide levels (µg/kg) in roasted Arabica coffees (pooled Brazils and Colombia's) as measured for the normal range for consumption

Roast time Roast degree	135–150 s	290–320 s	460–525 s	670–870 s
LRU >95 (very light)	403	300	260	No data
LRU 85–95	367	240	233	233
LRU 75–85	336	200	196	200
LRU 65–75	343	208	196	195
LRU <65 (very dark)	283	193	145	No data

Delatour *et al.* [6] reported that a sample of roasted coffee with 203 µg/kg acrylamide after ambient storage for 7 months contained only 147 µg/kg. Hoenicke *et al.* [14] reported a reduction from 305 to 210 µg/kg for 3 months storage at 10–12°C. In the present study, the acrylamide reduction in vacuum-packed roast and ground coffee was measured over 12 months at four different temperatures (Fig. 6).

A sample of corresponding roasted coffee (whole beans) stored at room temperature showed a decreasing curve par-

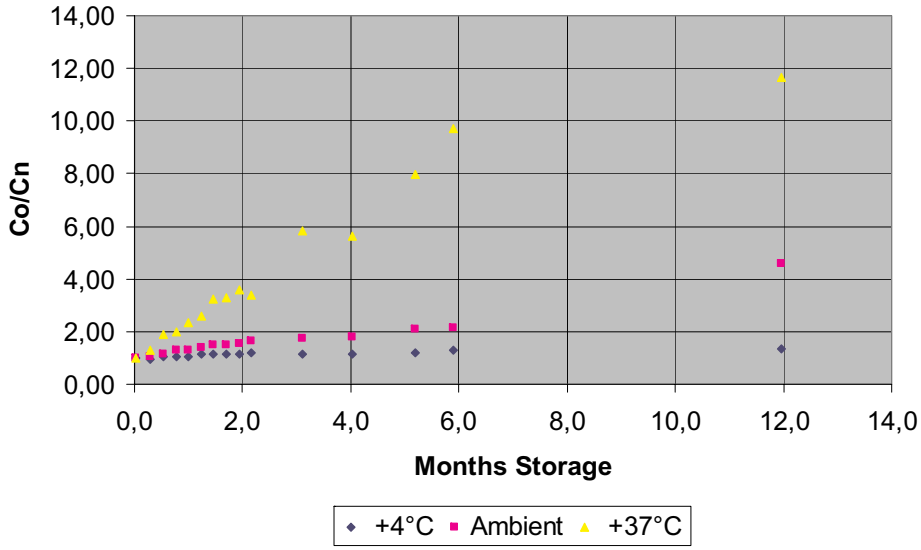

Figure 7. Kinetics of acrylamide reduction during storage of vacuum packed roasted coffee.

allel to the room temperature curve for roast and ground coffee in Fig. 6, at a slightly lower level (on average 33 µg/kg lower). This difference could be due to the further handling of the sample. The data for acrylamide reduction during storage of vacuum-packed roast and ground coffee allowed checking for the kinetics of the reduction reaction.

The function 1/Cn (Cn = concentration at "n" months) being linear in time (Fig. 7) indicates that the reduction of acrylamide during storage of vacuum packed roast and ground coffee followed second order reaction kinetics, at least for a considerable number of months. The rate difference between +4 and +37°C indicates an activation energy of about 73 KJ/mole for the acrylamide reduction reaction during storage.

The concentration of acrylamide in market samples of roast and ground coffee was reported to range from 45 to 539 g/kg [4–6, 9]. Part of this observed variation in commercial samples will be actually due to differences in freshness of the coffee.

A cross-section of generally available brewing systems was used to test extraction of acrylamide from the roast and ground coffee into the brew. The results are presented in Table 3.

At-home brewing strengths range from about 30 g/L upward. The tested brewing methods showed complete extraction of acrylamide into the brew up to the double of this brewing strength. Only for espresso (146 g/L) the extraction of acrylamide was incomplete. The lower extraction efficacy of espresso brewing might be due to the combination of the higher coffee-to-water ratio plus the much shorter extraction time used in espresso brewing.

Table 3. Extraction of acrylamide into coffee brew

Brewing system	Coffee/water (g/L)	Extraction efficiency (%)
Horeca pour-over system (5-L capacity)	46	104
Household drip-filter (1-L capacity)	49	102
Plunger pot	49	99
Fresh-brew filter coffee (vending machine)	62	102
Espresso machine (manual equipment)	146	75

No reduction of acrylamide was observed at holding the coffee beverage from the household drip-filter coffee in a thermos-jar for 1.5 h (data not shown).

4 Concluding remarks

In coffee, the acrylamide level went through a peak level during roasting. Both formation and reduction of acrylamide occurred during the roast process. The remaining levels in the fully roasted product for brewing of coffee were only a small fraction of the intermediately observed peak levels.

The main factors in affecting the acrylamide level in roasted coffee appeared to be the Arabica/Robusta ratio in the blend, with Robusta giving higher levels; time and degree of roast, with both shorter and lighter roasting at the edges of the normal roasting range giving the higher levels; conditions and time of storage after roasting, with clear reduction by ambient storage during a few months. Acrylamide, pre-

sent in the roast and ground coffee at the moment of brewing, was largely extracted into the brew. This extracted acrylamide was stable in the beverage within the normal time of consumption. The Arabica/Robusta ratio in the blend, the time of roast and the degree of roast have very distinct effects on the sensorial characteristics of the final product. Therefore, within the accepted boundaries of product-specific taste profiles, only relatively small effects on the acrylamide level are expected to be achievable.

These results leave a number of quite relevant and interesting questions for further research. The European coffee sector already initiated a study into the mechanism and kinetics of the acrylamide reduction reaction. Further research has to address the starting levels in freshly roasted coffee, as most of the so-far available studies did not take the reduction during storage into consideration at design of the study. In addition, part of the variation observed in commercial samples might be actually due to differences in freshness of coffee. Another subject needing investigation is the co-variance of other desired/undesired coffee components with any changing of the roast conditions.

Present study investigated the chain from green coffee to the coffee beverage for the factors affecting the acrylamide level. Together, it can be concluded that within the sensorial range, as accepted by the consumers, only relatively small reduction of acrylamide levels appears achievable.

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